# THE EFFECTS OF SYNERGISTIC EXTRACTANTS ON THE DISPOSAL OF ARSENIC IN PRODUCED WATER FROM CRUDE OIL PRODUCTION VIA HOLLOW FIBER CONTACTOR MODULES

**[1]CHANET WORABOOT, [2]URA PANCHAROEN**

[1,2]Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University,
Patumwan, Bangkok 10330, Thailand
E-mail: chanetwr@hotmail.com, ura.p@chula.ac.th

**Abstract-** This research proposes the effectiveness of synergistic extractants on the separation of arsenic ions in produced water from crude oil production via hollow fiber contactors modules (HFCM). Aliquat 336 and Cyanex 921 dissolved in kerosene were used as the organic extractants. The maximum extraction was obtained 84% by using 0.15 M Aliquat 336 mixed with 0.1 M Cyanex 921.

**Keywords-** Synergistic Extractant, Arsenic, Hollow Fiber Contactor Modules

## I. INTRODUCTION

The petroleum production system brings about waste by-products such as water which is contaminated. This water is known as “produced water” and contains significant amounts of heavy metal such as mercury, arsenic and cadmium. The presence of arsenic is detrimental to the petroleum production system and can be damaging for both people’s health and the environment. So, the development of water treatment processes is necessary for obtain greater efficiency for remove hazardous material prior discharged to the environment. In terms of water treatment standard, produced water from crude oil operation processes must be passed according to the legislation discharge of industrial effluent which must be less than 0.25 mg/L which is the permissible discharge limit of industrial wastewater in Thailand.
Carbon adsorption, air stripping, solvent extraction, chemical oxidation and biological treatment are general processes used for water treatment prior re-injected into the reservoir.

Arsenic is one hazardous material from produced water. Many researchers have studied and found out the way to improve the separation efficiency of arsenic. Pérez et al. used synthetic feed solution from sulphuric acid extracted arsenic via supported liquid membrane with Cyanex 921 as an extractant. Poonkum et al. used waste water from gas separation plant and chose Aliquat 336 to study via hollow fiber supported liquid membrane. This work reported the highest removal rate of 91%. Papasawat used Cyanex923 as organic extractant for remove As(III) and As(V) from synthetic water via hollow fiber supported liquid membrane; the extraction results were 40% and 64% respectively. Ballinas et al. used Ailquat 336 as an organic reagent for extracted As(v) via polymer inclusion membrane (PIM) ,highest extraction was obtained 90%.

Hollow fiber contactor is noted as a device, which have higher rate of mass transport because of its contact area per volume is about 10,000 m2 per m3 and capable to remove metal ion in very low concentration level. Mass transport mechanism of the separation via hollow contactor module consists of 2 phases. The first phase is the feed phase and the second phase is the organic phase. The extractant in the organic phase will be circulated in the shell cavity and poured into the microporous membrane. The type of extractant used should be is one that can influence extraction efficiency. Other researchers have found that a combination of one or more extractants made its efficiency increase. This research therefore aims to study the effect of synergistic extractants on arsenic separation via hollow fiber modules.

## II. THEORY

The extraction of Arsenic by Aliquat 336 at the feed–liquid-membrane interface is described by Eq. (1) , Eq. (2) Eq. (3)

As(III) $$H_3AsO_3 + \overline{CH_3R_3NCl} \rightleftharpoons \overline{(CH_3R_3NCl)(H_3AsO_3)} \quad (1)$$

As(V) $$H_2AsO_4^- + \overline{CH_3R_3N^+ \cdot Cl^-} \rightleftharpoons \overline{(CH_3R_3N^+)(H_2AsO_4^-)} + Cl^- \quad (2)$$

$$HAsO_4^{2-} + \overline{2(CH_3R_3N^+ \cdot Cl^-)} \rightleftharpoons \overline{(CH_3R_3N^+)_2(HAsO_4^{2-})} + 2Cl^- \quad (3)$$

2.1 Calculation of experimental result

The following formula is reference for calculation percentage of extraction of arsenic ion

$$\%Extraction = \frac{Cf,in - Cf,out}{Cf,in} x100$$

$$\%\ Recovery = \frac{Cs,out}{Cf,in} x\ 100$$

where Cf,in, Cf,out are the inlet and outlet of metal ions concentration in the feed phase. Cs,out is concentration of metal ion at outlet stripping solution

## III. EXPERIMENTAL

3.1 Chemical

Aqueous feed is produced water from crude oil production process. Inductively Coupled Plasma Spectroscopy (ICP) used as equipment for check chemical compositions.

Methyltrioctylammonium chloride (Aliquat 336),Trioctylphosphine oxide (Cyanex921) and Mixture of tertiary octyl and hexyl phosphine oxides (Cyanex923) were the extractants chosen for study and kerosene was used as diluent. Stripping solution is triourea dissolved in De Ionized water.Hydrochoric acids, Sulpuric acid were used for pH adjustment.

