ORIGINAL ARTICLE

Separation of homogeneous palladium catalysts from pharmaceutical industry wastewater by using synergistic recovery phase via HFSLM system

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Abstract   Separation of homogeneous palladium catalysts from pharmaceutical industry wastewater by using synergistic recovery phase via hollow fiber supported liquid membrane (HFSLM) system is presented. HFSLM impregnated with N-methyl-N,N,N-trioctylammonium chloride (Aliquat 336) as the extractant dissolved in cyclohexane. The influence of various chemical parameters, including the concentration of extractant and recovery phases as well as recovery selector concentration in recovery phase, were also studied. A mixture of hydrochloric acid and thiourea was used as synergistic recovery phase. The highest percentage of extraction and recovery was 99.95% and 88.12%, respectively. Furthermore, the kinetics of recovery reaction was studied to provide reaction order, reaction rate constant, equilibrium constant and distribution ratio.

1. Introduction

The treatment of pharmaceutical industry wastewater presents a real challenge for wastewater engineers. Pharmaceutical wastewater from chemical synthesis-based process contains a variety of organics, including solvents, additives, reactants, pharmaceutically active compounds and trace precious metal catalyst (Nakada et al., 2008, Coimbra et al., 2019, Mahmoudian et al., 2020). Although trace precious metal catalysts are present in low concentrations in the environment, there is no data as yet available to assess the effect of this exposure. A major source of health concern is the sensitization risk of precious metal catalysts as very low doses are sufficient to cause allergic reactions in susceptible individuals (Chen et al., 2008, Domínguez et al., 2011, Ali et al., 2019).

Palladium (Pd) is the one of precious metal which is widely applied in diverse fields such as homogeneous catalysts in chemical synthesis-based pharmaceutical process (Kato et al., 2016). Homogeneous palladium catalysts (palladium(II) chloride (PdCl$_2$)) was used as catalyst for the carbonylation of organic tellurides by reaction with carbon monoxide (Nishibayashi et al., 1996). The great increase in industrial demand for palladium causes its low abundance in the earth's

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Nomenclature

A	effective area of hollow fiber (cm^2)
BOD	Biochemical oxygen demand (mg/L)
COD	Chemical oxygen demand (mg/L)
C	concentration (mol/L)
C_f	the feed concentration (mol/L)
$C_{f,in}$	the inlet feed concentration of component i (mol/L)
$C_{f,out}$	the outlet feed concentration of component i (mol/L)
C_m	the concentration of component i in the membrane phase (mol/L)
$C_{Pd,0}$	the initial concentration of palladium (mol/L)
C_{Pd}	the concentration of palladium (mol/L)
C_r	the concentration of component i the recovery phase (mol/L)
$C_{r,out}$	the outlet recovery concentration of component i (mol/L)
D	distribution ratio [–]
D_{12}	distribution ratio obtained from the synergistic extractant or recovery [–]
D_1	distribution ratio obtained from a single extractant or recovery no. 1 [–]

D_2	distribution ratio obtained from a single extractant or recovery no. 2 [–]
K_r	the recovery equilibrium constant Extraction rate constant (L/mol)
$k_{r,f}$	the reaction rate constant
n	the reaction order
N	number of hollow fibers in the module (-)
R^2	coefficient of determination
S.C.	the synergistic coefficient
t	time (min)
TSS	total suspended solids (mg/L)
T	temperature (K)
V	volume (cm^3)

Subscripts

f	feed phase
i	component
r	recovery phase
m	membrane phase
0	initial concentration

crust and highlights its economic significance (Zereini and Alt, 2006, Xie et al., 2018, Hasegawa et al., 2018). However, palladium which is not only precious but also toxic metals is non-biodegradable and can contaminate in water resource. Without the suitable treatment, it can cause both environmental and health problems (Gebel et al., 1997, Nakajima et al., 2009, Afzali et al., 2012). Both issues attract many researchers to investigate the extraction and recovery of palladium. The effective recovery of palladium from both natural ore and industrial waste is important from the standpoint of full utilization of resources. Solvent extraction (Truong and Lee, 2018) is a method traditionally used for palladium recovery. However, several chemical reagents were used to solve the wastewater problem, which seems not sustainable for the modern society. The chemical reagents were also partially stayed in the water (Danlami et al., 2014). Alternatively, reverse osmosis (Hoffman, 1988), evaporation (Brooks, 1991), ion exchange (Hubicki et al., 2008), chemical precipitation (Ozturk et al., 2011), adsorption and biosorption (Ramakul et al., 2012, Cataldo et al., 2016, Huang et al., 2020) by some biomass such as wasted microorganism have been developed for the recovery of palladium from wastewater. However, the drawback of biosorption methods is that the extracted palladium would be contaminated by the biomass. In case of pharmaceutical industry, an effective simultaneous process to recover the compound from a much diluted solution by single-unit operation is important in close-control system. This is to prevent cross contamination and further use of the extracted palladium as a pharmaceutical catalyst (Sunsandee et al., 2012a, Vijayalakshmi et al., 2015, Chaudhury et al., 2018).

