

**SORPTION CHARACTERISTICS OF AQUEOUS Co(II) ON  
PREFORMED IRON FERRITE IMPREGNATED INTO  
PHENOLSULPHONIC FORMALDEHYDE RESIN**

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**ABSTRACT**

A series of stepwise procedures to prepare a new organic-inorganic composite magnetic resin with phenolsulphonic-formaldehyde and freshly formed iron ferrite was established, based upon wet-and-neutralization method for synthesizing iron ferrite and pearl-polymerization method for synthesizing rigid bead-type composite resin. The composite resin prepared by the above method shows stably high removal efficiency (maximally over 3.1 meq./g-resin) to Co(II) species from wastewater in a wide range of solution pH. The wide range of applicable solution pH (i.e. pH 4.09 to 10.32) implies that the composite resin overcomes the limitations of the conventional ferrite process that is practically applicable only to alkaline conditions. It has been found that both ion exchange (by the organic resin constituent) and surface adsorption (by the inorganic adsorbent constituent) are major reaction mechanisms for removing Co(II) from wastewater, but surface precipitation results in the high sorption capacity to Co(II) beyond normal ion exchange capacity of the phenolsulphonic-formaldehyde resin. Standard enthalpy change derived from van't Hoff equation is  $32.0 \text{ kJ}\cdot\text{mol}^{-1}$  conforming to the typical range for chemisorption or ion exchange. In a wide range of equilibrium Co(II) concentration, the overall isotherm is qualitatively explained by the generalized adsorption isotherm concept proposed by McKinley. At the experimental conditions where the composite resin shows equivalent selectivity to Co(II) and other competing reagents (i.e. EDTA and Na), the ratios of Co(II) to other chemicals turn out to be 2:1 and 1:221, respectively. In addition, the selectivity of the PSF-F to Co(II) species is very high (about 72% of Co(II)-removal efficiency) even when the molar ratio of Co(II) to Ca(II) is 1:30. It is anticipated that the composite resin can also be used for column-operation with process-control by applying external magnetic field, since the rigid bead-type composite resin shows magnetic-susceptibility due to its paramagnetic inorganic constituent (i.e. iron ferrite).

## INTRODUCTION

Wastewater containing transition metals is generated as a byproduct in various industries and many investigators have studied to develop more effective processes to treat such waste streams. Especially, a series of radioactive transition metal elements (e.g.  $^{58}\text{Co}$ ,  $^{60}\text{Co}$ ,  $^{54}\text{Mn}$ ,  $^{51}\text{Cr}$ ,  $^{59}\text{Fe}$ ,  $^{63}\text{Ni}$ ,  $^{65}\text{Zn}$ , etc.) is generated from nuclear power reactors as fission products or through corrosion and activation of structural materials. (1) Some of the above radioactive transition metals such as  $^{60}\text{Co}$  and  $^{54}\text{Mn}$  are high-energy gamma ray-emitters and play roles as major radiation source terms in nuclear industries. Removal of such radioactive transition metal elements has been an important issue in radioactive waste management, since they mainly contribute to the operational radiation exposure.

Ion exchange process has been widely adopted in liquid radioactive waste treatment systems, and most of the ion exchangers (i.e. ion exchange media) currently being used are commercially mass-produced organic resins. (2) Although the organic ion exchangers have a wide applicability, a few limitations of the organic resins have been reported. One of the severest limitations of the organic resin is its poor thermal stability; for instance, the mechanical strength and removal capacity of ordinary organic ion exchange resins tend to decrease under high temperature conditions which are frequently encountered in processing liquid radioactive waste streams. (2,3) In addition, degradation of ion exchange properties under high radiation field is also known to be another defect of the organic resins.

Recently, the conventional organic resins have been partly replaced with inorganic adsorbents in liquid radioactive waste treatment systems in a few countries' nuclear power plants. (4) It is anticipated that usage of the inorganic adsorbents in nuclear industry will be steadily expanded, since they have higher thermal-and-radiological resistances and higher selectivity toward certain radionuclides (e.g.  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$ , etc.), and they are more compatible with ultimate immobilization matrices than the conventional organic ion exchange resins. However, the inorganic adsorbents have their own limitations. For instance, fabrication of the inorganic adsorbents into rigid bead-type media suitable for column-operation is quite difficult, and they have generally worse mechanical strength than the organic counterparts. (5) Therefore, continuous column-operation using inorganic adsorbents has been seldom accomplished.

In order to overcome the above limitations of organic resins and inorganic adsorbents, many investigators have introduced composite resins consisting of inorganic sorbents and organic binding matrices. It is known that phenolic resin, phenolsulphonic-formaldehyde (PSF), sulphonated polystyrene-divinyl benzene (SPS-DVB), hydrophilic polyacrylic hydrazide (PAH), and polyacrylonitrile (PAN) are major organic binding matrices used for preparing composite resins. (5,6) Also there exist a wide variety of types of inorganic adsorbents (e.g. zeolites, metal hydrates, metal phosphates, etc.) adopted in preparation of the composite resins.