3.2 Apparatus

Hollow fibers contactor module made by Liqui_Cel®. 35,000 fibers microporous polypropylene built inside the fabric and wrapped around a central feeder tube in order to supply the shell-side fluid. Two modules of Liqui_Cel® were applied on these experimental. Characteristic of Liqui_Cel® modules show in table 1.

| Properties | Details |
|---|---|
| Material | Polypropylene |
| Pore size | 0.05 µm |
| Porosity | 30% |
| Contact Area | 1.4 $m^2$ |
| Area per Unit volume | 29.3 $cm^2/cm^3$ |
| Length | 20.3 cm |
| Inside diameter (fiber) | 0.24 mm |
| Outside diameter(fiber) | 0.30 mm |

Table 1: Characteristic of Liqui_Cel® modules

3.3 Procedure

Set up two modules of Celgard®x-30 240 micro porous polypropylene hollow fibers as shown in figure 1. Feed solution is fed inlet to tube side of the first column. Feed‘s pH were checked by pH meter, and value was adjusted by hydrochloric acid or Sodium hydroxide. Organic reagents are vary between Methyltrioctylammonium chloride (Aliquat 336),Trioctylphosphine oxide (Cyanex921) and Mixture of tertiary octyl and hexyl phosphine oxides (Cyanex923) dissolved in kerosene then counter - current fed into shell cavity of the first column. The outlet organic solution is defined to travel in shell side of second hollow fiber column. Meanwhile, in tube cavity of this column is conducted by stripping solution, which was pumped in from its reservoir.

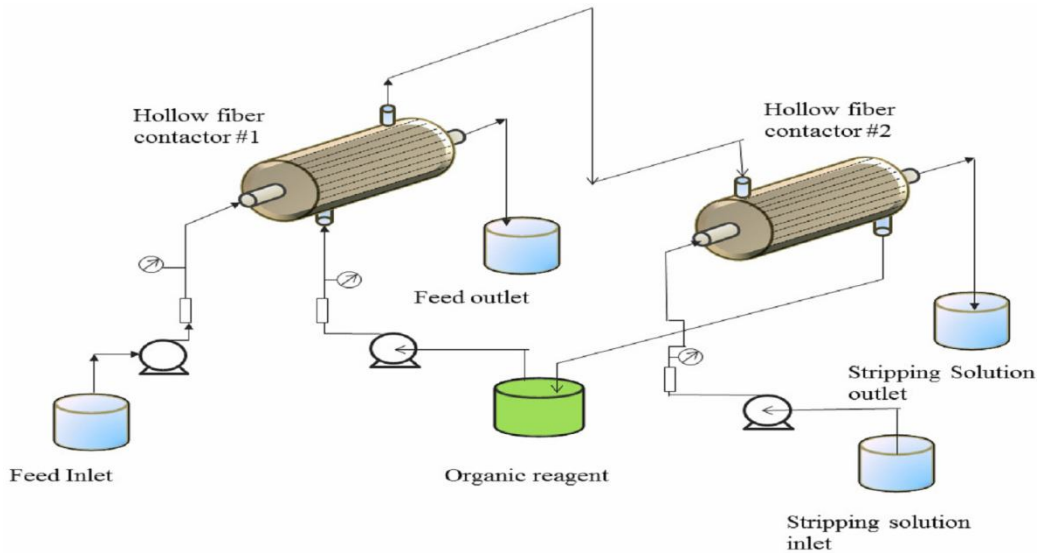


**Fig. 1. Schematic of hollow fiber contactor operation system, Celgard®x-30 240 microporous polypropylene hollow fibers**

## IV. RESULT AND DISCUSSION

4.1 Effect of extractants

Laboratory reported extraction percentage of arsenic are 68% with Cyanex 921, 48% with cyanex923 and 80% by Aliquat 336. Percentage of stripping by used Triourea 0.1 M dissolved in de ironized water as a stripping solution shown as 39%, 33% and 43% respectively.

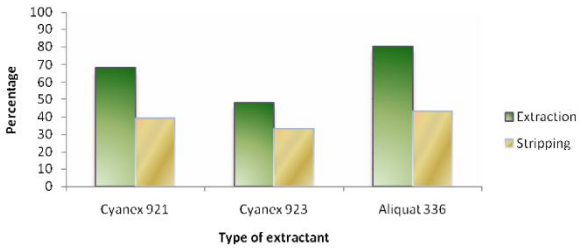


**Fig. 2: Effect of each extractants on arsenic separation, With initial arsenic concentration in feed phase was 350 ppb ,Triourea 0.1 M dissolved in DI water used for stripping reagent. Flow rate of feed was 100 ml/min**

4.2 Effect of Mixture

Experimental determined effect of synergistic extractant by vary each mixture of extractant types and find out the optimum mixed rate .Testing result shown mixture between 0.9M Aliquat 336 and 0.1M Cyanex 923 is 63%, 0.15 M Aliquat 336 with 0.1M is 84% and 0.2 M Cyanex 921 with 0.1 M Cyanex 923 is 72%.In order to percentage of stripping are 31%,43% and 39% respectively.