In recent years, the use of a liquid membrane in wastewater treatment has become increasingly important. A liquid membrane offers several advantages, such as high selectivity, high efficiency of separation, high enrichment efficiency, and less use of the organic phase, compared with the classical solvent extraction process (Es'haghi and Azmoodeh, 2010, Lothongkum et al., 2012, Es'haghi, et al., 2017). Hollow fiber supported liquid membrane (HFSLM), one of the liquid membrane systems, combines the extraction, recovery and regeneration processes, which are normally carried out in two separate steps in conventional processes (Panja et al., 2011, Sunsandee et al., 2012a, Chaudhury et al., 2018). as an effective simultaneous process to extract and recover compound from a very dilute solution of interested component in the feed by a single-unit operation (Sunsandee et al., 2012a, Vijayalakshmi et al., 2015, Chaudhury et al., 2018). The advantages of the HFSLM system over the traditional separation processes include lower capital and operating costs (Sunsandee et al., 2012a, Wannachod et al., 2016), lower energy consumption (Wannachod et al., 2016, Pirom et al., 2017), less solvent used, and the possibility of achieving a high overall separation factor (ChusnunNi'am et al., 2020, Kedari et al., 2020). The HFSLM process has much potential for precious metal ions separation (Wongsawa et al., 2020, Mohdee et al., 2020).

The prime objective of this work is to study the improvement of recovery efficiency by synergistic recovery phase for separation of homogeneous palladium catalysts from pharmaceutical industry wastewater via HFSLM system. Specific separation methods for homogeneous palladium catalysts uses HFSLM system based on Aliquat 336 as extractant. The recovery phase was prepared using the different solutions of hydrochloric acid, thiourea and mixture of hydrochloric acid and thiourea. The optimum conditions of the influencing parameters such as pH in feed phase, extractant concentration in organic phase, type of recovery phase, extraction and recovery time were determined in order to provide the highest extraction and recovery efficiency of homogeneous palladium catalysts. Moreover, the determination of the reaction order and the reaction rate constant in kinetics exhibited the behavior of recovery phase reaction was studied.

2. Theory

2.1. Hollow-fiber supported liquid membrane

The hollow fiber supported liquid membrane (HFSLM) system contains many micro-porous polyethylene fibers. The HFSLM system consists of a feed solution consisting of a precious metal ion and a recovery solution. The liquid membrane is in the process of entering and recovery and consists of an organic carrier that reacts with precious metal ion. The organic membrane phase consists of an extractant dissolved in organic phase embedded into porous material in order to enhance separation. The feed solution and recovery solution are in contact with the organic membrane. The hollow fiber module consists of a large number of hollow fibers arranged horizontally with the liquid membrane embedded. The organic phase will fill the pores of fibers with capillary forces. (Wannachod et al., 2016, Pirom et al., 2017).

2.2. Transport mechanism of homogeneous palladium catalysts (Pd(II)) using an extractant

The extractant (N-methyl-N,N,N-trioctylammonium chloride (Aliquat 336)) is embedded in the polymeric hydrophobic microporous fibers of the hollow fiber module by capillary action. The supported liquid membrane lies between the aqueous solution containing the wastewater, and the aqueous recovery phase containing recovery agents. The transport of homogeneous palladium catalysts (Pd(II)) takes place in consequence of the driving force of the concentration between the aqueous feed solution and the aqueous recovery phase. The feed solution and the recovery solution are pumped _counter-currently into the tube and shell sides of the module, respectively. In the liquid membrane phase, the extractant (N-methyl-N,N,N-trioctylammonium chloride (Aliquat 336)) takes place via extraction reactions in the system. The reaction is the reaction between N-methyl-N,N,N-trioctylammonium chloride (Aliquat 336), and Pd(II) in the feed phase, as shown in Eq. (1) (Chaturabul et al., 2013, Wongkaew et al., 2015). The extractant and Pd(II) are formed as $\overline{((C_{25}H_{54})N^+)_2 \cdot PdCl_4^{2-}}$ and transported across the membrane phase to the recovery phase.

$$PdCl_4^{2-} + 2(C_{25}H_{54})N^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \overline{((C_{25}H_{54})N^+)_2 \cdot PdCl_4^{2-}} \quad (1)$$
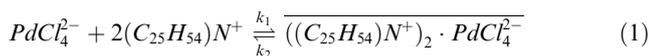
where k_1 and k_2 are the apparent extraction reaction rate constants, respectively.