Main objectives of this study are to establish a stepwise method for synthesizing a new organic-inorganic composite resin, and to experimentally prove the efficiency of the composite resin as an ion exchange media for removing transition metal elements from wastewater. Ferrite was chosen as an inorganic constituent of the proposed composite resin, because it is known as a good adsorbent for removing heavy metal or transition metal elements from liquid

waste streams. (7) In addition, the ferrite has high removal capacity toward some important radionuclides, and shows paramagnetic properties implying possible magnetic control of the process. (8) In turn, PSF was selected as an organic binding matrix, since its ion exchange properties have been well characterized and its preparation methods are also fully established. (9)

## **SYNTHESIS AND CHARACTERIZATION OF THE COMPOSITE RESIN**

### **Materials**

All chemicals listed in this study were of reagent grade or higher, and they were used as received. Iron ferrite was synthesized from ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), according to the wet method as described in related literatures. (10,11) A series of pH titration and pH-adjustment for aqueous solution was performed with NaOH and HCl standard solutions (0.1 N and 1.0 N), as required. Organic binding matrix (i.e. PSF) was prepared by polymerization of sulphonated phenol and formaldehyde (37%), and the sulphonated phenol was synthesized from phenol and concentrated sulphuric acid (95%), in advance. Inert mineral oil (Dow Corning DC550) was used in the process of pearl-polymerization for synthesizing bead-type PSF-F composite resin.

### **Apparatus and Instruments**

The pH measurement was done by use of Orion pH meter (SA 720) while the solution was being sufficiently agitated with magnetic stirring device. Equilibration of each batch system was accomplished by a shaker equipped with water bath (Lauda MS/2). Separation between aqueous and solid phases was done with Beckman centrifuge (J2-21M/E), and the concentration of metal species in the supernatant was analyzed by atomic absorption spectrophotometer (Perkin Elmer 3100). All liquid reagents requiring precise volume control were handled with a micro pipet (Gilson Pipetman P200). An electric heating mantle (supplied by domestic vendor, Hana) equipped with temperature-controller was used for supplying heat and controlling temperature during polymerization process.

### **Preparation of the PSF-F Composite Resin**

A series of steps to synthesize PSF-F composite resin used in this study is summarized and conceptually displayed in Fig. 1.

Iron ferrite as an inorganic adsorbent was prepared by wet method at ambient temperature, as proposed by Wang and Takada. (10,11) At first, 0.25 mol of ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) as  $\text{Fe}^{2+}$ -source and 0.5 mol of ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) as  $\text{Fe}^{3+}$ -source were dissolved in 1.0 dm<sup>3</sup> of water, and then NaOH was added into the solution until the pH was set to the target point (i.e. pH 11.0). Blackish particles were observed in the mixture when the

solution pH approached around pH 11.0. After complete precipitation, the supernatant was removed by suction-and-filtration method in the Buchner funnel and only precipitated wet iron ferrite was obtained on the filter paper. The wet particles of iron ferrite were washed until no chemical impurities were detected in the washed solution, and then dried at 80°C in the electric oven for 2 d. The washed-and-dried blackish conglomerates were crashed into relatively homogeneous particles and stored in a desiccator for further extraction of the water content that may exist in the iron ferrite structure, and then used as an inorganic constituent for synthesizing the PSF-F composite resin.

In order to prepare the ultimate organic matrix of the PSF-F composite resin, sulphonation of phenol was performed in advance. A bottle of solid phenol was crashed and 56.4 g of phenol was weighed. The weighed phenol was poured into a round-bottomed flask and melted at 70°C. The molten phenol was slowly added into 61.8 g of concentrated (95%) sulphuric acid, and the sulphonation of phenol was carried out for 2 h in a water bath while the temperature was being maintained at 100.0±2.0°C. The product, sulphonated phenol, was cooled down and maintained at 20.0±0.5°C in a water-circulating bath. And then, 48.0 g of 37% formaldehyde was slowly added into the cooled sulphonated phenol, while keeping the temperature less than 25°C. Addition of formaldehyde into sulphonated phenol naturally induces temperature increase, since the resultant reaction is highly exothermic. After the mixing process was finished, the mixture was maintained at 20.0±0.5°C for 10 min.

The final product of PSF-F composite resin was synthesized by introducing the preformed iron ferrite into the mixture of formaldehyde and sulphonated phenol. That is, 23.15 g of preformed iron ferrite was slowly poured into the mixture of formaldehyde and sulphonated phenol. And then, the inorganic-organic mixture was slowly poured into the pre-heated mineral oil. The temperature of the pre-heated mineral oil was maintained at 90.0±2.0°C. When the inorganic-organic mixture was added into the pre-heated mineral oil, the oil was being vigorously agitated by mechanical stirrer. The speed of the mechanical stirrer was set to 200±5 rpm. In this stage, an amount of bead-type composite resin was formed through so-called pearl polymerization of the mixture. During the polymerization, blackish and spherical beads were observed in the reactor. After 2 h, the synthesized composite resin was separated from the reactor, and the resin beads were washed with distilled water and small amount of surfactant until no oily constituents were observed. And then, the resin beads were dried in the electric oven at 40.0±0.5°C for 10 h, and classified into six groups based upon their diameters (Table I). Only 86.8 g of the formed PSF-F composite resin beads with diameter 0.6 to 1.0 mm (i.e. groups III to V) were used for additional batch experiments.

