

# The application and properties of composite sorbents of inorganic ion exchangers and polyacrylonitrile binding matrix

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## Abstract

A description is given of the preparation and properties of potassium hexacyanocobalt (II) ferrate (II) (KCFC) and the composite, potassium hexacyanocobalt (II) ferrate (II)–polyacrylonitrile (KCFC–PAN). The materials were dried at high temperatures and characterized by chemical analysis, scanning electron microscope, X-ray diffraction, inductively coupled plasma and infrared.

The ion exchange of alkaline earth metals and molybdenum on a nonstoichiometric compound  $K_2[CoFe(CN)_6]$  and its PAN based absorber was examined by batch methods. The adsorption of molybdenum from aqueous solutions on KCFC–PAN was investigated and optimized as a function of equilibration time and pH. The materials which were dried at optimum high temperature of 110 °C were found to be stable in water, dilute acids, alkaline solutions and relatively high temperature.

The distribution coefficient values  $K_d$  for alkaline earth metals, followed the same trend of increase for both sets of absorbers studied, i.e.  $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ , which closely resembles to the order of the size of the hydrated cations. However, the  $K_d$  values show a significant increase for PAN based absorbers in comparison to KCFC absorbers.

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**Keywords:** Hexacyanoferrates; Polyacrylonitrile binder; Sorption properties; Distribution coefficient

## 1. Introduction

The problem of radioactive waste treatment and management has been raised from the very beginning of the use of nuclear energy for different purposes. The waste streams from nuclear facilities include low, intermediate and high activity wastes, which may also include  $\alpha$ -emitting materials. The waste streams could be of different origin and contain, besides radionuclides, various toxic and hazardous materials, such as heavy metals, organic wastes from decontamination procedures, etc. [1–5].

Organic sorbents, commonly used for sorption of radioactive wastes, have certain drawbacks and among them is their ability to swell, which makes them incompatible for the final waste form.

Inorganic sorbents however have been used more extensively in the past two decades, due to their greater thermal and radiation stability, high chemical stability even in strongly acidic media

and their compatibility with final waste forms. Some of the inorganic sorbents have proved to have greater selectivity for trace radionuclides compared to organic ion exchangers, and much better operation over a wider pH range [6–9]. The major disadvantage of synthetic inorganic ion exchangers is the difficulty in preparing granulated materials with sufficient strength and suitable mechanical properties for use in column applications [10–12]. In this paper as part of a series of studies on inorganic composite absorbers, the group of inorganic ion exchangers modified by a binding material in order to prepare larger particles with higher granular strength is considered. Many different methods have been proposed for preparing granules of inorganic ion exchangers and for improving their granular strength.

Polyacrylonitrile (PAN) based composite inorganic–organic absorbers represent a group of inorganic ion exchangers modified by using PAN binder to produce larger size particles. In the view of stability and treatment for final disposal, the composite absorbers represent a separate group of absorbers similar both to the organic and inorganic ion exchange resins [13–17]. Their main feature is that the organic binding polymer (PAN) is inert and all the radionuclides are bound to inorganic active

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component (inorganic ion exchanger). As a result, contrary to organic ion exchange resins even in the case of decomposition of organic binding matrix (radiation, chemical, thermal or biological decomposition) no radionuclides are released.

Preparation of composite absorbers with organic binding matrices involves dispersing an exchanger in a solution of a matrix/matrix–monomer/matrix–component, followed by coagulation/polymerization/polycondensation of the dispersion and separation of a product. Modified polyacrylonitrile has been proposed as a universal binding polymer for practically any inorganic ion exchanger, and the principal scheme for the preparation was proposed by Šebesta [18].

Several authors published papers on the use of PAN as a binding polymer for granulating hydrous oxides of polyvalent metals, such as titanium oxide [19–21]. Nakamura et al. [22] used a commercial PAN-HTO (Asahi Chemical Industry Co. Ltd.) containing hydrous titanium oxide granulated with PAN to study the uptake of uranium from sea water.

In the following parts of this contribution, composite absorbers, potassium cobalt hexacyanoferrate with polyacrylonitrile binding matrix is prepared and its properties and technological application are evaluated. Furthermore, the advantages and disadvantages of the absorber are considered.