2.3. The transport mechanism of Pd(II) and extractant complex by using acid agent hydrochloric acid, organic carrier (thiourea) and synergistic recovery phase

The recovery of Pd(II) and extractant complex by recovery phase occurred the recovery reaction in the system. At the interface of the organic membrane phase and the recovery phase, the complex species, $\overline{(C_{25}H_{54})N^+)_2 \cdot PdCl_4^{2-}}$, react with the recovery solution and release Pd(II) to the recovery phase. The recovery of Pd(II) and extractant complex by acid agent hydrochloric acid and organic carrier (thiourea) occurred the recovery reaction in the system as shown in Eqs. (2)–(3),

respectively (Mohdee et al., 2018, 2019, 2020). The synergistic recovery of Pd(II) and extractant complex react with a mixture of the acid agent hydrochloric acid and thiourea solution and release Pd(II) to the recovery phase in reductive recovery of Pd (II) as shown in Eq. (4) (Mohdee et al., 2018, 2019, 2020). The schematic representation of the counter-current flow diagram for batch mode operation in HFSLM is presented in Fig. 1.

$$\overline{((C_{25}H_{54})N^+)_2 \cdot PdCl_4^{2-}} + 2Cl^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \overline{2N^+(C_{25}H_{54})Cl^-} + PdCl_4^{2-} \quad (2)$$
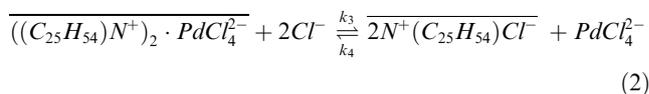
where k_3 and k_4 are the apparent recovery reaction rate constants, respectively.

$$\overline{((C_{25}H_{54})N^+)_2 \cdot PdCl_4^{2-}} + CS(NH_3)_2$$
$$\times \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \overline{2N^+(C_{25}H_{54})Cl^-} + PdCl_2 \cdot CS(NH_3)_2 \quad (3)$$
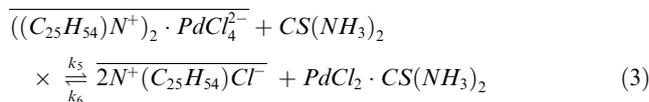
where k_5 and k_6 are the apparent recovery reaction rate constants, respectively.

$$((C_{25}H_{54})N^+)_2 \cdot PdCl_4^{2-} + CS(NH_3^+)_2 + 2Cl^-$$
$$\times \underset{k_8}{\overset{k_7}{\rightleftharpoons}} 2N^+(C_{25}H_{54})Cl^- + PdCl_4^{2-} \cdot CS(NH_3^+)_2 \quad (4)$$
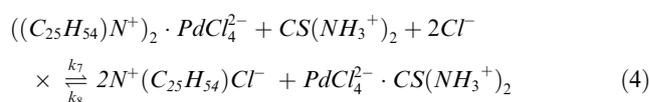
where k_7 and k_8 are the apparent recovery reaction rate constants, respectively.

2.4. Synergistic recovery

The application of synergistic recovery for metal ion separation is the phenomenon whereby two recovery reagents combine together to recover target metal ion from metal ion-extractant complex. Synergistic recovery is an important method which enhances recovery efficiency (Sunsandee et al., 2012b, Mohdee et al., 2019).
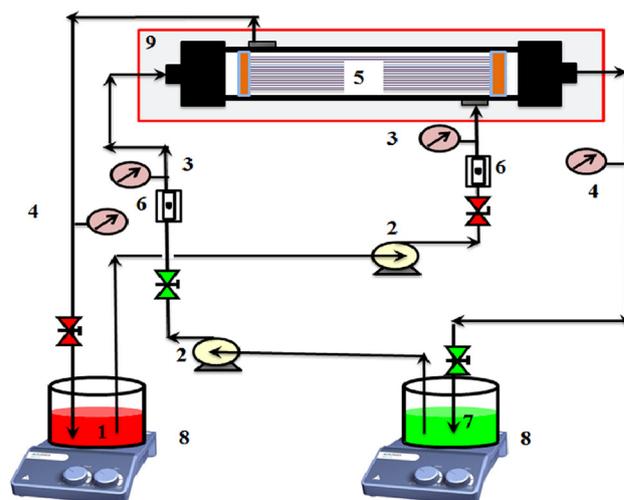
Fig. 1 Schematic representation of the counter-current flow diagram for batch mode operation in HFSLM: (1) feed reservoir; (2) gear pumps; (3) inlet pressure gauges; (4) outlet pressure gauges; (5) hollow-fiber module; (6) flow meters; (7) stripping reservoir; (8) stirrer with temperature control; and (9) temperature control box.

It is more efficient than using recovery separately. The effect of synergistic recovery (expressed as the synergistic coefficient, S.C.) as a function of the distribution ratio is shown as reported elsewhere (Sunsandee et al., 2012b, Mohdee et al., 2019).

$$S.C. = \frac{D_{12}}{D_1 + D_2} \tag{5}$$

where D_{12} is a distribution ratio from the synergistic extractant or recovery and D_1 or D_2 is the distribution ratios obtained from a single extractant or recovery.

Based on S.C. behavior, the synergistic extractant or recovery is defined as follows (Luo et al., 2004).

(a) S.C. > 1, there is a positive synergic effect;
(b) S.C. < 1, there is an antagonistic effect (negative synergism);
(c) S.C. = 1, there is no synergic effect

Distribution ratio (D) was calculated by Eq.(6). The distribution ratio (D) from IUPAC compendium of chemical terminology (Berthod and Mekaoui, 2011) was given by

$$D = \frac{C_r}{C_m} \tag{6}$$

where C_r denotes the concentration of component i the recovery phase. C_m denotes the concentration of component i in the membrane phase.