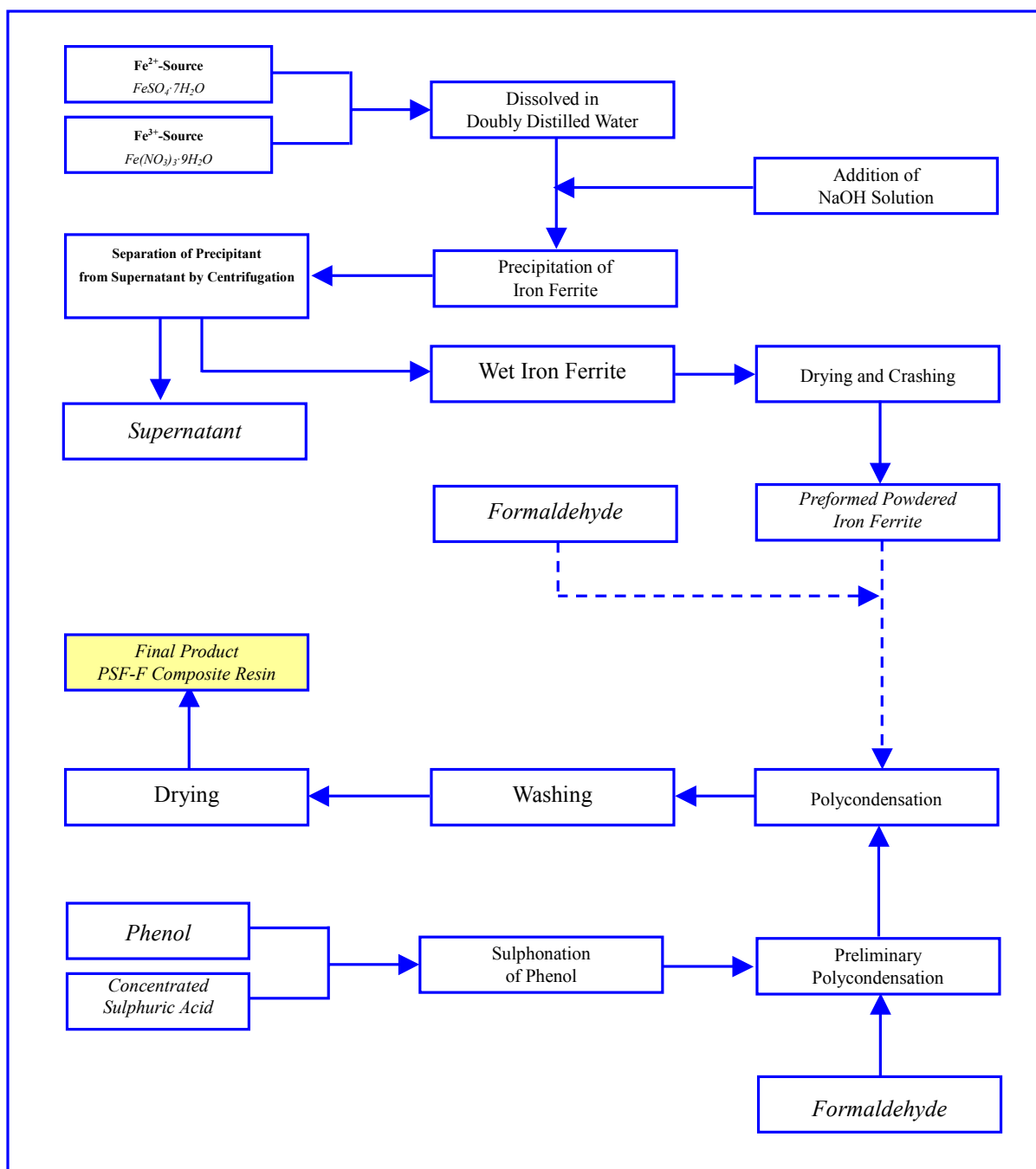


Fig. 1. Simplified preparation scheme for synthesizing PSF-F composite resin (The solid line represents the whole stepwise process for synthesizing PSF-F composite resin. The dotted line, especially, represents a step for introducing the inorganic adsorbent (i.e. preformed iron ferrite) and formaldehyde into the PSF organic binding matrix.).