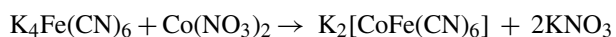
## 2. Experimental

### 2.1. Preparation of potassium hexacyanocobalt (II) ferrate (II)

Hexacyanoferrates are generally prepared by mixing a solution of a transition metal salt with a solution containing ferrocyanide ions, usually Na<sup>+</sup> or K<sup>+</sup> salts and ferrocyanic acid. Since the mechanical properties of hexacyanoferrates and their chemical behaviour vary according to the method of preparation, experiments were performed in order to find the optimum conditions, such as the concentration of solutions, temperatures of precipitation and drying and effects of a mechanical carrier. The method of preparation chosen and described as below, gives sufficiently large crystalline particles, which could directly be used as column bed material. A technical advantage of the described procedure is that the granules produced do not undergo decomposition during the contact with the treated solution (for example, by peptisation), which may cause decreased flow rate or even column clogging. Another important advantage of the procedure is the possibility to granulate mixtures of various active components, and thus the properties of such mixed absorbers can be tailored to the special features of the applications.

All the reagents and chemical used were of Analar grade obtained from Merck. The final method chosen is described in detail below.

A nonstoichiometric potassium hexacyanocobalt (II) ferrate (II) abbreviated as KCFC was prepared by slowly adding 200 mL of 0.5 M K<sub>4</sub>[Fe(CN)<sub>6</sub>] to 480 mL of 0.3 M Co(NO<sub>3</sub>)<sub>2</sub> under continuous stirring at room temperature at a molar ratio of Co/Fe = 2.44. The reaction was as below:



It must be pointed out that the composition of the product depends upon the proportions of the two reagents used. In order to prevent the formation of colloidal products or slimes, that are difficult to centrifuge, Co(NO<sub>3</sub>)<sub>2</sub> must be added in excess and the optimum amount of excess was found to be 40%. The KCFC was green precipitate, which was filtered, washed with deionised water and dried in an oven at 120 °C. The product was ground and sieved to 50–100 mesh.

### 2.2. Preparation of composite absorber based upon polyacrylonitrile binding matrix

A weighed amount of potassium hexacyanocobalt (II) ferrate (II) (KCFC) which had been synthesized as above was measured in a weight ratio of 1:1 to polyacrylonitrile (PAN).

A weighed amount of PAN was dissolved in 12 M HNO<sub>3</sub> with gentle heat and continuous stirring, till a viscous solution was obtained. KCFC was added to the mixture at room temperature, and finally poured into a deionised water bath. KCFC–PAN was formed instantly. This was filtered and washed with deionised water and dried at 80 °C in an oven for 24 h. The PAN absorber was ground and sieved to 50–100 mesh.

This procedure can be modified or simplified in several ways. The initial components (or their solutions) for preparing the inorganic ion exchanger can in some cases be mixed directly with solution of the binding polymer, instead of using the ready made dried and powdered exchanger. The active component of the composite ion exchanger is then formed during (or after) the coagulation of the binding polymer. Another possibility is to mix one of the components of the inorganic ion exchanger with the solution of the binding polymer while the other component is dissolved in the coagulation bath. These methods enable incorporation of very fine to colloidal particles of the active component in the binding polymer, which increases the capacity and improves the ion exchange kinetics of the resulting sorbent. The final product can be shaped as grains, beads, fibers, membranes, etc.

### 2.3. Chemical stability of PAN-based composite sorbents

A PAN binding polymer is stable in all aqueous solutions of common electrolytes, except concentrated solutions of ZnCl<sub>2</sub>, LiBr, CaCl<sub>2</sub> and NaSCN, which are known to dissolve polyacrylonitrile. This polymer also dissolves in acids more concentrated than 8 M HNO<sub>3</sub>, 5 M H<sub>3</sub>PO<sub>4</sub> or 5 M H<sub>2</sub>SO<sub>4</sub>.

The chemical stability of the PAN binder is excellent in neutral to weakly acidic solutions. In acid media with a pH of 0, and in alkaline media with pH up to 13, no deterioration of the sorption properties of composite sorbents was observed.

