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Study on highly hydrophilic cellulose hollow fiber membrane contactors for thiol sulfur removal

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Abstract

Dispersion-free reactive extraction of thiol compounds from high-sulfur-contained naphtha products into alkali solutions has been studied in a cellulose microporous hollow fiber membrane contactor. A steady extraction was achieved under a long-term operation of one month. The constant partition coefficient of thiol in an infinite dilution between the alkali solution and the oil phase was over 940. In addition, the effects of the tube and shell side hydrodynamics on the mass transfer were investigated. The results indicated that the mass transfer resistance in the oil phase boundary layer contributed to more than 95% of the overall mass transfer resistance, while the membrane resistance only accounted for 2% under the operating conditions. The mass transfer flux of thiol extracted from the real naphtha stream containing 883.4 μg·g⁻¹ of sulfur came to 2.40 ×10⁻⁵ kg·m⁻²·s⁻¹, and the mass transfer coefficient reached 3.91 ×10⁻⁵ m·s⁻¹. The removal
efficiency was up to 99% with octane loss less than 3mg·L⁻¹ when the liquid-liquid volume ratio was 1:1. Furthermore, it was also found that the oil phase flowing at the shell was favorable in fast extraction. A diagram predicting the performance of the contactor for the extraction of sulfur from real naphtha streams was established and the prediction showed a good agreement with the experimental data.

**Key words:** cellulose membrane; hollow fiber membrane contactor; thiol sulfur removal; reactive extraction; mass transfer
1. Introduction

Environmental regulations are becoming increasingly more stringent with respect to the allowable sulfur level in fuels for internal combustion engines. The presence of sulfur impurities in gasoline is undesirable as the fuel combustion results in the release of \( \text{SO}_2 \) which are noxious, corrosive, and therefore, present a serious pollution problem. Moreover, sulfur is a well-known poison for catalytic converters, leading to the increase of the volatile organic compounds (VOCs), \( \text{NO}_x \) and total toxic or foul-smelling emissions \([1,2]\). The sulfur content in motor gasoline has to meet a new sulfur limit of 30ppm with possible further reduction mandated in the near future. As such, it is imperative to explore new and effective technologies for sulfur removal from gasoline to meet emission standards.

Being one of the main components of motor gasoline, naphtha derived from the fluid catalytic cracking (FCC) process contains a substantial amount of sulfur. The levels of sulfur compounds may be up to 4000 ppm or higher. In order to minimize the hydrogenation of alkanes and octane reduction, the naphtha feed has to be pretreated by selective hydrodesulfurization. Over 75 wt. % of the sulfur compounds are normally present as thiol sulfur in the hydrotreated feed \([3]\), which along with other sulfur compounds such as sulfides, disulfides and thiophenes can be converted to hydrogen sulfide. In the various forms of sulfur compounds, thiol sulfur is of fatal toxicity and its upper limit in the atmosphere should be controlled at a level of lower than 10 ppm.
Although columns and other traditional liquid/liquid contactors have been the workhorses for thiol removal in industry for decades, there exist major drawbacks of phase dispersion because of the two liquid phases to be contacted, and limited mass transfer areas. An alternative technology that is expected to have potential to overcome the disadvantages of the conventional equipment is non-dispersive contact via a microporous hollow fiber membrane contactor (HFMC) [4]. In a membrane contactor, the two phases flow on each side of the membrane without phase dispersion, thus avoiding the problems often encountered in the conventional apparatus such as emulsions, foaming, unloading and flooding [5]. The solvent holdup is low, which is an attractive feature when using expensive solvents. Besides, the energy consumption is low and able to treat a large amount of dilute solutions with a small footprint of the equipment. Additionally, the scale-up is more straightforward with membrane contactors.

The attractive characteristics of the membrane contactors have driven considerable research to apply HFMC extraction for the recovery of organic pollutants [6-8], proteins and pharmaceuticals [9, 10], volatile [11-15] and non-volatile [16-19] compounds using hydrophobic polypropylene (PP) membranes; and for the separation of alcohols and organic acids or enzymatic transformation using hydrophilic regenerated cellulose hollow fibers or composite flat membranes [20-25].

However, to our best knowledge, there has been rare report on reactive extraction separation of thiol sulfur from petroleum products using HFMCs, especially for using hydrophilic hollow fiber membranes such as cellulose or chitosan membranes. Cellulose
is known to be the most abundant organic material [26]. It exhibits remarkable hydrophilic property due to three active hydroxyls in each repeating unit of cellulose molecules, which can be seen from its chemical structure formula in Fig.1. Because of the strong hydrogen bonds that occur between cellulose chains, cellulose does not melt or dissolve in ordinary solvents, but solvent N-methylmorpholine N-oxide can physically dissolve cellulose, which was used as the solvent to prepare cellulose membranes via phase inversion method. The details of the membrane preparation can be found elsewhere [27]. It can be seen that the membranes made from cellulose have the characteristics of strong hydrophilicity, solvent resistance and low fouling tendency.