In this work, the extractability of homogeneous palladium catalysts was determined by the percentage of extraction:

$$\%\text{Extraction} = \frac{C_{f,in} - C_{f,out}}{C_{f,in}} \times 100 \tag{7}$$

The percentage of recovery was calculated by:

$$\% \ \text{Recovery} = \frac{C_{r,out}}{C_{f,in}} \times 100 \tag{8}$$

where $C_{f,in}$ and $C_{f,out}$ are the inlet and outlet feed concentrations of component i, and $C_{r,out}$ is the outlet recovery concentration of component i.

3. Experiment

3.1. Pharmaceutical industry wastewater from chemical synthesis-based process

The wastewater used in this study was taken from a chemical synthesis-based of Sevenstar Pharmaceutical Company, Thailand. The wastewater was generated from the synthesis and separation processes, containing approximately 10 ppm (0.01×10^{-6} mol/L) of homogeneous palladium catalysts at pH 2 to 4 was pretreated by filter paper (No. 41, pore size 20 µm, Whatman™) and used as the feed phase. The generation rate of the wastewater was 20 L per batch. The properties of the wastewater are shown in Table 1.

3.2. Chemicals and reagents

The aqueous phase was pharmaceutical industry wastewater containing homogeneous palladium catalyst (Sevenstar Pharmaceutical Company, Thailand). The organic phase was prepared by mixing Aliquat 336 (purity 90.5%, Acros Organics, USA) in organic diluent of cyclohexane (purity 99.5%, Merck, Thailand). For the recovery phase, thiourea (purity AR grade, Merck, Thailand), hydrochloric acid solution (purity 37.0%, Merck, Thailand) and their mixtures were dissolved in doubly deionized water. Standard solution for the ICP analysis was prepared by diluting the solution of Pd (Merck, Thailand) + 10% HCl (1000 µg/mL, PerkinElmer Pure) in doubly deionized water. All chemicals were used without further purification. All analytical reagents were provided by Merck, Thailand. Doubly deionized water (Millipore®, USA) was used in all experiments.

3.3. Apparatus

Hollow fiber supported liquid membrane (HFSLM) system (Liqui-Cel® Extra-Flow 2.5 in × 8 in membrane contactor) manufactured by Membrana/Celgard (Charlotte NC, USA). This module uses polypropylene fibers. The micro-propylene fabric is woven into the fabric and wrapped around the central tube feeder, which supplies liquid to the shell. Woven fabrics provide a more uniform spacing that leads to a higher mass transfer coefficient than those obtained from single fibers (Wannachod et al., 2016, Pirom et al., 2017). The properties of the hollow fiber module are specified in Table 2. The fibers were inserted into the tube sheet. Polyethylene with a solvent resistant solvent with polypropylene shell casing.

3.4. Procedures

The single-module operation was shown in Fig. 1. The organic phase was prepared by mixing Aliquat 336 in organic diluent of cyclohexane (500 mL) individually. Liquid membrane was prepared by pumping the mixture of the mixing Aliquat 336 and diluent into the HFSLM module for 50 min. in order that the organic phase became enmeshed in the micro-porous fibers. Then, 5000 mL of the feed solution and 5000 mL of the recovery solution were driven counter-currently into the HFSLM system. The extraction and recovery solution of homogeneous palladium catalyst was carried out using solvent extraction processes at room temperature (303.15 K) to determine the optimum condition for each influencing parameter. Separation time was studied in the range of 0-120 min. All experiments were repeated three times. The concentrations of Pd (II) ions in the sampling solutions were analyzed by a Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) (Thermo Scientific, iCapQ, Laser ablation ESI NWR-213, USA).

Table 1 Characteristics of the raw pharmaceutical industry wastewater.

Parameter	Value
Color	Brownish
Homogeneous palladium catalysts (ppm)	~10
Temperature (K)	298.5
pH	2–4
TSS (mg/L)	790
BOD (mg/L)	1850
COD (mg/L)	3160
Conductivity (µs/cm)	2870

3.5. Analytical procedures

Feed pH was measured by pH meter (SevenMulti™ Mettler-Toledo). The element analysis of Pd(II) samples, in the feed and recovery solutions aqueous phases, were kept before and after experiments to measure the initial and final concentration of palladium ions respectively. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) (Thermo Scientific, iCapQ, Laser ablation ESI NWR-213, USA) was used to determine the concentrations of palladium (Pd(II)) ions, according to USP 42 chapters ⟨232⟩ and ⟨233⟩ on elemental impurities in pharmaceutical products (USP, 2019) and analytical method was proposed by previous study (Prudnikov and Barnes, 1998, Sun et al., 2004, Rajput et al., 2015). The limit of detection was found as 0.05 μg/ml for palladium while the limit of quantitation was found to be 0.1 μg/ml for palladium (Prudnikov and Barnes, 1998, Sun et al., 2004, Rajput et al., 2015). All analyses were repeated three times. Each experiment was duplicated under identical conditions. Owing to the change of volume is very small and can be neglect, the concentration of palladium (Pd(II)) complex in organic phase were determined from a mass balance method.