In alkaline solutions at pH >13, chemical stability of PAN is negatively affected by its hydrolysis. The influence of the hydrolysis increases with increasing pH and temperature. The binding polymer subsequently hydrolyses to gel, becomes hydrophilic and finally dissolves. The hydrolysis itself does not deteriorate the sorption properties of composite sorbents; it affects only their mechanical stability.

Due to the high sorption rate achievable with most PAN-based composite sorbents, their sorption capacity will usually be exhausted earlier. Furthermore, most active components (inorganic ion exchangers) are not sufficiently stable in media with high alkalinity. Therefore, the stability of PAN binder in alkaline solution, even though limited, is sufficient for most of the practical applications.

#### 2.4. Chemical and instrumental analysis

The elemental analysis of the material was accomplished by decomposing 0.05 g of hexacyanoferrates in 1 mL of concentrated H<sub>2</sub>SO<sub>4</sub> with heating and the resulting solution was evaporated to dryness. The residue was taken up in 10 mL of 0.1 M H<sub>2</sub>SO<sub>4</sub> and diluted to 50 mL with deionized water. An aliquot was then used for measuring the amount of K, Co and Fe, using a Perkin-Elmer model 5500 inductively coupled plasma (ICP-AES) spectrometer.

The infrared runs were carried out for the absorbers, a Perkin-Elmer spectrophotometer being used for these studies.

Scanning electron microscope (SEM) of the samples of the absorbers synthesized was carried out using a Philips model XL30 SEM.

X-ray powder diffractometry was carried out using an 1800PW Philips diffractometer with Cu K $\alpha$  beam in order to determine the structures of KCFC and KCFC–PAN absorbers. The finely powdered samples of the absorbers were packed in to a flat aluminium sample holder, where the X-ray source was a rotating anode operating at 40 kV and 30 mA with a copper target. Data were collected between 4° and 60° in 2 $\theta$ .

The solubility of the exchanger was determined at room temperature by equilibrating 0.1 g of the sieved material in various solutions overnight. The supernatant was analyzed by ICP spectrophotometer.

#### 2.5. Batch distribution coefficient ( $K_d$ )

The batch distribution coefficient ( $K_d$ ) is an equilibrium measure of the overall ability of the solid phase ion exchange material to remove an ion from solution under set conditions. The batch distribution coefficient,  $K_d$ , is an experimental way of determining the affinity of a sorbent material for a specific ion. The batch distribution coefficient can also be used as an indicator of the selectivity and affinity for a particular ion in the presence of a complex matrix of interfering ions. Larger  $K_d$  values indicate a greater amount of ions, which are concentrated on to the sorbent material. To ensure accurate comparison of  $K_d$  results, experimental conditions, such as liquid volume to solid mass ratio, temperature, solution composition and material pre-treatment were analogous for all experiments. Distribution coefficient ( $K_d$ ) values were calculated by

$$K_d = \frac{C_i - C_f}{C_f} \frac{V}{M} \text{ mL g}^{-1}$$

where  $C_i$  is the initial ion concentration of the solution,  $C_f$  the ion concentration in solution after equilibrium with the absorber,  $V$

the volume of solution (mL) and  $M$  is the weight of the absorber in contact with  $V$  mL of solution (g).

The rate of adsorption was determined by equilibrating 0.2 g of KCFC and KCFC–PAN absorbers (50–100 mesh) in 20 mL of respective solutions of 0.005 M alkaline metals, Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> ions and radionuclide molybdenum-99, using a thermostated shaker for 24 h, at 25 °C. The solution was separated and an aliquot of 1 mL of supernatant solution was withdrawn and its concentration (activity in case of <sup>99</sup>Mo) was measured by ICP (gamma spectrometry) and compared with the initial concentration (activity) of the solution. The adsorption was calculated using the above formula.