Table I. Size Distribution of the Prepared PSF-F Composite Resin Beads

Group	Size (Diameter) Range	Mass [g]	Fraction
I	> 1.18 mm	0.9040	0.0090
II	1.00 - 1.18 mm	3.2543	0.0325
III	850 $\mu\text{m}$ - 1.00 mm	53.7012	0.5361
IV	710 - 850 $\mu\text{m}$	17.6585	0.1763
V	600 - 710 $\mu\text{m}$	15.4632	0.1544
VI	500 - 600 $\mu\text{m}$	9.1851	0.0917
Total		100.1663	1.0000

### Analysis of pH Titration Curve – Ion Exchange Capacity

Ion exchange capacity of the PSF-F composite resin was investigated through the analysis of pH titration curve. At first, 45 ml of water was poured into the 250ml of polyethylene (PE) bottle, and pre-determined dose of NaOH or HCl solution was applied for pH-adjustment. While the pH-adjusted solution was vigorously agitated by magnetic stirrer, the system volume was messed up to 50 ml and 0.1 g of the PSF-F composite resin was poured into the bottle. The batch system was equilibrated for 24 h with reciprocating mechanical shaker at 120 rpm. The equilibrium reaction (i.e. complete pH-titration) time was determined by referring to various literatures. (7,12) After equilibration, complete separation of solid and solution phases was accomplished by centrifuge at 12,000 rpm for 15 min. The supernatant was collected into test tubes and stabilized for a while.

Fig. 2 displays the result of the pH-titration of the PSF-F resin with NaOH solution. In the case of strong-acid cation exchange resin, the pH-titration curve usually shows a steep edge; that is, the  $\text{-H}$  functional groups on the resin are depleted and replaced with  $\text{Na}^+$  ions at that point and the number of  $\text{-H}$  sites are the same as the amount of NaOH added. The curve shows slow increase when NaOH is added 0.3 to 0.5 meq./g-resin, and relatively steep increase when NaOH is added 0.8 to 1.2 meq./g-resin. In the region where more NaOH is added, the equilibrium pH further increases but much slowly. For comparison, another pH titration curve for pure iron ferrite is simultaneously displayed in Fig. 2. The curve shows slow pH-edge when NaOH is added 0.3 to 0.6 meq./g-sorbent, where the first pH-edge for the PSF-F resin was also observed.

The two pH-titration curves imply that the composite resin shows the characteristics as inorganic and organic ion exchangers, at the same time. The first pH-edge implies that the inorganic constituent (i.e. iron ferrite) contributes to the  $\text{Na}^+$ -sorption in the region. In addition, the slow and continuous increase of the equilibrium pH after passing the second pH-edge point implies contribution of the inorganic sorbent (i.e. iron ferrite). The slowness of the pH-titration curve in the region where much NaOH is added can be ascribed to the surface precipitation at the iron ferrite, and more detailed descriptions are to be given in later part of this paper. It is anticipated that the second pH-edge showing sorption capacity of 1.0 meq./g-resin can be mainly attributed to ion exchange of cobalt ions onto the PSF organic constituent.

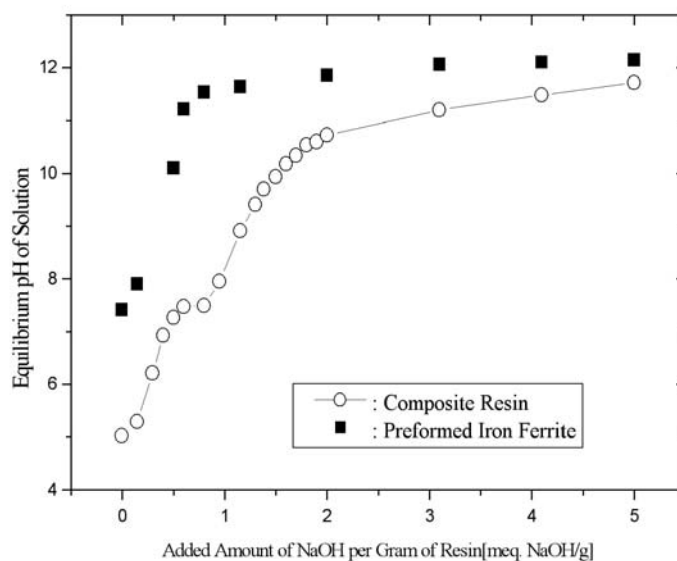


Fig. 2. Titration curve for the PSF-F composite resin with NaOH and comparison to the pH-titration curve for pure iron ferrite sorbent (Slow increase of the pH-titration curve after passing the second pH-edge point, around 1.0 meq./g-resin, implies reactions (e.g. surface precipitation) other than ion exchange are involved.).