4. Results and discussion

4.1. Optimization of initial parameters for palladium separation via HFSLM

The separation efficiency causes the total transfer of analytes to spread throughout HFSLM. This is controlled by several initial parameters, including: pH, feed phase concentration, feed flow rate and recovery solution via HFSLM. The optimum conditions are shown in Table 3 (Patthaveekongka et al., 2003, Chaturabul et al., 2013, Wei et al., 2016, Mohdee et al., 2018, 2019, 2020). Some of these parameters can be determined by examining the physical properties of the compound. The feed procedure is carried out at an optimized pH of feed solution 2.0. The phase feed concentration approximately 10 ppm (0.01×10^{-6} mol/L). The flow rate of the feed solution and solution is 100 mL/min.

4.2. Effect of extractant (Aliquat 336) concentration in liquid membrane

It has been established that transport of metal ions through HFSLM depends on the concentration of the extractant in the membrane phase. The concentrations of Aliquat 336 in the range of 0.2–1.4 mol/L were studied and the results have been represented graphically in Fig. 2. The results indicated that the percentage of extraction of Pd(II) clearly increased when extractant concentration increased from 0.2 mol/L to 0.8 mol/L. The highest percentage of Pd(II) extraction was achieved at the extractant concentration of 0.6 mol/L. This result was in agreement with a report by (Wei et al., 2016, Mohdee et al., 2018, 2019, 2020). However, the rate of separation decreased when the Aliquat 336 concentration reached over 1.0 mol/L. This can be explained by the fact that the viscosity of the liquid membrane phase increases (Wannachod et al., 2016, Pirom et al., 2017). The increasing tendency of liquid membrane viscosity causes low diffusivity and obstructs mass transfer of $\overline{((C_{25}H_{54})N^+)_2 \cdot PdCl_4^{2-}}$ (which ultimately reduces extraction and recovery percentages of Pd(II)). Consequently, the concentration of 0.6 mol/L Aliquat 336 was accepted as the best extractant concentration.

4.3. Effect of acid recovery agent (hydrochloric acid) concentration in recovery phase

The effect of hydrochloric acid concentration in the recovery solution on the efficiency of Pd(II) recovery were also investigated. The concentration of hydrochloric acid varied from 0.1 to 1.0 mol/L, the results are shown in Fig. 3. It can be inferred that the Pd(II) ion can be recovered using any hydrochloric acid concentration because the Pd(II) and extractant complex react with proton in the recovery solution (El-Hefny and Daoud, 2013, Nguyen et al., 2016, Mohdee et al., 2018, 2019, 2020). However, when the hydrochloric acid concentration in the recovery solution was increased from 0.1 mol/L to 0.3 mol/L, the recovery percentage of palladium increased, which is in accordance with Eq. (2). The recovery of palladium ions reached a maximum value with 0.3 mol/L concentration of hydrochloric acid solution. Above this concentration, the recovery of palladium ions increased only slightly (El-Hefny and Daoud, 2013, Nguyen et al., 2016). Therefore, 0.3 mol/L concentration of hydrochloric acid was accepted as the best recovery solution concentration.

Table 2 Physical characteristics of the hollow-fiber module.

Properties	Description
Material	Polypropylene
Inside diameter of hollow fiber	240 μm
Outside diameter of hollow fiber	300 μm
Effective length of hollow fiber	15 cm
Number of hollow fibers	35,000
Average pore size	0.03 μm
Porosity	30%
Effective surface area	1.4×10^4 cm²
Area per unit volume	29.3 cm²/cm³
Module diameter	6.3 cm
Module length	20.3 cm
Contact area	30%
Tortuosity factor	2.6
Operating temperature	273.15–333.15 K

Table 3 Optimized operation using HFSLM in palladium separation.

Phase	Chemical reagent	Concentration	Flow rate
Feed	Pharmaceutical industry wastewater contains homogeneous palladium catalysts pH 2.0	10 ppm (0.01×10^{-6} mol/L)	100 mL/min
Membrane	Aliquat 336	0.6 mol/L	–
Recovery	Hydrochloric acid Thiourea	Result report in this study	100 mL/min
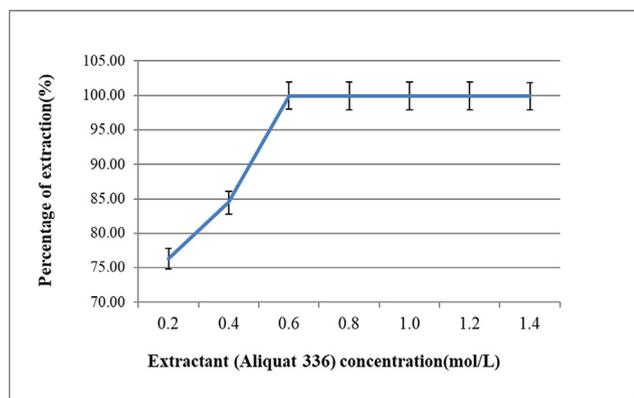
Fig. 2 Effect of extractant (Aliquat 336) concentration in liquid membrane on separation of homogeneous palladium catalysts under the error of extraction percentage at ±3%.