In present work, the separation of thiol sulfur in a simulated naphtha stream using a cellulose membrane hollow fiber contactor has been theoretically and experimentally studied. Based on the quantitative analyses of various mass transport resistances including the oil phase boundary layer diffusion, the membrane diffusion, the aqueous boundary layer diffusion and the interfacial chemical reaction, the dominant resistance and the mass transfer mechanism in the process were discussed. Finally, a diagram prediction for the performance of the contactor to extract sulfurs from real naphtha streams was established and compared with the experimental results.

2. Theory

2.1 Mass transfer with chemical reaction

Membrane extraction is a concentration-driven operation. The mechanism for
extracting thiol with aqueous alkali solutions in the cellulose hollow fiber membrane contactor can be illustrated in Fig.2. Several assumptions have to be made in order to develop the model: (a) the interface is perfectly stable, even at the beginning of extractions when the mass transfer rates are the highest, (b) pore-filling by fluid is uniform throughout the membrane, (c) the two fluids are immiscible with each other, (d) the curvature of the fluid/fluid interface hardly influences the mass transfer, the equilibrium solute distribution or the interfacial area, (e) the partition coefficient of the solute is constant over the concentration range of interest, (f) the mass transfer is described adequately by the simple film type mass transfer coefficients. According to Eq. (1) [28, 29], a typical plot can be built up for the solvent concentration varying semi-logarithmically with time and the overall mass transfer coefficient, $K_{OV}$, can be calculated.

$$\ln\left(\frac{C_e^0}{P-C_f^0}\right) = \ln\left[1 - \exp\left(-4K_{OV}V_m|/d_{m}V_e\right)\right] + (V_f/PV_e)(C_f^0-C_e^0)$$

$$= t \times \frac{1}{1/Q_f - 1/Q_e} \exp\left(\frac{-4K_{OV}V_m|/d_{m}V_e}{1/Q_f - 1/Q_e}\right)$$

During the liquid-liquid extraction, the hypothetical concentration $C_f^*$ in the oil phase is in equilibrium with the actual aqueous phase $C_{ex}$. They are related by the partition coefficient $P$, which expresses the equilibrium state as:

$$P = \frac{C_{ex}}{C_f^*} = \frac{C_{eq}}{C_f^{eq}}$$

This equilibrium parameter $P$ is dependent upon temperature and concentration.
Moreover, $P$ is one of the main criteria for choosing the extractant. The equilibrium state can displace far more towards the extract phase when the partition coefficient is higher.

### 2.2 Model development

#### 2.2.1 Resistance-in-series model in a hollow fiber contactor

The mass transfer in the system involves the following four sequential steps when the oil phase flows in the lumen of the hollow fiber (tube side) and the aqueous phase flows at the shell side: (1) mass transfer from the bulk oil boundary layer to the inside surface of the hollow fiber membrane; (2) interfacial reaction taking place at the interface between the oil phase and the extracting phase; (3) diffusion through the porous membrane and (4) diffusion to the alkali aqueous solution. A resistance-in-series model is used to relate the overall mass transfer coefficient, $K_{OV}$, to the local mass transfer coefficients as follows [30]

$$\frac{1}{K_{OV}} = \frac{1}{k_r} + \frac{1}{k_f} + \frac{1}{P k_m} \left( \frac{d_{i,in}}{d_{1,in}} \right) + \frac{1}{P k_{ex}} \left( \frac{d_{i,in}}{d_{1,out}} \right)$$

where $k_r$ is the effective rate of interfacial reaction at the surface, $k_f$, $k_m$ and $k_{ex}$ are the mass transfer coefficients in the oil boundary layer, the membrane and the aqueous phase, respectively, and $d_{i,in}$, $d_{i,out}$ are the internal and external diameters of the hollow fiber, respectively, and $d_{1,in}$ is logarithmic mean value [31].
2.2.2 Estimation of local mass transfer coefficients

The overall mass transfer coefficient can be calculated based on the individual transfer coefficients $k_r, k_f, k_m$ and $k_{ex}$. $k_f$ is a function of the oil phase flow as it often varies with flow conditions in the fiber lumen, while the fourth term $k_{ex}$ depends on the shell fluid. $k_m$ does not vary with the flows, but it is a function of the hollow fiber properties such as the membrane thickness, porosity and tortuosity. For simplicity, this work focuses on $k_r$ separately. Thus, the contributions of local terms can be normally separated. The following reaction is assumed as the main reaction:

$$RSH(A) + OH^-(B) \rightarrow RS^-(C) + H_2O(D)$$

For hydroxyl concentrations below some critical values, the reaction front is within the aqueous boundary layer. The front would move closer to the liquid/liquid interface as the $[OH^-]$ increases, finally reach the interface when a critical concentration is exceeded. Therefore, it is assumed this chemical reaction occurs instantaneously and fast enough to enhance the mass transfer process with excessive $[OH^-]$. The reaction can be supposed to be a pseudo-one-order chemical reaction; and the rate expression is given by:

$$-r_A = k_r C_{A0} C_{B0} = k_r C_{A0}$$

where $k_r$ denotes the effective rate of the interfacial reaction at the surface, then $(1/k_r)$ is the resistance to this interfacial reaction.