## REMOVAL OF COBALT SPECIES FROM WASTEWATER

### Batch Experimental Systems

In order to disclose the sorption characteristics of the PSF-F resin toward cobalt species in aqueous wastewater, a series of batch experiments was performed. Otherwise specifically mentioned, the initial concentration of cobalt in the wastewater was  $3.40 \times 10^{-4}$  M ( $\approx 20$  ppm), and the initial solution pH was adjusted to  $6.7 \pm 0.2$ . The amount of sorbent (i.e. PSF-F resin) added was 0.5 g and the total volume of the solution was set to  $5.0 \times 10^{-2}$  dm<sup>3</sup>. The solution was equilibrated at  $25.0 \pm 0.2^\circ\text{C}$  by reciprocal shaking at 120 rpm for 12 h, and then the solid and aqueous phases were completely separated by high-speed centrifuge at 12,000 rpm for 15 min. The removal efficiency was evaluated by analyzing the concentration of cobalt species in the supernatant by AAS at 240.7 nm.

The generalized experimental conditions are displayed in Table II, and the representative parameters are adopted in each batch system, otherwise specified.

Table II. Representative Batch Experimental System Parameters Adopted in This Study

Parameters	Value
Temperature	25.0±0.2 $\pi$
Initial solution pH	6.7±0.2
Initial concentration of cobalt species	3.40×10 <sup>-4</sup> M ( $\approx$ 20 ppm)
Amount of sorbent (PSF-F resin)	0.5 g
Solution volume	5.0×10 <sup>-2</sup> dm <sup>3</sup>
Ionic strength	1.0×10 <sup>-2</sup> N
Equilibrium reaction time	12 h
Equilibrium solution pH	4.0±0.2

### Determination of Optimal Reaction Time

In order to determine the optimal equilibration time for Co(II)/PSF-F batch system and to analyze the Co(II)-removal efficiency as a function of reaction time, a series of batch experiments was performed at the reaction time ranged from 3 min to 48 h. As shown in Table III, the reaction proceeds rapidly until 60 min, and after that, the Co(II)-removal efficiency increases much slowly and is almost saturated at 360 min. This phenomenon implies that the PSF-F composite resin shows typical properties of the well-known two-step process; that is, rapid initial ion exchange/sorption followed by much slower reaction in which the equilibrium sorption density approaches asymptotically. (12)

It is anticipated that the rapid reaction step results from both ion exchange of Co(II) at the PSF organic resin's -H functional groups and surface complexation of Co<sup>2+</sup> or CoOH<sup>+</sup> at the iron ferrite's surface sites. (7) In addition, the slow reaction step may be ascribed to the contribution of other surface reactions occurred at the iron ferrite's surface sites. (7,12) The reaction times for further experimental systems were set to 12 h, since the batch system reaches the so-called quasi-equilibrium state after 6 h as shown in Table III.

### Equilibrium pH and Its Impacts to the Removal Efficiency

The effect of solution pH on the Co(II)-removal efficiency was studied as shown in Table IV, and the optimal pH range was determined based upon the experimental results.

While the initial solution pH in each batch system varies from 3.04 to 12.88, the final solution pH after equilibration for 12 h lies on 3.21 to 11.76. At first, Table IV shows that the Co(II)-removal percentage is kept high (90.55 to 99.85%) over the wide pH range. In the low pH region where the initial pH is 3.04 to 3.57, the equilibrium pH varies almost as much (from 3.21 to 3.7) and a local increase of Co(II)-removal efficiency was observed. This phenomenon may be attributed to the fact that cobalt species exist as only divalent ionic form (i.e. Co<sup>2+</sup>) favorable to be removed by both PSF resin and iron ferrite, in the given solution pH range. In the high pH region, however, the equilibrium pH rapidly increases from 5.05 to 11.76 and the Co(II)-removal percentage decreases 99.1 to 90.55%, while the initial solution pH varies slightly from 11.68 to 12.88. Although quantitative description is not addressed in this



study, it is anticipated that the possible dissolution of the PSF-F resin and the variety of chemical forms of cobalt (e.g.  $\text{CoOH}^+$ ,  $\text{Co(OH)}_2$ ,  $\text{Co(OH)}_3^-$ , etc.) existing at the high pH region may play roles in diminishing the overall Co(II)-removal efficiency. (13)

It has been reported that high Co(II)-removal efficiency through the ferrite process can be attained only for the alkaline (e.g.  $\text{pH} > 8$ ) waste streams. (7) Through the broad middle range of initial solution pH (4.09 to 10.32), however, the equilibrium pH remains almost constant (3.85 to 4.08) and its relevant Co(II)-removal percentage is also kept to be stably high (99.45 to 99.5%) in this study. This implies that the applicability of the newly prepared PSF-F composite resin is better and additional pre-treatment steps such as pH-adjustment of wastewater are less required than the conventional ferrite process.

Based upon the experimental results as above, the optimal pH was determined to be  $6.7 \pm 0.2$  of initial solution (conforming to  $\text{pH} 4.0 \pm 0.2$  at the final equilibrium state) and the pH condition was consistently adopted to the following batch experimental systems.

Table III. Effect of Equilibrium Time on the Co(II)-Removal Efficiency in the Co(II)/PSF-F Batch System (All Experimental Conditions Listed in Table II Were Adopted Except for the Reaction Time Ranging from 3 min to 48 h.)