4.4. Effect of organic carrier (thiourea) concentration in recovery phase

As expected, the extraction and recovery of Pd(II) through HFSLM was found to be largely dependent on the nature and concentration of the recovery ligand selected in the recovery solution. Therefore, several recovery agents had been reported as having outstanding performance for use as a recovery solution for Pd(II) recovery, for example, thiourea with large anion in the structure was reported that thiourea have strong enough to recover Pd(II) complex ion from Aliquat 336, which is in accordance with Eq. (3) (Mohdee et al., 2018, 2019, 2020).

Thiourea is a chemically interesting ligand in that it has several different possible modes of binding to a metal ion. Three types of the compounds are described: clathrates, ion complexes and coordination compounds. The main attention is paid to thiourea complexes of transition metals. The structure of the complexes is considered, using X-ray structural analysis and other physicochemical methods. Stability and lability of thiourea coordination compounds and its *N*- and *N, N'*-substituted derivatives are characterized, as well as peculiarities of the given ligands in substitution reactions. Acid-basic, redox and thermal properties of thioamide complexes are discussed (Khairul et al., 2018).
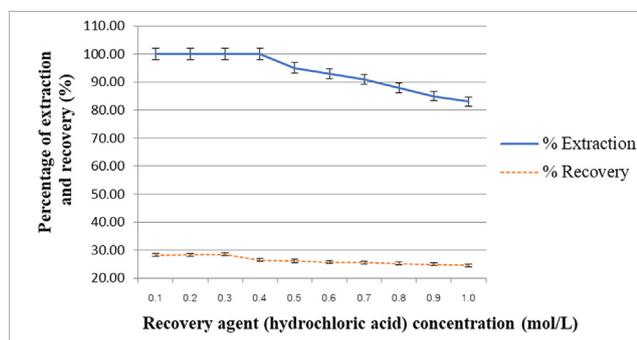
The previous works exhibited finding indicated that the expected coordination of ligand to the palladium metal center took place via N and S atoms (Cotton, et al, 1964, Khairul et al., 2018). Thiourea has C-S and C-N bond lengths of 1.720(9) Å and 1.340(6) Å, respectively (Cotton, et al, 1964). It may coordinate through the mostly nonbonding electron pairs of the nitrogen or via the sulfur atom. The sulfur itself may donates electrons by the two different mean: (a) electron from the nonbonding sp^2 lobes. (b) electron from the S-C π molecular orbitals. Thiourea is actually coordinating and helping in the back-extraction of the recovery process of Pd(II). Thiourea ligands are coordinated to the Pd(II) ion.

The effects of thiourea concentration in the recovery solution on the efficiency of Pd(II) recovery were also investigated and results were shown in Fig. 4. The concentration of thiourea varied in the ranges of 0.1–1.0 mol/L. Recovery percentages increased suddenly when concentration of thiourea increased up to 0.6 mol/L. Higher concentration of thiourea more than 0.6 mol/L provided constant percentage of the recovery. Thus, the results indicated that thiourea had the capability to form the coordinating bonds through both sulfur and nitrogen atoms (Mohdee et al., 2018, 2019, 2020). In addition, concentration of thiourea at 0.6 mol/L was the maximum amount to recover palladium complexes. Higher concentration greater than 0.6 mol/L was the excess amount (Mohamed Noah et al., 2016).

4.5. Synergistic effects of the combination of acid recovery agent (hydrochloric acid) and organic carrier (thiourea) in recovery phase

The effect of the concentration of combination of acid recovery agent (hydrochloric acid) and organic carrier (thiourea) in recovery phase was studied. Thiourea mixed with hydrochloric acidic solution was also reported that is the most effective recovery agents of precious metals such as platinum ion as reported elsewhere (Chaturabul et al., 2013, Wongkaew et al., 2015). In this work, hydrochloric acid and thiourea has been investigated for synergistic recovery of Pd (II) from the liquid membrane phase. Hydrochloric acid concentration was adjusted from 0.1 to 1.0 mol/L and the concentration of thiourea was also varied in a range of 0.1–1.0 mol/L. The influences of the synergistic recovery compositions were summarized in Fig. 5. When thiourea was not added to the

Fig. 3 Effect of acid recovery agent (hydrochloric acid) concentration in recovery phase on separation of homogeneous palladium catalysts under the error of extraction percentage at ± 3%
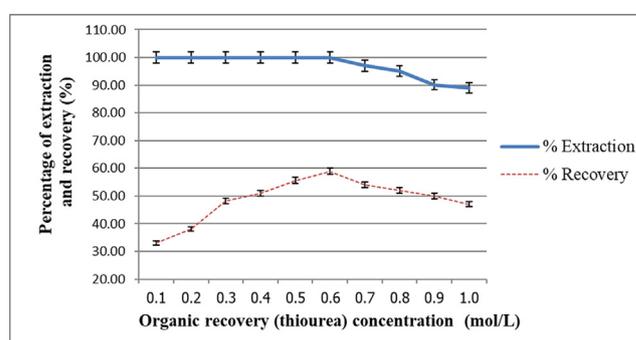
Fig. 4 Effect of organic carrier (thiourea) concentration in recovery phase on separation of homogeneous palladium catalysts under the error of extraction percentage at ±3%.

recovery, hydrochloric acid showed recovery effect on recovery of Pd(II) from the liquid membrane phase, but with very small value. With the increase of the thiourea content, the percentage of recovery of Pd(II) was greatly enhanced. Increase of thiourea concentration resulted in continuously increase of the recovery activities until thiourea concentration reached 0.6 mol/L, when the recovery activities started to decline. This is because thiourea is actually coordinating and helping in the back-extraction of the recovery process of Pd(II). Thiourea ligands are coordinated to the Pd(II) ion. Therefore, when there is more thiourea, the recovery activity will be enhanced.

