

# Removal of Toxic Organic Compounds contained in Water using Magnetic Particles

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水中に含まれる有害有機化合物の磁性粒子による除去

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まず、四酸化三鉄の超微粒子に両親媒性のグラフト共重合体を被覆した構造の磁性粒子を調製し、磁性粒子(重合体部分)–水間における有機化合物(トルエンおよびフェノール)の平衡関係を実測した。有機化合物の分配は磁性粒子側に大きく偏っていた。ついで、この平衡関係を用いて向流多段接触による水中の有機化合物の除去計算を行った。本分離法により水中の有機化合物を低濃度にまで除去できる結果を得た。

## 1. Introduction

Removals of contaminants in water are quite important in various aspects such as drinking water, industrial water, and wastewater. Although there are a lot of water treatment techniques, the problems of the water contaminants have become so diverse that new techniques should be developed and applied to the respective problems.

To remove the organic contaminants in water, Moeser et al. proposed the treatment with hydrophilic magnetic nanoparticles<sup>1)</sup>. The magnetic fluids are colloidal dispersions of magnetic nanoparticles (<10 nm) which are coated with amphiphilic graft copolymer. Due to this structure, the particles disperse stably in an aqueous phase as colloid, extract organic components into their lipophilic polymer part, and can be recovered with a magnetic field from water.

In this study, the magnetic particles were prepared, the solubility of toxic organic compounds, toluene and phenol, in the magnetic particles were measured, and with these experimental results, the calculation of multi-stage countercurrent contact operation was carried out to know the feasibility of this technique.

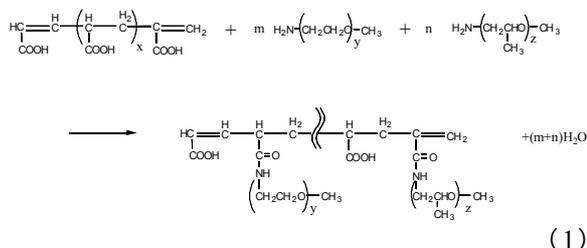
## 2. Equilibrium of Organic Compounds between Water and Magnetic Particles

### 2.1. Experiments

Poly(acrylic acid)(PAA;  $M_w=5000$ ), iron(III) chloride hexahydrate(99%), iron(II) chloride tetrahydrate(99%), sodium hydroxide(96%), heptane(99.0%), phenol(99.0%), toluene(99.5%) were obtained from Wako Corp.. Ammonium hydroxide(29.5 wt% in water) was obtained from Aldrich. Jeffamine XTJ-506(PEO/PPO-NH<sub>2</sub>, EO:PO=6.3:1,  $M_w=1000$ ) and Jeffamine XTJ-507(PEO/PPO-NH<sub>2</sub>, EO:PO=1:4.8,  $M_w=2000$ ) were obtained from Huntsman Corp..

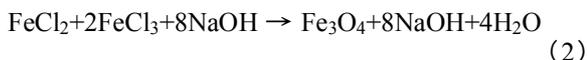
The amino-terminated PEO and PPO polymers used in this work consisted of random copolymers of ethylene oxide(EO) and propylene oxide(PO) repeats units. XTJ-506 contained 6.3 EO units per PO unit, so its character is similar to that of a pure PEO chain. The polymer designated XTJ-507 is a random copolymer with 4.8 PO units per EO unit. In this work, we consider the polymer to be equivalent to pure PEO and PPO polymer chains and designate XTJ-506 as PEO-NH<sub>2</sub> and XTJ-507 as PPO-NH<sub>2</sub> for simplicity.

The graft copolymers were produced by reacting PAA with amino-terminated PEO and PPO, as follows:



The graft copolymers were prepared with varying mass of PEO and PPO. "x/y" means that x% of the carboxylic acid groups on PAA were reacted with PEO-NH<sub>2</sub> and y% reacted with PPO-NH<sub>2</sub>. In this work, 8/8 and 12/4 were synthesized.