The membrane mass transfer coefficient can be determined by the following
equation [32]:

\[ k_m = \frac{Dc}{\varepsilon} \]  

(5)

For the solute used here, \(D = 9.26 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}\), calculated at 303K using the Wilke and Chang method [33]; Membrane porosity \(\varepsilon\) of the cellulose hollow fiber is tested as 0.9 and tortuosity \(\tau = 1\).

The fluid through the hollow fibers is always at laminar flow. Thus, the local mass transfer coefficient \(k_f\) is dependent on the flow velocity. The Lévêque solution was widely used in the literature [4] to predict tube side mass transfer when the \(Gz > 4\). The Lévêque solution is as follows:

\[
S_{hube} = 1.62 \text{Re}^{0.33} \text{Sc}^{0.33} \left(\frac{d_{h im}}{\ell}\right)^{0.33}
\]  

(6)

Thus, the expression of the tube side mass transfer coefficient \((k_{tube})\) can be:

\[
k_{tube} = 1.62 \left(\frac{Dc^2 \nu}{l d_{im}}\right)^{0.33}
\]  

(7)

At present work, the \(Gz\) number ranges from 20.9 to 104.5.

The shell side mass transfer coefficients in the hollow fiber module can be similarly estimated by adopting the relationships between these dimensionless groups. The prediction of the shell side mass transfer coefficients can be expressed as [34, 35]:

\[
S_{h shell} = \frac{k_{shell} d_h}{D_s} = \beta (1 - \phi) \text{Re}_{shell}^{0.6} \text{Sc}^{0.33} \left(\frac{d_h}{\ell}\right)
\]  

(8)

\(\beta\) is 6.1 for hydrophilic membranes; the ranges of interest are \(0 < Re < 500\) and \(0.04 < \varphi < 0.04\).
0.4. In this work both terms are fulfilled, as Re ranges between 0.18 and 17.5 and $\varphi = 0.357$.

In addition, Kreith & Black [36] studied heat transfer phenomena and deduced a similar correlation for mass transfer in L-L membrane contactor:

$$Sh_{\text{shell}} = 0.39 \text{Re}_{\text{shell}}^{0.59} Sc^{0.33}$$

Therefore, the mass transfer coefficient of shell side could be predicted by the above two correlations, respectively.

3. Experimental

3.1 Reagents and membrane modules

Since the real naphtha is a veritable complex mixture composed of alkanes, cyclopentanes, aromatics and olefins ranging from C$_4$ to C$_{12}$, n-octane was selected as a substitute for naphtha, while ethyl-thiol and octanethiol were chosen as the representative thiol sulfurs in this study.

Experiments were conducted at room temperature (20±2°C) using a hollow fiber UF membrane module. The simulated feedstock solution consisted of n-octane (Medicine Group, Shenyang Chemical Reagent Corporation, China) and 930µg/g thiol (ethyl-thiol 98%, Fluka, France; 1-octanethiol 97%, Acros Organic, US). During the test, the thiol was marked as RSH for short, and R can be any alkyl moiety containing from about 1 to
about 22 carbon atoms. NaOH (Tianjin Kermel Chemial Reagent Development Center, analytical grade) was used as the extractant. The main physicochemical properties of the chosen compounds are given in Table 1.

A dry/wet spinning technique was employed to prepare the cellulose hollow fibers according to the previous work [27]. The details of contactors and UF cellulose fibers are listed in Table 2.

### 3.2 Partition coefficient of RSH

The partition coefficient of RSH between the oil phase and the alkali aqueous solution was determined by contacting 150mL oil phase containing the RSH solute with an equal volume alkali aqueous solution, aiming to reach equilibrium in a separating funnel. Tests were conducted at three different concentrations. The range of initial organic concentrations (from 200 to 1200 ppm) was chosen to cover the range of equilibrium aqueous concentrations obtained during the extraction experiments. After a period of 24h settlement at 20 ± 2°C without mixing, both phases were carefully separated and analyzed by a micro-coulomic instrument accompanied with GC. Mutual mixing of the two phases should be avoided in order to prevent any loss of octane in the aqueous phase. The equilibrium curve of RSH partitioning between the NaOH aqueous solution and the simulated petroleum at 20°C is shown in Fig. 3. According to Eq. (2), the partition coefficient $P$ of RSH was calculated to be over 940 due to the interfacial
reaction at the surface.