Reaction Time [min]	Equilibrium Solution pH	Removal Efficiency [%]
0	6.7	28.55
3	4.06	77.05
30	3.82	95.1
60	3.78	98.5
120	3.74	99.3
360	3.72	99.55
720	3.72	99.55
1440	3.72	99.55
2880	3.73	99.7

Table IV. Relation Between Initial/Equilibrium Solution pH and Its Impacts to Co(II)-Removal Efficiency (All Experimental Conditions Listed in Table II Were Adopted Except for the Initial Solution pH Ranging from 3.04 to 12.88, Which Result in the Equilibrium Solution pH Ranging from 3.21 to 11.76)

Initial Solution pH	Equilibrium Solution pH	Removal Percentage [%]
3.04	3.21	98.85
3.47	3.67	99.6
3.57	3.7	99.85
4.09	3.85	99.45
10.32	4.08	99.5
11.68	5.05	99.1
11.91	6.44	98.7
12.05	6.85	98.6
12.23	7.06	98.35

Table IV. Relation Between Initial/Equilibrium Solution pH and Its Impacts to Co(II)-Removal Efficiency (All Experimental Conditions Listed in Table II Were Adopted Except for the Initial Solution pH Ranging from 3.04 to 12.88, Which Result in the Equilibrium Solution pH Ranging from 3.21 to 11.76) (Continued)

Initial Solution pH	Equilibrium Solution pH	Removal Percentage [%]
12.43	8.26	91.8
12.66	10.67	90.55
12.88	11.76	95

### Isotherm and Experimental Sorption Capacity

The phase distribution characteristics of cobalt at equilibrium were analyzed by varying the initial concentration of cobalt species from  $1.70 \times 10^{-5}$  to  $1.70 \times 10^{-2}$  M (i.e. 1 to 1,000 ppm).

Fig. 3 shows the relation of  $\log X_S$  vs.  $\log C_f$ ; where  $X_S$  is the equilibrium concentration of cobalt in unit mass of PSF-F resin (i.e. mg-cobalt/g-solid) and  $C_f$  is the equilibrium concentration of cobalt in solution (i.e. ppm). At a glance, the overall plot can be divided into three regions having different linear slopes and the linearity of  $\log X_S$  vs.  $\log C_f$  generally represents the well-known Freundlich isotherm as:

$$\log X_S = \log P + \frac{1}{n} \log C_f, \quad (\text{Eq. 1})$$

where  $P$  and  $n$  are empirical constants to be attained from the intersect and slope of the plot of  $\log X_S$  vs.  $\log C_f$ . It seems plausible to conclude incautiously that the sorption characteristics of the PSF-F resin toward Co(II) can be simulated by three Freundlich isotherms in the given experimental conditions.

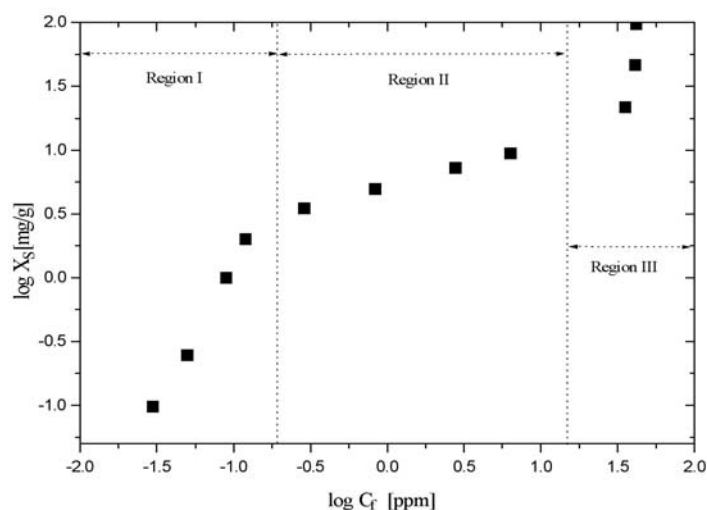


Fig. 3. Relation between equilibrium Co(II) concentration in solution and removed amount of Co(II) species in unit mass of the PSF-F composite resin (All experimental conditions listed in Table II were adopted except for the initial concentration of Co(II) ranging from  $1.70 \times 10^{-5}$  to  $1.70 \times 10^{-2}$  M: that is, 1 to 1,000 ppm.).

However, it is more adequate to interpret the plot into a linear sorption region, a non-linear sorption region, and a surface precipitation-dominant region, respectively. This interpretation is completely compatible with the generalized adsorption isotherm for radionuclides in a wide range of equilibrium concentration as proposed by Langmuir and McKinley. (14,15) The first linear sorption region may be dominantly attributed to the sorption of cobalt species onto the iron ferrite constituent, as Cheong (7) proved the linearity of  $\log X_S$  vs.  $\log C_f$  in interpreting the sorption characteristics of ferrite material toward aqueous transition metal elements. It is anticipated that the second non-linear sorption region results from both sorption and ion exchange phenomena on the iron ferrite and PSF constituents, respectively. In the last region where all ion exchange sites are to be depleted, the precipitation of aqueous cobalt onto the surface of iron ferrite constituent may play an important role in removing more cobalt species from aqueous solution.