The magnetic particles were synthesized by chemical precipitation in a graft copolymer solution. This synthesis involved two reactions. First, the colloidal nanoparticles of magnetite were produced by reacting FeCl<sub>2</sub>, FeCl<sub>3</sub>, and NaOH as follows:



The nanoparticles grew up to approximately 10 nm in diameter. Secondly, the carboxylic acid groups of graft copolymer coordinated to the surface of nanoparticles. The PEO and PPO side chains on the graft copolymer form a shell around the magnetite particle. The magnetic particles were washed with water by centrifugal filtration (Millipore, Centricon Plus-20) to remove unreacted polymers etc..

Graft copolymer was analyzed by nuclear magnetic resonance analysis (NMR) and by ninhydrine reaction to know the fractions of PEO and PPO in the side chains of graft copolymer. The magnetic particles were observed by a transmission electron microscopy (TEM; JEOL, JEM-2010). Samples were prepared with formvar support films on TEM grids. Three hundred and fifty samples of the particles were extracted from the observation to know the distribution of the nanoparticles size.

The original magnetic fluid was diluted by water into specified concentrations to be provided for the equilibrium runs.

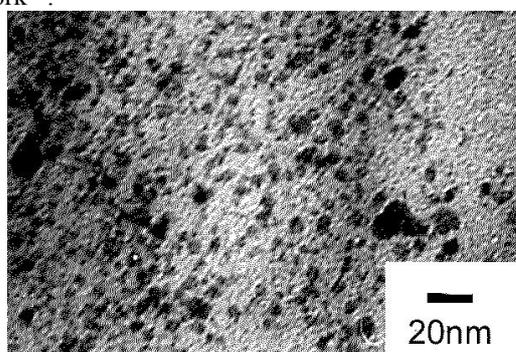
The magnetic fluid (12 ml) and the organic compound (toluene 12 ml or phenol 10 g) were brought into contact for 48 hours to be equilibrium. After equilibration, the magnetic fluid and organic phases were separated into each other to be weighed. The organic compounds contained in magnetic fluid phase was extracted with appropriate hydrocarbons (20 ml) sufficient times and this hydrocarbons were analyzed by a gas chromatograph (Shimadzu, GC-17A). The results of

these analyses and simple material balance relationships allowed to give the concentration of organic compound in the magnetic fluid phase with the assumption that the mutual solubilizations among the magnetic particles, water, and hydrocarbon were negligible.

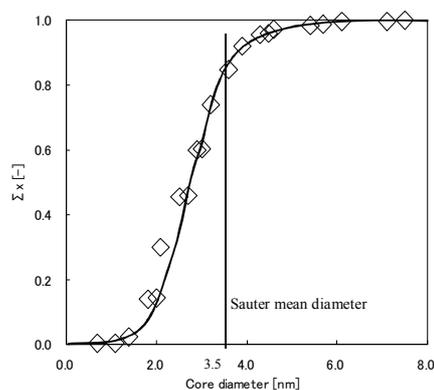
## 2.2 Results and Discussion

Although the existences of  $-CH_2-$  and  $-C(CH_3)H-$  groups in graft copolymer were detected by NMR spectrum, the fractions of PEO and PPO could not be determined, because the concentration of  $-C(CH_3)H-$  group could not be calculated because the signal of  $-C(CH_3)H-$  group was indistinct.

**Figure 1** shows a TEM image of 8/8 nanoparticles. The black parts are the magnetite cores. An example of the cumulative distribution of magnetic particle diameter is illustrated in **Figure 2**. The particle diameter was distributed up to 7.5 nm. The sauter mean diameter of the particles was 3.5 nm and was smaller than that in the previous work<sup>1)</sup>.