3.3 Experimental set-up

A schematic drawing of the membrane-based RSH extraction process is shown in Fig. 4. This system utilized two constant flow pumps to control the flow and stainless steel pressure gauges to measure inlet/outlet pressures. Both the oil phase feedstock and NaOH aqueous solutions from two 250 ml reservoirs respectively were recycled counter-currently. The oil phase flowed through the lumen of the fibers, while the extracting phase circulated through the shell side, wetting the wall of the hydrophilic fibers. The sulfur concentrations in both phases were measured as a function of time by the micro-coulomic instrument.

In order to compare two different patterns of flowing, the feed steam would flow in the tube and then the shell side of the membrane respectively. When feeding in the tube side, a positive static pressure was applied to the organic phase to avoid emulsion formation. It was not necessary to implement accurately since many authors have demonstrated that the pressure difference between the two phases had no influence on the mass transfer [31, 32]. Furthermore, it would be harder to apply such a pressure from the shell side if the aqueous phase running in the tube side.

3.4 Analytical methods
Samples after desulfurizing were analyzed by the micro-columic instrument (WK-2D, Jiangsu, analytical company) and impurities existed in the RSH original reagents were analyzed by a Gas Chromatography (GC7892, Shanghai Tianmei Company) with a flame photometric detector (FPD).

4. Results and discussion

4.1 Structure of the cellulose hollow fiber membrane

SEM images of the cellulose membrane prepared are shown in Fig.5. The cross-sectional structure in Fig.5 (a) and (b) indicates that finger-like micro-voids started from the inner surface towards the exterior of the fiber. Fig.5 (c) shows that the outer top skin layer with a thickness of about 3 μm was supported by a porous substrate and Fig.5 (d) reveals that the outer surface had no visible pores at 10,000 times of magnification. Fig.5 (e) illustrates that the inner surface was microporous. It may be concluded that the outer skin dominated the mass transport resistance of the hollow fiber UF membrane.

4.2 Effects of process parameters on extraction performance

4.2.1 Effect of operating temperature

The relationship between the permeation flux and operating temperature can be normally described by the Arrhenius-type formula: \( J = A \exp(-E_p / RT) \), where \( A \) is the pre-exponential factor, \( E_p \) is the activation energy of permeability, \( R \) is the gas constant, and \( T \) is the absolute temperature. As shown in Fig.6, a linear correlation
existed between the logarithm of the mass transfer flux and the reciprocal of the absolute operating temperature with a slope \( (E_p) \) of 7.18 kJ·mol\(^{-1}\), and the pre-exponential factor \( A \) was 1.7 kg·m\(^{-2}\)·h\(^{-1}\).

### 4.2.2 Effect of alkali aqueous solution concentration

Variations of RSH overall mass transfer coefficient and flux as a function of the NaOH concentration are shown in Fig. 7. The extraction module didn't perform well when the NaOH concentration was low. When the concentration increased to 0.2 mol·L\(^{-1}\), the performance started to improve, and the best result was observed at the concentration range of 0.5~1.25 mol·L\(^{-1}\) where the performance of the system was relatively stable. With a further increase of the concentration to 2 mol·L\(^{-1}\) or higher, the mass transfer flux increased dramatically. It was not surprising to see such results. As the membrane used was very hydrophilic, it was wetted completely by pore-filling fluid (NaOH solution). The interface of the oil/NaOH phases was at the inner surface of the membrane. Thus, the thiol solute in the oil phase at the lumen of the membrane can react with NaOH directly without any hindrance by the membrane.

In order to ensure a stable and long-term running of the module, 0.75 mol·L\(^{-1}\) was chosen as the test concentration and the interfacial reaction at this NaOH concentration level was assumed to be instantaneous and fast. Based on Eq. (1), the experimental overall mass transfer coefficient was estimated to be 3.50 \( \times \) 10\(^{-5}\) m·s\(^{-1}\), which was at the same magnitude as that (3.81 \( \times \) 10\(^{-5}\) m·s\(^{-1}\)) predicted by the model using \( k_f \), \( k_m \) and \( k_s \) terms
and ignoring $k_r$ term in Eq. (3). Thus, the resistance caused by reaction at the interface was negligible and not considered in the following experiments. Moreover, this result would be testified by the theoretical values according to Eqs. (4), (5), (7) and (8) later.

4.2.3 Effects of feeding and extracting flow rates

Fig. 8 depicts the extraction kinetic curves obtained for (a) different extracting phase flows at the shell side and (b) different oil phase flows at the tube side. During the tests, the flow rates of both phases were alternately adjusted with other parameters being kept constant. The shell side $Re$ number ranged from 0.18 to 18, and the tube side (the oil phase) $Re$ number ranged from 3.1 to 76.3. It was found that the extraction efficiency was hardly influenced by the variation of the extracting flow rate, while it changed dramatically with increasing the flow rate of the oil phase, as shown in Fig. 8 (b).