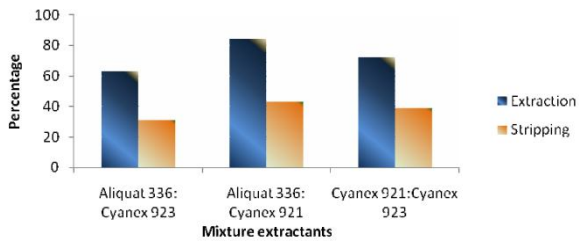


**Fig. 3: Effect of synergistic extractants on extraction of arsenic, With initial arsenic concentration in feed phase was 450 ppb, Triourea 0.1 M dissolved in DI water used for stripping reagent. Flow rate of feed was 100 ml/min**

## CONCLUSION

Hollow fiber contactor modules are capable to separated arsenic from produced water. The optimum synergistic extractants is mixture of 0.15M Aliquat 336 and 0.1 M Cyanex 921, Percentage of extraction is presented at 84 % and stripping by using triourea 0.1M is 43%.

## REFERENCE

[1] S.Frankel, J.Concannon, K.Brusky, E.Peitrowicz, S.Giorgianni, W.Douglas Thompson,Douglas A Currie, Arsenic exposure disrupts neurite growth and complexity in vitro: Neuro Toxicology 30(2009)529-537.

[2] Chung-Min Liao, Arsenic cancer risk posted to human health from tilapia consumption in Taiwan, Ecotoxicology and Environmental Safety 70 (2008) page 27-37.

[3] Jack C.Ng, Jianping Wang, Amjad Shraim.A global health problem cause by arsenic from natural sources: Chemosphere 52 page 1353-1359 (2003).

[4] M.E.M.Parez, J.A.RAgulilera, T.I.Saucedo, M.P.Gonzales, R.Navarro, M.A.Rodriguez, Study of As(V) transfer through a supported liquid membrane impregnated with trioctylphosphin oxide (Cyanex -921),Journal of Membrane Science 302 (2007) page 119-126.

[5] W.Poonkum, U.Pancharoen, A.W.Lothongkum, Treatment of arsenic ions from produced water through hollow fiber supported liquid membrane, Journal of Alloy and Compounds 482 (2009) 328-334.

[6] M.E.M Pere, J.A.R.Aguilera, T.I.Saucedo, M.P.Gonzalez, R.Navarro, M.A.Rodriguez, Study of As (V) transfer through a supported liquid membrane impregnated with trioctylphosphine oxide (Cyanex921);Journal of membrance science 302 (2007) page 119-126.

[7] Tatchanok Prapasawat, Prakorn Ramakul, Chairit Satayaprasert, Ura Pancharoen and Anchaleeporn W. Lothongkum, Separation of As(III) and As (V) by hollow fiber supported liquid membrane based on the mass transfer theory,Korean J.Chem.Eng 25(1) page 158-163 ( 2008).

[8] M.L.Ballinas, E.R.De san Miguel,M.T. De jess rodriguez,O.Silva,M.Muoz,J.de gyves,Arsenic(V) removal with polymer inclusion membranes from sulfuric acid media using BBP as carrier;Enviromental Science Technology 38(2004) page 886-889.

[9] S.K.Gupta, N.S.Rathore, J.V.Sonawane,Anil Kumar, R.R.Sinh, A.K.Venugopalan and P.K.Dey, Hollow fiber membrane contactor:Novel extraction device for plutonium extraction, Nuclear Recycle Group, Radiation Chemistry & Chemical Dynamic Devision,Bhabha Atomic Reseach Center, Tarapur.

[10] R.Klaassen, P.H.M.Feron and A.E.Jansen, Membrane contactors in industrial application;Chemical Engineering Research and Design 83 (A3) 234-246.

[11] K.Soldenhoff, M.Shamieh, A.Mains, Liquid Liquid extraction of cobalt with hollow fiber contactors;Journal of Membrane Science 252 (2005) 183-194.

[12] S.Bey, A.Criscuoli, A,Figoli, A.Leopold, S.Simone, M.Benamor, E.Drioli, Removal of As(V) by PVDF hollow fibers membrane contactors using Aliquat-336 as extractant;Desalination264(2010) page 193-200.

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