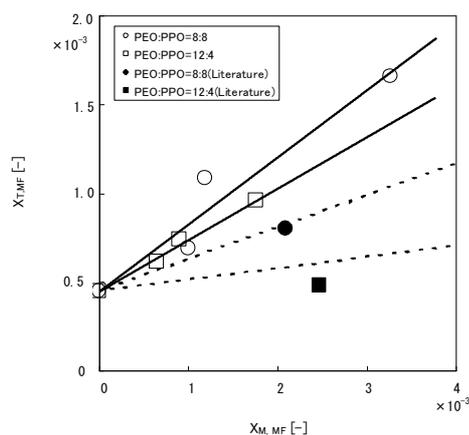


**Figure 1.** TEM image of 8/8 magnetic particles.

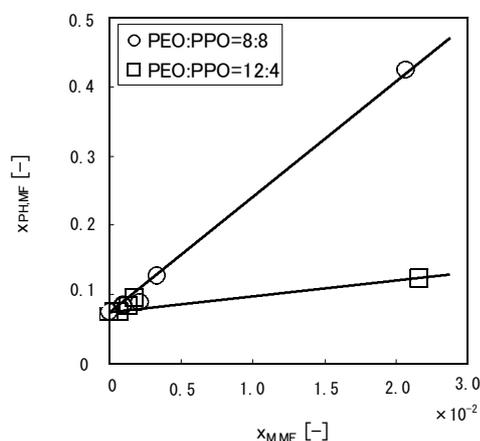


**Figure 2.** Cumulative distribution of 8/8 magnetic particles.

The mass fractions of toluene and phenol in the magnetic fluids are plotted against the that of magnetite in **Figures 3** and **4**. The intercepts of these figures correspond to the solubility of toluene and phenol into pure water. These solubilities are summarized in **Table 1** with the previous results<sup>2,3)</sup>. The solubilities obtained here were almost equivalent to those in the previous work in spite of quite simple method of measurement in this work. The solubilities of organic compounds in the magnetic fluid increased with mass fraction of magnetite. The organic compounds transferred into the polymer layers of the magnetic particles. The magnetic particle with 8/8 polymer extracted the



**Figure 3.** The mass fraction of toluene solubility in 8/8 and 12/4 magnetic fluids.



**Figure 4.** The mass fraction of phenol solubility in 8/8 and 12/4 magnetic fluids.

**Table 1.** Solubilities in water, in polymer layer of magnetic particles(mass fraction), and distribution coefficients,  $K_i$ , of organic compounds

	Solubility [-]				$K_i$ [-]	
	In water		Polymer layer			
	This work	Previous work <sup>2,3)</sup>	8/8	12/4	8/8	12/4
Toluene	$4.51 \times 10^{-4}$	$5.15 \times 10^{-4}$	0.32	0.27	711	592
Phenol	0.074	0.090	0.96	0.77	13	10

organic compounds more than that with 12/4 polymer. The previous results of toluene<sup>1)</sup> are also shown in **Figure 3**. The magnetic particles prepared in this study extracted toluene more than those in the previous work. These differences in the extraction extents may be attributed to the differences in the particle sizes mentioned above and in molecular weight of PEO.

The solubilities of organic compounds in the polymer layer can be calculated with the intercept, i.e., the solubility in water, the slop of the plot in **Figure 3** and **4**, and the mass ratio of polymer layer relative to magnetite<sup>1)</sup>. The distribution coefficient of the organic compounds were defined as,

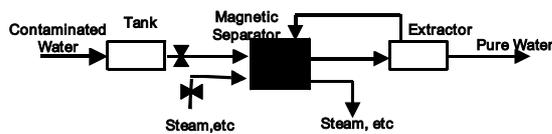
$$K_i = \frac{X_{i,\text{water}}}{X_{i,\text{polymer}}} \quad (3)$$

These solubilities and distribution coefficients are also summarized in **Table 1**. It was reconfirmed that the organic compounds are more distributed in the polymer layer than in aqueous phase. Consequently, organic compound contaminating water would be able to remove by adding the magnetic particles into the water.

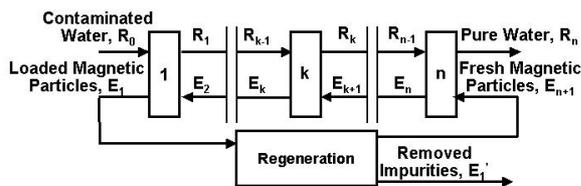
### 3. Countercurrent Multi-stage Extraction

#### 3.1 Process Configuration

The conceptual diagram of single stage continuous contact was illustrated in **Figure 5(a)**. For simplicity, it was assumed that magnetic particles do not leak from magnetic separator and that were separated from water completely. The overall process of multi-stage countercurrent contact is illustrated in **Figure 5(b)**. The extractor was fed the contaminated water intermittently. An aqueous phase and magnetic particles can contacted with each other countercurrently in each stages. The purpose of this operation is to remove organic compounds from water, so that the cascade becomes quite simple without the reflux concentrating the impurities.