This result suggested that the predominant resistance of the whole transfer process lied in the oil boundary layer. It might be attributed to the effect of the much higher equilibrium concentration of the RSH in the NaOH aqueous solution than in n-octane, and the highly hydrophilic property of the cellulose membrane. The high partition coefficient made the diffusion steps that took place in the extractant phase much faster compared with the diffusion of the RSH solute from the bulk oil phase to the organic–aqueous interface, which was the controlling step of the whole transfer process.

4.2.4 Effect of the oil phase flowing at the tube side or the shell side
Fig. 9 shows the overall mass transfer coefficients $K_{OV}$ obtained from the simulation using the resistance-in-series model and from two sets of experiments. In these experiments, the oil phase flowed at either the tube side or the shell side, while the flow rate of the NaOH aqueous phase was maintained constant. It can be seen that the simulated results presented a good agreement with the experimental data.

Though the $Re$ number was about ten times lower at the shell side compartment than at the tube side (mainly due to the calculation being based on a superficial velocity), the two sets of experiments gave a similar tendency of the overall mass transfer coefficients varying with the feed flow rate or $Re$. However, the contacting interfacial areas offered to the mass transfer were different in the two cases. The membrane was entirely wetted by the aqueous phase when it flowed outside the fibers. Thus, the oil phase contacted with the aqueous extracting phase through the inner surface of the fibers with a surface area of 62.4 cm$^2$. On the other hand, the contact surface area was 93 cm$^2$ when the oil phase flowed at the shell side. Obviously, the larger contacting area is favorable for the mass transfer and the oil phase flowing at the shell was thus preferred for a higher flow rate.

4.2.5 Long-term operation of extraction

In order to find out whether the physical structure of the membranes or the overall mass transfer flux was changed after contacting the organic solvent for a long time, the batch experiment was repeated over one month of time. As shown in Fig. 10, the
extraction performance was excellent and stable during the long time operation of one month, which indicated that the membranes made from cellulose possessed the characteristics of solvent resistance and anti-fouling, as they were able to resist the oil pollution and endure severe alkali solutions. Thus, the cleaning cost of the membrane contactor can be reduced significantly.

4.2.6 Distribution of the local mass transfer resistances

Fig.11 shows the distribution of the local mass transfer resistances as a function of NaOH concentration. The reaction resistance \(1/k_r\) could reach more than 80% of the overall resistance when the concentration was lower than 0.25 mol\(\cdot\)L\(^{-1}\), suggesting that it was the controlling step at a low NaOH concentration. When the NaOH concentration was around 0.75~2.5 mol\(\cdot\)L\(^{-1}\), the resistance in the oil phase \(1/k_f\) represented more than 95% of the total mass transfer resistance. Meanwhile the membrane resistance \(1/k_m\) contributed to about 2% of the total resistance for the transfer of thiol at any NaOH concentration used. This is because the surface reaction in the membrane-based extraction system was instantaneous or fast enough at a higher NaOH concentration. Therefore, the local resistance caused by the reaction can be ignored.

The experimental overall mass transfer coefficients \(K_{OV}\) obtained with different NaOH concentrations and the corresponding local mass transfer coefficients calculated using Eqs. (4), (5), (7) and (8), respectively, are also presented in Table 3. The mass transfer coefficient of the surface reaction was two-magnitude larger than the overall
coefficient $K_{OV}$ when the NaOH concentration was as high as 1.5 mol·L⁻¹.

4.3 Comparison of different empirical correlations

The resistance-in-series model (Eq. (3)) was used to predict the overall mass transfer coefficient by estimating each local mass transfer coefficient. The Lévêque equation was chosen to determine the tube side mass transfer coefficient. The relation given by Kiani et al. [32] was also used widely in the literature for determining the mass transfer coefficients of various microporous membranes. Eq. (8) proposed by Prasad and Sirkar [34] and Eq. (9) proposed by Kreith and Black [36] were used to predict the shell side mass transfer coefficient, respectively, for comparison.

The mass transfer coefficients predicted by either Eqs. (5), (7) and (8) (dash lines) or Eqs. (5), (7) and (9) (solid lines) are given in Fig.12 and 13 along with the experimental data as a function of the flow rates of the oil phase and the aqueous extracting phase, respectively. It was found that the experimental overall mass transfer coefficient varied from $2 \times 10^{-5}$ to $7 \times 10^{-5}$ m·s⁻¹, which were at the same order of magnitude as those given in the literature for different systems [18, 37]. In addition, it can be seen that the mass transfer coefficients predicted by the two sets of the empirical correlations were in a good agreement with the experimental data, especially at a higher flow rate of the oil or the aqueous phase.