The equilibrium load of cobalt in unit mass of PSF-F resin linearly increases with increasing the initial concentration of cobalt species in solution from  $1.70 \times 10^{-5}$  to  $1.70 \times 10^{-2}$  M. According to the plot, the cobalt removal capacity of PSF-F resin is experimentally disclosed to be over 3.1 meq./g-resin at the initial Co(II)-concentration of  $1.70 \times 10^{-2}$  M. In the region, the nominal cation exchange capacity of PSF organic constituent would be depleted and the high Co(II)-removal capacity of the PSF-F resin can be ascribed to the surface precipitation of cobalt species. (14,15)

#### **Derivation of van't Hoff Equation – Temperature Effect**

The standard enthalpy change of the overall reaction can be correlated with the distribution coefficient by van't Hoff equation as:

$$\ln K_d = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + C, \quad (\text{Eq. 2})$$

where  $\Delta H^0$  is the standard enthalpy change in  $\text{J}\cdot\text{mol}^{-1}$ ,  $T$  is the absolute temperature at which the reaction proceeds in Kelvin,  $R$  is the gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ),  $C$  is the constant, and  $K_d$  is the distribution coefficient defined as:

$$K_d = \frac{(C_0 - C_f) \cdot V}{C_f \cdot m}, \quad (\text{Eq. 3})$$

where  $C_0$  and  $C_f$  are initial and equilibrium concentrations of cobalt species in solution, respectively in ppm,  $V$  is the volume of solution in  $\text{dm}^3$ , and  $m$  is the mass of PSF-F resin in g.

The overall reaction was turned out to be highly endothermic, since the standard enthalpy change calculated from the slope of the (Eq. 2) is  $32.0 \text{ kJ}\cdot\text{mol}^{-1}$ . The magnitude of  $\Delta H^0$  calculated in this study is within the range of chemisorption or ion exchange; that is, 8 to  $42 \text{ kJ}\cdot\text{mol}^{-1}$  as proposed by Helfferich. (9) However, the value is much higher than the standard enthalpy changes for the Co-sorption systems by pre-formed iron ferrite (i.e.  $25.0 \text{ kJ}\cdot\text{mol}^{-1}$ ) and by commercially supplied magnetite (i.e.  $16.8 \text{ kJ}\cdot\text{mol}^{-1}$ ). (7,16) The much higher value of  $\Delta H^0$  in this study can be attributed to the ion exchange at the PSF organic resin, which is one of the representative characteristics of strong-acid ion exchangers.

**Relative Affinity toward Cobalt Species Compared to Competing Reagents**

In general, the fraction of Co(II) removed diminishes when other competing agents (i.e. Na<sub>2</sub>EDTA, Ca(II) and Na, in this study) exist in the solution (Fig. 4).

The initial concentration of ethylene-diamine-tetra-acetic acid (EDTA) as a form of disodium salt (Na<sub>2</sub>EDTA) was varied from 2.00×10<sup>-6</sup> to 2.00×10<sup>-3</sup> M, while the concentration of Co(II) was kept at 3.40×10<sup>-4</sup> M. The Co(II)-removal efficiency decreases to a half at Na<sub>2</sub>EDTA concentration of 1.70×10<sup>-4</sup> M, compared to the case where no Na<sub>2</sub>EDTA is added. This implies that the affinities of the PSF-F composite resin toward Co(II) and Na<sub>2</sub>EDTA are almost equivalent when the molar ratio of them is around 2.

The effects of calcium and sodium ions (as CaCl<sub>2</sub> and NaOH, respectively) on the removal of Co(II) by the PSF-F resin were studied by varying the concentration of Ca(II) from 1.00×10<sup>-5</sup> to 1.00×10<sup>-2</sup> M and that of Na from 2.00×10<sup>-2</sup> to 2.00 M. Fig. 4 shows that the fraction of Co(II) removed decreases with increasing the initial concentration of Ca(II), but the Co(II)-removal efficiency still remains relatively high (≈ 72%) even when the molar ratio of Co(II) to Ca(II) is 1/30. A divalent cation, Ca(II), competes against Co(II) through the ion exchange process at the -H functional groups of the PSF organic constituent of the composite resin. On the other hand, it has been reported that the affinity of iron ferrite for transition metals including Co(II) is much higher than that for Ca(II) in aqueous solution. (7)