Results were shown by generating the dimensional surface plot from the concentration effect data in Fig. 5. It was observed that the percentage of Pd(II) recovery increased when the concentration of hydrochloric acid increased up to 0.1 mol/L and the concentration of 0.6 mol/L thiourea. This result was in agreement with the fact that the driving force for the present coupled transport is supplied by the proton concentration gradient between the feed and the recovery phases. However, the recovery of Pd(II) decreased at a higher recovery concentration than 0.1 mol/L hydrochloric acid and 0.6 mol/L thiourea. This can be attributed to the fact that the excess amount of recovery solution for Pd(II) recover from the complex species. It blocked the membrane pores, resulting in the membrane fouling and poor transport performance in the membrane phase (Chaturabul et al., 2013, Wongkaew et al., 2015, Mohdee et al., 2018, 2019, 2020). The results indicated that the combination of hydrochloric acid and thiourea showed the excellent recovery ability as illustrated in Fig. 5. Under the optimum condition, the percentage of recovery of Pd(II) reaching 88.12% was obtained. The optimized condition is the concentration ratio between thiourea: hydrochloric acid of 0.6 mol/L: 0.1 mol/L. The excellent reproducibility of the experimental data was observed at the standard deviation of 2% under identically optimum operating conditions in three different extraction operations.

4.6. Recovery equilibrium constant (Kr), distribution ratio (D) and synergistic coefficient (S.C.)

The equilibrium constant (K_r) of homogeneous palladium catalysts recovery was determined using the reaction in Eq. (9) and calculated by the slope of the graph in Fig. 6. This deriva-

tion followed the work of Rydberg et al and Mohdee et al (Rydberg et al., 2004, Mohdee et al., 2018, 2019, 2020). This consideration corresponded to the highest recovery results of 88.12% and found to be 7.8568 L/mol.
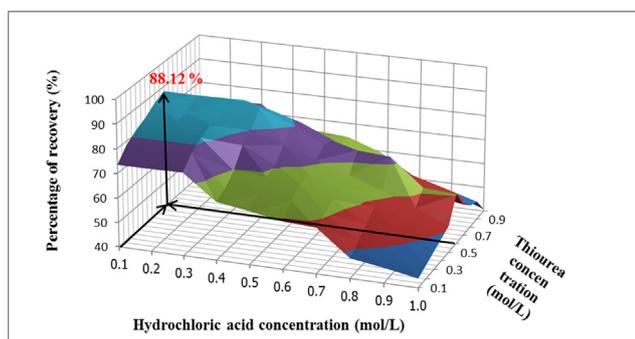
$$K_r = \frac{[PdCl_4^{2-} \cdot CS(NH_3^+)_2]^2 \left[N^+(C_{25}H_{54})Cl^-\right]^2}{\left[((C_{25}H_{54})N^+)_2 \cdot PdCl_4^{2-}\right][CS(NH_3^+)_2][Cl^-]^2} \quad (9)$$

The distribution ratio (D) at the concentration ratio between thiourea: hydrochloric acid varied (ratio 0.3 mol/L: 0.1 mol/L, 0.3 mol/L: 0.2 mol/L, 0.3 mol/L: 0.3 mol/L, 0.6 mol/L: 0.1 mol/L, 0.6 mol/L: 0.2 mol/L, 0.6 mol/L: 0.3 mol/L) were calculated by Eq. (6) as shown in Table 4.

It was noted that the distribution ratio increased with concentration ratio between thiourea: hydrochloric acid, agreed with the earlier report by Mohdee et al. (2018, 2019, 2020) the optimized condition is the concentration ratio between thiourea: hydrochloric acid of 0.6 mol/L: 0.1 mol/L found to be 7.42.

The synergistic coefficient (S.C.) as a function of the distribution ratio is shown in Eq. (5). Where synergistic coefficient (S.C.) increased from 1, it can be concluded that using the mixture of recovery agent led to higher percentage recovery than using a single recovery agent (Sunsandee et al., 2012b, Mohdee et al., 2019). It is calculated that S.C. for separation of homogeneous palladium catalysts from pharmaceutical industry wastewater by using synergistic recovery phase via HFSLM system was 4.17. under 0.6 mol/L thiourea: 0.1 mol/L hydrochloric.