The two sets of the empirical correlations gave very close predictions of the overall
mass transfer coefficient. Actually, the selection of a correction for predicting the shell side mass transfer was not so critical as the operation was controlled by the diffusion in the oil boundary layer at the tube side. Indeed, whatever the shell side correlation was used, the local oil mass transfer resistance represented about 95% of the total resistance.

4.4 Sulfur removal from real FCC naphtha streams

Fig. 14 shows the sulfur extraction results from real fluid catalytic cracked (FCC) naphtha streams at Dalian refinery in China using the cellulose hollow fiber membrane contactor. By using the correlations justified from the simulated naphtha, the mass transfer fluxes of the thiol from the different FCC naphtha streams with different initial sulfur contents were also estimated theoretically.

The mass transfer flux obtained in the experiment came to $2.40 \times 10^{-5}$ kg·m$^{-2}$·s$^{-1}$ with initial sulfur content of 883.4 µg·g$^{-1}$ in the naphtha, and corresponding mass transfer coefficient reached $3.91 \times 10^{-5}$ m·s$^{-1}$. The removal efficiency was up to 99% with an oil loss less than 3mg·L$^{-1}$ (tested by Chemical Oxygen Demand Meter, LOVIBON) when the liquid-liquid volume ratio was 1:1. The predicted results were also in a good agreement with the experimental data, especially for the streams containing high sulfur contents.

5. Conclusions

The removal of thiol from simulated naphtha could be steadily conducted by
reactive extraction using a cellulose hollow fiber UF membrane contactor. The constant partition coefficient of thiol in an infinite dilution between the alkali solution and the oil phase was over 940. The parameters that influenced the performance of the membrane contactor have been investigated. It was found that the overall mass transfer coefficient increased rapidly with increasing the alkali solution concentration to 0.5 mol•L⁻¹ and then reached a relatively stable stage in the range of 0.5 ~1.25 mol•L⁻¹, where the interfacial reaction became instantaneous and fast so that its local resistance \(1/k_r\) could be ignored. The overall mass transfer coefficient was also influenced significantly by the oil phase flow rate at the tube side, while the variation of the aqueous phase flow rate had almost no impact on it. The oil phase resistance represented up to 95% of the overall mass transfer resistance, while the membrane resistance only contributed to 2%. The oil phase flow at the shell was favorable in fast extraction. The comparison of different empirical correlations shows that the two sets of the correlations agreed well with experimental results. The membrane contactor exhibited a stable extraction performance over one month of operation, indicating that the membranes made from cellulose possessed the characteristics of solvent resistance and anti-fouling. It was also used for sulfur extraction from real fluid catalytic cracked naphtha streams in industry. A diagram predicting the performance of the contactor for the extraction of sulfur from real naphtha streams was established and it showed a good agreement with the experimental data.

Acknowledgements

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Nomenclature

$A$  
pre-exponential factor of Arrhenius formula, $\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$

$A_m$  
membrane area in the module, $\text{m}^2$

$C_{40}$  
concentration of reactant thiol at instant $t$, $\text{kg} \cdot \text{m}^{-3}$

$C_{80}$  
concentration of reactant NaOH at instant $t$, $\text{kg} \cdot \text{m}^{-3}$

$C_{ex}^0$  
concentration of the solute in extract solution at a given instant $(t = 0)$, $\text{kg} \cdot \text{m}^{-3}$

$C_{ex}$  
concentration in extracting phase, $\text{kg} \cdot \text{m}^{-3}$

$C_{ex}^{eq}$  
equilibrium concentration in extracting phase, $\text{kg} \cdot \text{m}^{-3}$

$C_f$  
concentration of the solute at instant $t$, $\text{kg} \cdot \text{m}^{-3}$

$C_f^0$  
concentration of the solute in feed, at a given instant $(t = 0)$, $\text{kg} \cdot \text{m}^{-3}$

$C_f^*$  
hypothetical concentration in oil phase in equilibrium with extracting phase, $\text{kg} \cdot \text{m}^{-3}$

$C_f^{eq}$  
equilibrium concentration in oil phase, $\text{kg} \cdot \text{m}^{-3}$

$d_h$  
hydraulic diameter, $\text{m}$

$d_{in}$  
internal diameter of the hollow fiber, $\text{m}$

$d_{lm}$  
logarithmic mean value, $\text{m}$

$d_{out}$  
external diameter of the hollow fiber, $\text{m}$

$D_s$  
diffusion coefficient of the solute in shell side, $\text{m}^2 \cdot \text{s}^{-1}$

$D_t$  
diffusion coefficient of the solute in tube side, $\text{m}^2 \cdot \text{s}^{-1}$

$e$  
membrane thickness, $\text{m}$

$E_P$  
activation energy of permeability, $\text{kJ} \cdot \text{mol}^{-1}$

$G_z$  
Graetz number

$k_{ex}$  
local mass transfer coefficient in extracting phase, $\text{m} \cdot \text{s}^{-1}$