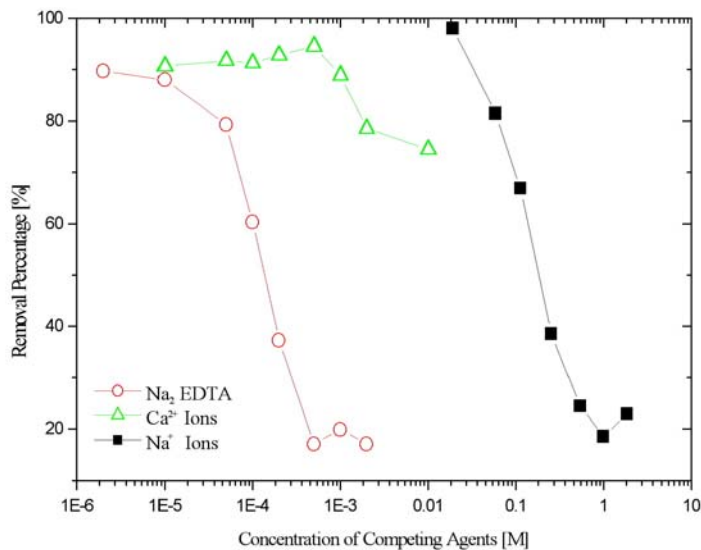


Fig. 4. Competitive phenomena of Ca(II), Na and Na<sub>2</sub>EDTA against Co(II)-removal efficiency in the Co(II)/PSF-F batch system.

Decrease of Co(II)-removal efficiency is observed when the concentration of Na is over sixty times higher than that of the initial concentration of Co(II), based upon molar concentration. In addition, the fraction of Co(II) removed diminishes to a half when the equivalent ratio of Co(II) to Na is 4.50×10<sup>-3</sup> (i.e. 6.80×10<sup>-4</sup> N of Co(II) to 0.15 N of

Na). It is natural that the PSF-F resin show much higher selectivity to the divalent cation (i.e.  $\text{Co}^{2+}$ ) rather than to the monovalent cation  $\text{Na}^+$ , since the above phenomenon is common to both organic and inorganic constituents of the composite resin. (7,9)

## CONCLUSIONS

A series of systematic procedures to synthesize the PSF-F resin (an organic-inorganic composite resin) was newly established, and the ion exchange/sorption characteristics of the resin at various conditions were experimentally disclosed. As the results, the composite resin simultaneously shows the properties of its constituents (i.e. PSF and iron ferrite), but the resin generally turns out to have much better characteristics to remove Co(II) species in aqueous solution than its constituents. Overall reaction turned out to be endothermic, as proved by the slope of van't Hoff equation, and its standard enthalpy change (i.e.  $32.0 \text{ kJ}\cdot\text{mol}^{-1}$ ) conforms to the typical range of  $\Delta H^\theta$  for chemisorption or ion exchange.

In the given experimental conditions, the maximum sorption capacity of the PSF-F resin toward Co(II) species is over  $3.1 \text{ meq./g-resin}$ . As the result of titration with NaOH standard solution, two pH-edges (i.e. the first is at pH 0.3 to  $0.5 \text{ meq./g-resin}$ , and the second at pH 0.8 to  $1.2 \text{ meq./g-resin}$ ) were observed. Even in the case where much more volume of NaOH is added, the equilibrium pH increases much slowly, which implies that reaction mechanisms other than conventional ion exchange or surface adsorption are to be involved.

The plot of  $\log X_s$  vs.  $\log C_f$  in the wide range of equilibrium Co(II) concentration, was successfully explained by implementing the generalized adsorption isotherm proposed by McKinley. (15) Accordingly, the rapid increase of the removed fraction of Co(II), under the condition where all ion exchange sites are to be depleted, implies that surface precipitation contributes to the high Co(II)-removal capacity of the PSF-F resin.

It is anticipated that one of the limitations of the conventional ferrite process (i.e. practically applicable only to alkaline wastewater) can be overcome by introducing the PSF-F composite resin, which shows high Co(II)-removal efficiency through the wide pH range (i.e. pH of wastewater at 4.09 to 10.32).

The affinities of the PSF-F composite resin toward Co(II) species compared to some competing chemicals (e.g.  $\text{Na}_2\text{EDTA}$ , Ca(II) and Na) are slightly lower than those of its inorganic constituent (i.e. iron ferrite). However, the PSF-F resin shows still high selectivity to Co(II), since the affinities of the PSF-F to Co(II) species and to other competing reagents show equivalence in the following conditions: EDTA (at molar ratio of Co(II) to  $\text{Na}_2\text{EDTA}$  is 2:1) and Na (at equivalent ratio of Co(II) to Na is 1:221). And also, the Co(II)-removal efficiency still remains relatively high ( $\approx 72\%$ ) even when the molar ratio of Co(II) to Ca(II) is 1:30.

In this study, it has been emphasized to develop a stepwise method for synthesizing a composite resin with PSF and iron ferrite, and to disclose the basic characteristics of the composite resin by performing a series of batch experiments. Since the composite resin was prepared into the form of magnetic-susceptible rigid beads, however, we are currently planning to perform further studies on the column operation and on the process-control by applying external magnetic field.

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