Adsorption performances of an acid-stable 2D covalent organic framework towards palladium(II) in simulated high-level liquid waste

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Reasons for Urgent Publication

For “Rapid Communications” present the reason(s) for urgent publication here.

Covalent organic frameworks (COFs), which are mainly composed of light H, C, N, O elements through covalent bonding, have been attracted much attention in recent years as a novel kind of porous crystalline materials and exhibit a great potential in various fields such as catalysis, gas storage and separation, and drug carriers etc. While, synthetic procedures of COFs have been mainly focused on reversible condensation reactions, such as the Schiff base reaction, Spiro-borane condensation, Knoevenagel condensation and imide condensation etc., the gradual collapse of predesigned crystalline framework structure of COFs in highly acidic condition makes its application to be frustrating in the practical reprocessing process of high-level liquid waste (HLLW). Up to now, still a few articles regarding to the utilization of COFs as adsorbent have been reported to recover metal ions in aqueous phase, not even to mention selective recovery of radionuclides from HLLW. **The reason for urgent publication of this manuscript is to our best knowledge, there is still few (or even no) publications regarding the selective recovery of metal ions using COFs from high-level liquid waste** due to its inherent high concentration of nitric acid and co-existence of various competing elements.

Therefore, in view of the potential sense of our new results and their critical environmental implications, we think our manuscript would be suitable for its fast publication on “Analytical Sciences”.

Finally, we deeply appreciate your consideration of our manuscript, and we are
also looking forward to receiving any comments from the reviewers. If you have any queries, please don’t hesitate to contact us through the address below.

Thank you and best regards.

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Abstract

An acid-stable 2D covalent organic framework (COF TpPa-1) was synthesized by reversible Schiff base reaction and the following irreversible enol-keto tautomerism. The adsorption behaviors of COF TpPa-1 towards Pd(II) in simulated high-level liquid waste (HLLW) were investigated under the effect of contact time, concentration of nitric acid etc. The obtained experimental results supported that the utilization of this type of acid-stable COF in HLLW to recover metal ion was feasible.
Due to various excellent properties, covalent organic frameworks (COFs), which are mainly composed of light H, C, N, O elements through covalent bonding, have been attracted much attention in recent years as a novel class of porous crystalline materials and exhibit a great potential in various fields such as catalysis, gas storage and separation, and drug carriers etc. While, synthetic procedures of COFs have been mainly focused on reversible condensation reactions, such as the Schiff base reaction, Spiro-borane condensation, Knoevenagel condensation and imide condensation etc., the gradual collapse of predesigned crystalline framework structure of COFs in highly acidic condition makes its application to be frustrating in the practical reprocessing process of high-level liquid waste (HLLW). Up to now, still a few articles regarding to the utilization of COFs as adsorbent have been reported to recover metal ions in aqueous phase, not even to mention selective recovery of radionuclides from HLLW due to the inherent high concentration of nitric acid and co-existence of various competing elements. Palladium (Pd) as one member of fission products, plays an important role in a variety of fields (catalyst, photography, fuel cell, electronics, dental alloys etc.) because of its superior merits of chemical activity, biological importance and so on. The natural deposit of Pd is reported to be only 0.0063 ppm in the earth’s crust, while the quantity of Pd generated in nuclear power plant each year is reported to be significant, which could easily meet the desired amount of daily consumption. COF TpPa-1 is reported to be prepared by a combination of reversible and irreversible reactions using 1,3,5-triformylphloroglucinol (Tp) with p-phenylenediamine (Pa-1). The first reversible Schiff base reaction facilitates to the formation of a crystalline framework. Exceptional resistance towards acid treatment could be realized through enhancing its chemical stability by the following irreversible enol-to-keto tautomerization and this is also the main reason for selecting COF TpPa-1 as the target adsorbent in this study. Further,
COF TpPa-1 is composed of only light C, H, O, and N elements, which are considered to be burnable and difficult to form secondary high-level waste. Therefore, the objective of this study is to exhibit some representative adsorption behaviours of COF TpPa-1 when utilizing as a promising adsorbent for Pd(II) adsorption from simulated high-level liquid waste.

All chemical reagents used in this study were directly purchased from commercial suppliers in the highest grade that could be obtained and used without any further purification. All aqueous solutions were made with deionized water. COF TpPa-1 was synthesized by the facile routes introduced from previously published articles as shown in Scheme 1.7

Due to the large consumption of adsorbents in the batch experiments, the synthesis procedures of COF TpPa-1 was slightly modified from previous reports in order to enlarge the amounts of products obtained. For instance, 0.3 g of 1,3,5-triformylphloroglucinol was dispersed into 15 mL super dehydrated dioxane in a 20 mL glass vial in the presence of 0.5 mL of 3 M acetic acid, followed by sonicating for 10 min. Next, 0.228 g of p-phenylenediamine was added into the above suspension and sonicated for 5 min. The glass vial was sealed for 3 days at 25 °C without stirring. After the reaction, the red solid formed at the bottom of glass vial was isolated by filtration and washed several times with acetone, THF, methanol, respectively. Then dried at 150 °C under vacuum for 24 h to give a deep red coloured powder. On the other hand, the working solution used in batch experiment was dissolving 1 mM of 14 types of tested metal ions (Pd(II), Ru(III), Rh(III), Zr(IV), Mo(VI), Re(VII), Sr(II), Ba(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III)) with a variable concentration of nitric acid from 0.6–4 M. Batch experiments were carried out by mixing 4 mL of working
solution with 0.05 g of COF TpPa-1. The concentration of metal ions in aqueous phase
before and after adsorption were determined by ICP-AES. The removal percentage ($R$
/ %) and amount ($Q$ / mmol/g) were calculated using the following equations,
respectively.