$k_f$  
local mass transfer coefficient in oil boundary layer, $\text{m} \cdot \text{s}^{-1}$

$k_m$  
Local mass transfer coefficient in membrane, $\text{m} \cdot \text{s}^{-1}$

$K_{ov}$  
overall mass transfer coefficient, $\text{m} \cdot \text{s}^{-1}$
\( k_r \) effective rate of interfacial reaction at the surface, m\( \cdot \)s\(^{-1} \)

\( \ell \) fiber length, m

\( J \) mass transfer flux, kg\( \cdot \)m\(^{-2} \)\( \cdot \)s\(^{-1} \)

\( P \) liquid–liquid partition coefficient

\( Q_f \) volumetric feeding flow rate, m\(^3\)\( \cdot \)s\(^{-1} \)

\( Q_e \) volumetric extracting flow rate, m\(^3\)\( \cdot \)s\(^{-1} \)

\( R \) gas constant, kJ/(kmol\( \cdot \)K)

\( Re \) Reynolds number, \( \nu d/\eta \)

\( Sc \) Schmidt number, \( \eta /D \)

\( Sh \) Sherwood number, \( kd/D \)

\( t \) time, s

\( T \) absolute temperature, K

\( \nu \) fluid velocity, m\( \cdot \)s\(^{-1} \)

\( V_e \) extract volume, m\(^3\)

\( V_f \) feed volume, m\(^3\)

**Greek letters**

\( \beta \) constant in Eq. (8)

\( \varepsilon \) membrane porosity

\( \varphi \) module packing density

\( \eta \) dynamic viscosity, Pa\( \cdot \)s\(^{-1} \)

\( \mu \) kinematic viscosity, m\(^2\)\( \cdot \)s\(^{-1} \)

\( \rho \) fluid density, kg\( \cdot \)m\(^{-3} \)

\( \tau \) membrane tortuosity
References:


Table 1. Representative properties of the compounds studied

<table>
<thead>
<tr>
<th>Compound</th>
<th>n-Octane</th>
<th>Ethyl-thiol</th>
<th>1-Octanethiol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural-formula</td>
<td>CH₃(CH₂)₆CH₃</td>
<td>C₂H₅SH</td>
<td>C₈H₁₇SH</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>Analytical grade</td>
<td>98%</td>
<td>97%</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>-56.795</td>
<td>-147.89</td>
<td>49.2</td>
</tr>
<tr>
<td>Freezing point (°C)</td>
<td>15.6</td>
<td>&lt;0</td>
<td>68</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>125.665</td>
<td>35</td>
<td>197-200</td>
</tr>
<tr>
<td>Density at 20°C(kg·m⁻³)</td>
<td>702.52</td>
<td>839.1</td>
<td>843</td>
</tr>
<tr>
<td>Refractive index, nD²⁰</td>
<td>1.397</td>
<td>1.431</td>
<td>1.452</td>
</tr>
<tr>
<td>Viscosity at 20°C(cP·s)</td>
<td>0.58</td>
<td>0.293</td>
<td>1.33</td>
</tr>
</tbody>
</table>

* The impurities in reagents could be analyzed by gas chromatography (GC)
Table 2. Details of the hollow fiber membrane and the contactor

<table>
<thead>
<tr>
<th>i) Hollow fiber membrane</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic diameter (mm)</td>
<td>15</td>
</tr>
<tr>
<td>Fiber inner diameter (mm)</td>
<td>1.2</td>
</tr>
<tr>
<td>Fiber wall thickness (μm)</td>
<td>300</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>89.95</td>
</tr>
<tr>
<td>Pore size (nm)</td>
<td>17.56</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ii) Membrane contactor</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of fibers</td>
<td>Cellulose</td>
</tr>
<tr>
<td>Type of potting</td>
<td>Epoxy</td>
</tr>
<tr>
<td>Module diameter (cm)</td>
<td>4</td>
</tr>
<tr>
<td>Module length (cm)</td>
<td>30</td>
</tr>
<tr>
<td>Effective fiber length (cm)</td>
<td>20</td>
</tr>
<tr>
<td>Number of fibers</td>
<td>10</td>
</tr>
<tr>
<td>Effective interfacial area (cm²)</td>
<td>62.4</td>
</tr>
</tbody>
</table>
Table 3. Overall and local mass transfer coefficients at different NaOH concentrations ($T=20^\circ\text{C}$, $Q_f=1\text{ mL/min}$, $Q_{ex}=5\text{ mL/min}$)