**Figure 5(a).** Conceptual diagram of single stage continuous contact of aqueous phase and magnetic particles.



**Figure 5(b).** Block flow sheet overall multi-stage countercurrent contact.

#### 3.2 Calculations

The material balance in stage  $k$  is expressed with flow rates and mass fractions of component  $i$  of aqueous phase and magnetic particles as follow;

$$R_{k-1} \cdot x_{k-1,i} + E_{k+1} \cdot y_{k+1,i} = R_k \cdot x_{k,i} + E_k \cdot y_{k,i} \quad (1 \leq k \leq n) \quad (4)$$

The material balance for the regeneration is,

$$E_1 \cdot y_{1,i} = E_{n+1} \cdot y_{n+1,i} + E_1 \cdot y_{1,i} \quad (5)$$

The constraints of mass fraction are written as the following equations;

$$\sum_i x_{k,i} = 1 \quad (1 \leq k \leq n) \quad (6)$$

$$\sum_i y_{k,i} = 1 \quad (1 \leq k \leq n+1) \quad (7)$$

$$\sum_i y_{1,i} = 1 \quad (8)$$

The equilibrium relationship in each stage is,

$$y_{k,i} = \frac{0.8}{1.8} K_{k,i} \cdot x_{k,i} \quad (1 \leq k \leq n) \quad (9)$$

where  $K_{k,i}$  is the distribution coefficient of component  $i$  between copolymer and water in stage  $k$ . The mass ratio of graft copolymer for a magnetite particle was assumed as 0.8. So,  $K_{k,i}$  was reduced to the distribution coefficient among magnetic particles and water.

The followings were assumed for simplicity besides the assumptions supplied to the above process configuring; (1) water does not transferred into magnetic particles; (2) magnetic particles do not dissolved into water; (3) the distribution coefficient of organic compounds is constant independently of the concentration, namely, stage number, since the concentration of organic compound in water is very low and the distribution law may hold. According to these assumptions, the followings are obtained:

$$y_{n+1,i} = 0 \quad (i=HC,W) \quad (10)$$

$$y_{n+1,MP} = 0 \quad (11)$$

$$K_{k,HC} = K_{HC} \quad (1 \leq k \leq n) \quad (12)$$

$$K_{k,W} = 0 \quad (1 \leq k \leq n) \quad (13)$$

$$\text{and Eq. (9) for magnetic particles are rewritten as,} \\ x_{k,MP} = 0 \quad (1 \leq k \leq n) \quad (14)$$

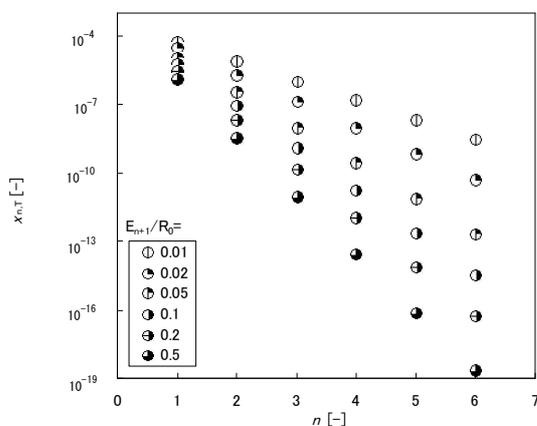
The other conditions of calculation are summarized in **Table 2**. The mass fractions of toluene and phenol in contaminated water feed,  $x_{0,PH}$  and  $x_{0,T}$ , were fixed at  $4.51 \times 10^{-4}$  and  $7.4 \times 10^{-2}$ , respectively. These values correspond to the experimental solubilities of toluene and phenol in water (see **Table 1**). The flow rate ratio of magnetic particles relative to the feed,  $E_{n+1}/R_0$ , and the number of extracting stages,  $n$ , were varied as shown in **Table 2**. Under these conditions, the mass fraction of organic compound remained in the product water,  $x_{n,HC}$ , was calculated.