$$R = \frac{(C_0 - C_t)}{C_0} \times 100$$  \hspace{1cm} (1)

$$Q = \frac{(C_0 - C_t) \times V}{m}$$  \hspace{1cm} (2)

where, $C_0$ is the concentration of metal ion at the initial condition in the aqueous phase
(mM); $C_t$ denotes the concentration at any time in the aqueous phase (mM); $m$ indicates
the mass of prepared COF TpPa-1 adsorbent (g); $V$ is the volume of the working
solution (mL).

Removal percentage of 14 types of tested metal ions under the effect of contact
time was firstly conducted and summarized as shown in Fig. 1. As a result, it was found
that the adsorption rate of COF TpPa-1 towards Pd(II) was fairly fast and almost 100%
of Pd(II) were adsorbed within 30 min. Therefore, all the other adsorption experiments
conducted in this study were all shaken for 5 h, which was considered to be long enough
for the adsorption equilibrium of Pd(II).

The result of adsorption performances of Pd(II) on the variation of concentration of
nitric acid was given in Fig. 2. Similar with the results introduced in Fig. 1, COF
TpPa-1 also exhibited an excellent adsorption performance towards Pd(II) without the
interference of [HNO$_3$] variation. Especially, in highly acidic condition when [HNO$_3$]$>1$,
the uptake percentage of Pd(II) still remained around 100%, which made it possible
for the practical application in the reprocessing process of HLLW. On the other hand,
from the results shown in Fig. 1 and 2, COF TpPa-1 exhibited moderate affinity towards Mo(VI) and Zr(IV) at some extent. With an increase in [HNO$_3$], the uptake percentage towards Mo(VI) decreased gradually while towards Zr(IV) increased. Moreover, COF TpPa-1 almost exhibited no adsorption ability towards other co-existing rare earth elements. Previous studies have shown that the O and N containing functional units remained in the linker which consisting of its main skeleton structure of COF TpPa-1 may play an important role in the complexation process. Further, the related adsorption mechanism will be elucidated in details in the next forthcoming full articles.

The result of adsorption capacity of COF TpPa-1 towards Pd(II) was shown in Fig. 3. With an increase in the concentration of Pd(II) in the aqueous phase, the adsorption amount of Pd(II) increased and gradually approached to a saturated state. The maximum adsorption capacity was calculated as a moderate 1.19 mmol/g. Next, the commonly used Langmuir and Freundlich isotherm models shown in equation (3) and (4) were adopted to evaluate the obtained experimental results with theoretical profiles.

\[
Q_{eq} = \frac{Q_{max} \times K_L \times C_{eq}}{(1 + K_L \times C_{eq})} \tag{3}
\]

\[
Q_{eq} = K_F \times C_{eq}^{(1/n)} \tag{4}
\]

where, $C_{eq}$ (mmol/L) means the equilibrium concentration; $Q_{eq}$ (mmol/g) denotes the amount of metal ion adsorbed in the equilibrium state; $Q_{max}$ (mmol/g) is the theoretical maximum of the adsorbed metal ion; $1/n$ is the Freundlich isotherm exponent constant; $K_L$ (L/mmol) and $K_F$ (mmol/g) are the Langmuir and Freundlich constants, respectively.

On the basis of the fitting results, it was found that the adsorption of Pd(II) onto COF TpPa-1 matched well with Freundlich isotherm model than Langmuir isotherm
model, with a high correlation coefficients of more than 0.98, which indicated that the adsorption processes occurred on a heterogenous surface consisting of various types of adsorption spots. In order to have a better understanding about the adsorption mechanism, further studies from the aspect of the structure of COF TpPa-1 should be considered.\textsuperscript{11}

In conclusion, an acid-stale 2D COF TpPa-1 prepared in this study exhibited enormously high adsorption ability towards Pd(II) in simulated high-level liquid waste without the interference of rare earth metals and slight co-adsorption of Mo(VI) and Zr(IV). Moreover, the adsorption performance of COF TpPa-1 was independent with the variation of nitric acid concentration which might promote its wide utilization as an alternative adsorbent in the nuclear waste reprocessing process. Further, the possible adsorption mechanism was considered as the N, O donor remained in the main skeleton of COF TpPa-1, which should be elucidated in future’s work.

Conflicts of interest
There are no conflicts to declare.

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Figure Captions:

Scheme 1. Brief synthesis procedures of COF TpPa-1

Fig. 1 The effect of contact time on the adsorption of Pd(II). Aqueous phase: [Metal] = 1 mM, [HNO₃] = 1 M, T = 298 K.
Fig. 2 The effect of concentration of nitric acid on the adsorption of Pd(II). Aqueous phase: [Metal] = 1 mM, [HNO$_3$] = 0.6−4 M, T= 298 K, shaking time= 5 h.

Fig. 3 Adsorption capacity and isotherm fittings of Pd(II). Aqueous phase: [Metal] = 1−20 mM, [HNO$_3$] = 1 M, T= 298 K, shaking time= 5 h.