<table>
<thead>
<tr>
<th>NaOH, (mol$\cdot$L$^{-1}$)</th>
<th>0.025</th>
<th>0.125</th>
<th>0.25</th>
<th>0.5</th>
<th>0.75</th>
<th>1</th>
<th>1.25</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^5K_{OV}, (\text{m}\cdot\text{s}^{-1})$</td>
<td>0.71</td>
<td>2.33</td>
<td>3.07</td>
<td>3.53</td>
<td>3.61</td>
<td>3.65</td>
<td>3.70</td>
<td>3.71</td>
</tr>
<tr>
<td>$10^5k_r, (\text{m}\cdot\text{s}^{-1})$</td>
<td>0.88</td>
<td>6.16</td>
<td>17.11</td>
<td>61.60</td>
<td>100.49</td>
<td>142.27</td>
<td>288.91</td>
<td>365.92</td>
</tr>
<tr>
<td>$10^5k_b, (\text{m}\cdot\text{s}^{-1})$</td>
<td>3.90</td>
<td>3.90</td>
<td>3.90</td>
<td>3.90</td>
<td>3.90</td>
<td>3.90</td>
<td>3.90</td>
<td>3.90</td>
</tr>
<tr>
<td>$10^5k_{ex}, (\text{m}\cdot\text{s}^{-1})$</td>
<td>34.20</td>
<td>34.20</td>
<td>34.20</td>
<td>34.20</td>
<td>34.20</td>
<td>34.20</td>
<td>34.20</td>
<td>34.20</td>
</tr>
<tr>
<td>$10^5k_m, (\text{m}\cdot\text{s}^{-1})$</td>
<td>262.0</td>
<td>262.0</td>
<td>262.0</td>
<td>262.0</td>
<td>262.0</td>
<td>262.0</td>
<td>262.0</td>
<td>262.0</td>
</tr>
</tbody>
</table>
Fig. 1. Chemical structure formula of cellulose ($\text{C}_6\text{H}_{10}\text{O}_5)_n$
Fig. 2. Concentration profiles of the reactive species in the extraction module
Fig. 3. Equilibrium curve of RSH partitioning between the NaOH aqueous solution and the simulated petroleum at 20°C
Fig. 4. Schematic diagram of the experimental setup
8, 9. Sampling points
Fig. 5. SEM images of the cellulose hollow fiber membrane.
Fig. 6. Effect of operating temperature on RSH mass transfer flux $J$
Fig. 7. Effect of NaOH concentration on RSH removal and overall mass transfer coefficient

\( T=20^\circ C, \text{ oil/aqueous volume ratio}=3:1, Q_f=5 \text{ mL•min}^{-1}, Q_{ex}=1 \text{ mL•min}^{-1} \)
Fig. 8. RSH extraction kinetics: RSH concentration in oil phase as a function of time
(20±2°C, oil/aqueous volume ratio=3:1):
(a) different extract phase flows ($Q_f=4.99\text{mL}\cdot\text{min}^{-1}$); (b) different oil phase flows ($Q_{ex}=5\text{mL}\cdot\text{min}^{-1}$).
Fig. 9. Influence of shell side (a) and tube side (b) feed phase flowrate on RSH overall mass transfer coefficient, oil/aqueous volume ratio=3:1 ( ■ : tube side; ▲ : shell side; - : simulated)
Fig. 10. Long-term operation of thiol sulfur removal in the membrane module with oil/aqueous volume ratio=3:1, $T=20^\circ$C, $Q_f=5$ mL•min$^{-1}$, $Q_{ex}=1$ mL•min$^{-1}$.
Fig. 11. Effect of NaOH concentration on distribution of local mass transfer resistances

\( T = 20^\circ C \), oil/aqueous volume ratio = 3:1, \( Q_f = 5 \text{ mL min}^{-1} \), \( Q_{ex} = 1 \text{ mL min}^{-1} \)

- ♦ - reaction resistance \( (1/k_r) \)
- ▲ - oil phase resistance \( (1/k_f) \)
- ● - membrane resistance \( (1/k_m) \)
Fig. 12. Predicted and experimental overall mass transfer coefficients as a function of oil phase Re ($T=20^\circ\text{C}$, $Q_{ex}=1\text{mL}\cdot\text{min}^{-1}$)

(×) experimental; (---) Eqs. (5), (7) and (8); (—) Eqs. (5), (7) and (9).
Fig. 13. Predicted and experimental overall mass transfer coefficients as a function of extracting phase Re ($T=20^\circ$C, $Q_f=5$ mL$\cdot$min$^{-1}$).

(*) experimental; (---) Eqs. (5), (7) and (8); (—) Eqs. (5), (7) and (9).
Fig. 14. Mass transfer flux $J$ of sulfur from real naphtha streams with different sulfur contents

$T=20^\circ C$, oil/aqueous volume ratio = 3:1, $Q_f = 5 \text{ mL}\cdot\text{min}^{-1}$, $Q_{ex} = 1 \text{ mL}\cdot\text{min}^{-1}$