**Table 2.** Calculation conditions

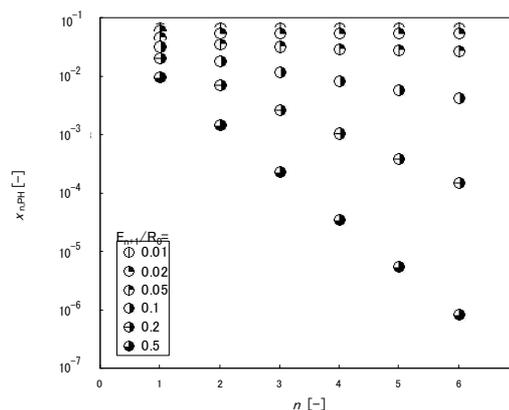
	Toluene	Phenol
Flow rate of feed, $R_0$	1kg·h <sup>-1</sup>	1kg·h <sup>-1</sup>
Mass fraction of organic compound in feed, $x_{0,HC}$	$451 \times 10^{-4}$	$7.4 \times 10^{-2}$
Flow rate ratio of magnetic particles to feed, $E_{n+1}/R_0$	0.01 - 0.5	0.01 - 0.5
The number of stages, n	1 - 6	1 - 6

### 3.3. Results and Discussion

Mass fraction of organic compounds remained in the product water,  $x_{n,HC}$ , is shown in **Figure 6** and **7** for toluene and phenol using 8/8 particles. They were reconfirmed that the organic compound contaminating water could be removed with the appropriate amount of the magnetic particles and the number of stages.  $x_{n,HC}$  decreased with the number of stages, n, and with the  $E_{n+1}/R_0$ .  $x_{n,HC}$  decreased remarkably with the n especially in the case with larger  $E_{n+1}/R_0$ , while the increases in n were not so effective with lower  $E_{n+1}/R_0$ . The removal of phenol could not be achieved effectively especially in the lower  $E_{n+1}/R_0$  range, whereas toluene was removed favorably as shown in the figures. These results were attributed mainly to the difference in distribution coefficients (see **Table 1**). Therefore, this technique would be useful for the treatment of aqueous diluted solution of component whose solubility in water is relative low and distribution coefficient is high.



**Figure 6.** Mass fraction of toluene remained in product water,  $x_{n,T}$  with 8/8 polymer.



**Figure 7.** Mass fraction of phenol remained in product water,  $x_{n,PH}$  with 8/8 polymer.

### 4. Conclusions

The solubility of organic compounds for magnetic particles is much larger than that for water. The multi-stage countercurrent contact using magnetic particles is useful for removal of the hydrophobic organic compound.

### 5. Nomenclature

- $E_1$  = flow rate of removed impurities [kg·h<sup>-1</sup>]
- $E_k$  = flow rate of magnetic particles from stage k [kg·h<sup>-1</sup>]
- $E_i$  = distribution coefficient of component i into magnetic particle from aqueous phase [-]
- $E_{k,i}$  = distribution coefficient of component i into magnetic particle from aqueous phase at stage k [-]
- $R_k$  = flow rate of aqueous phase from stage k [kg·h<sup>-1</sup>]
- n = the number of extraction stages [-]
- $x_{k,i}$  = mass fraction of component i in aqueous phase from stage k [-]
- $y_{k,i}$  = mass fraction of component i in magnetic particles from stage k [-]
- $y_{1,i}$  = mass fraction of component i in removed impurities [-]
- subscript
- HC = hydrocarbon
- M = magnetite
- MF = magnetic fluid
- MP = magnetic particles
- PH = phenol
- T = toluene
- W = water
- i = component i
- k = stage k
- n = stage n

### 6. References

- (1) Moeser, G. D. et al; "Water-Based Magnetic Fluids as Extractants for Synthetic Organic Compounds," *Ind. Eng. Chem. Res.*, 41, 4739-4749, 2002
- (2) S. M. Leshchev et al; "Estimation of the Free Energies of Hydration and Solvation of Organic Nonelectrolytes," *Russ. J. Phys. Chem.*, 67, (12), 2383-2387, 1993
- (3) Yu Yang et al; "Toluene Solubility in Water and Organic Partitioning from Gasoline and Diesel Fuel into Water at Elevated Temperatures and Pressures," *J. Chem. Eng. Data*, 42, 908-913, 1997