4.7. Determination of the reaction order and the reaction rate constant for recovery of homogeneous palladium catalysts from pharmaceutical industry wastewater by using synergistic recovery phase via HFSLM system

According to the concept of the reaction order (n) and the reaction rate constant ($k_{r,f}$) for recovery of homogeneous palladium catalysts was determined. The reaction order (n) and the reaction rate constant ($k_{r,f}$) of homogeneous palladium catalysts (Pd(II)) recovery were verified by integration and graphical method (Shukla et al., 2015, Lin and Wang, 2009). The best-fit result was obtained from the integrated first-order rate law at the semi natural logarithm plot between Pd(II) concentration and time. The linear curve was drawn tangentially along the plot, giving a calculated coefficient of determination (R^2) was higher than 0.99 for the recovery reaction. The coefficient of determination (R^2) is always between 0 and 100%:

(a) 0% indicates that the model explains none of the variability of the response data around its mean.
(b) 100% indicates that the model explains all the variability of the response data around its mean.

In general, the coefficient of determination (R^2) is more than 0.7 this value is generally considered strong effect size, the better the model fits the data (Moore et al., 2013). The metal recovery reaction is a reaction that proceeds at a rate that depends on Pd(II)-complex concentration. The results are shown in Table 5. Since the R^2 values of zero, first and second orders were low, pseudo-first order was determined following the literature (Shukla et al., 2015, Lin and Wang,

Fig. 5 Synergistic effects of the combination of acid recovery agent (hydrochloric acid) and organic carrier (thiourea) in recovery phase on separation of homogeneous palladium catalysts under the error of extraction percentage at ±3%.
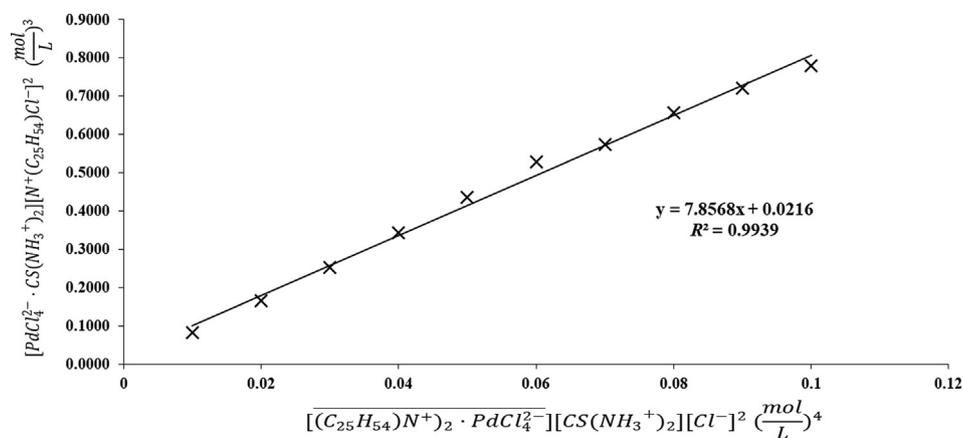
Fig. 6 The equilibrium constant (K_r) of homogeneous palladium catalysts recovery

Table 4 The distribution ratio (D) at the concentration ratio between thiourea: hydrochloric acid.

[thiourea:hydrochloric] (mol/L:mol/L)	0.3:0.1	0.3:0.2	0.3:0.3	0.6:0.1	0.6:0.2	0.6:0.3
The distribution ratio (D)	4.36	4.39	4.42	7.42	7.35	7.03
The synergistic coefficient (S.C.)	3.24	3.25	3.25	4.17	4.12	3.93

Table 5 Analysis of recovery reaction order and rate constants.

		Recovery			
Rate Order		Determination			
	Relationship	Rate constant		R^2	Remark
0	$C_{Pd,0}$ vs. Time*	0.0474	mmol·L^{-1}·min^{-1}	0.9572	
1	ln ($C_{Pd,0}/C_{Pd,}$) vs. Time*	0.0417	min^{-1}	0.9949	**Best Fit**
2	$1/C_{Pd}$ vs. Time*	0.0466	L·mmol^{-1}·min^{-1}	0.9068	

Note * Integral analysis.

2009): the highest R^2 value being 0.9949. Thus, the recovery reaction was pseudo-first order. The rate of molecular interactions between palladium complexes with thiourea in recovery phase is dependent on the concentration of thiourea, as previously reported by Mohdee et al. (2018, 2019, 2020). The reaction rate constant ($k_{r,f}$) for homogeneous palladium catalysts (Pd(II)) recovery is 0.0417 min^{-1}.

5. Conclusions

This study highlighted that the HFSLM system for separation of homogeneous palladium catalysts from pharmaceutical industry wastewater containing synergistic recovery agent (hydrochloric acid and thiourea) was carried out successfully. Percentages of extraction and recovery of homogeneous palladium catalysts were 99.95 and 88.12%, respectively. The kinetics of synergistic recovery phase presented pseudo-first order and a reaction rate constant of 0.0417 min^{-1}. This study confirmed that the optimized condition for the recovery reaction of the reactants is the concentration ratio between thiourea: hydrochloric acid of 0.6 mol/L: 0.1 mol/L. Finally, recovery equilibrium constant (K_r), distribution ratio (D) and synergistic coefficient (S.C.) were determined and provided the values of 7.8568 L/mol, 7.42, and 4.17 respectively.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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