### 3. Results and discussion

The results of scanning electron microscopic observation revealed that the particles were not homogeneous. A crust of PAN with many holes was observed, the pore size of the inner part of the particles was larger than that near the surface. The kinetics of sorption on these absorbers is very fast, because the finely divided particles of the active components are embedded into the macropores of the binding matrix. The deposition of the active component inside the macropores is well demonstrated by the comparison of scanning electron microscope photographs shown in Photos 1 and 2. These photographs show cross-sections

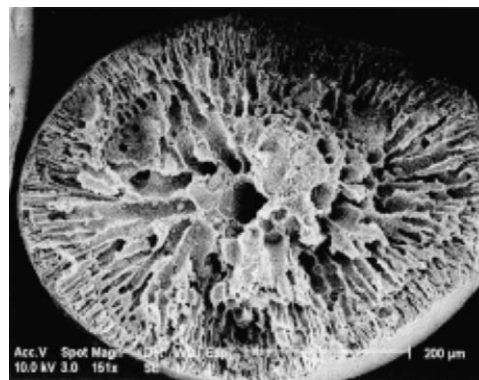


Photo 1. Scanning electron microscopic photograph of KCFC–PAN composite absorber bead cross-section.

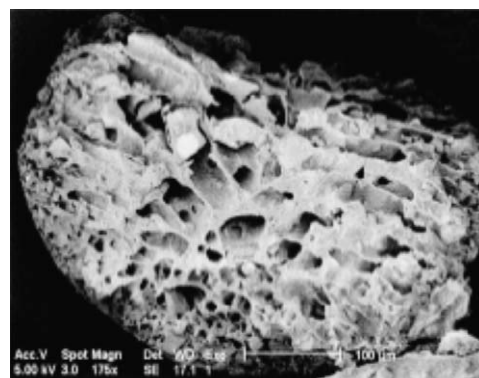


Photo 2. Scanning electron microscopic photograph of PAN binder bead cross-section.

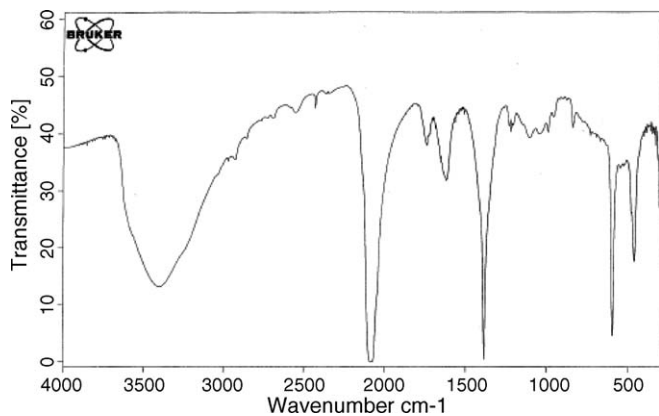


Fig. 1. IR spectrum of KCFC.

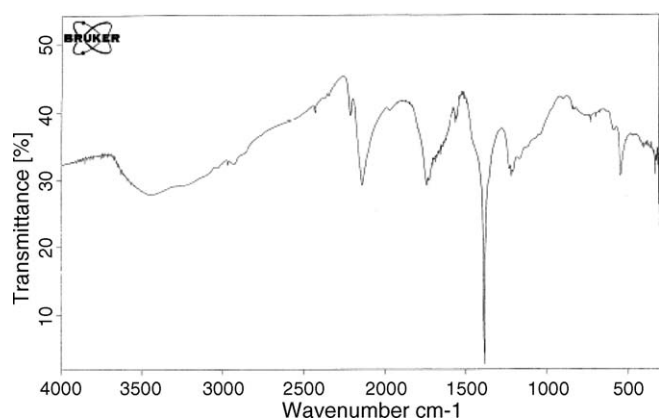


Fig. 2. IR spectrum of KCFC-PAN.

of the grains of a composite absorber KCFC-PAN and of polyacrylonitrile (PAN) binding polymer, respectively.

The IR spectrum of KCFC and KCFC-PAN are recorded in Figs. 1 and 2, respectively. The first peak at  $3450\text{ cm}^{-1}$  is due to interstitial water and hydroxyl groups. The sharp and strong absorption peak at  $2095\text{ cm}^{-1}$  corresponds to cyanide stretching region; and the peak at  $1620\text{ cm}^{-1}$  is due to the deformation vibration of the free water molecules. The bands in the  $350\text{--}500\text{ cm}^{-1}$  region are due to the M-C stretching. However, it must be pointed out that the IR spectrum of the samples heated to  $500^\circ\text{C}$  is typical of oxide spectra. Moreover, the samples are completely decomposed and no cyanide band, water molecule or OH group is observed in the heated samples. These samples are simple mixture of oxides.

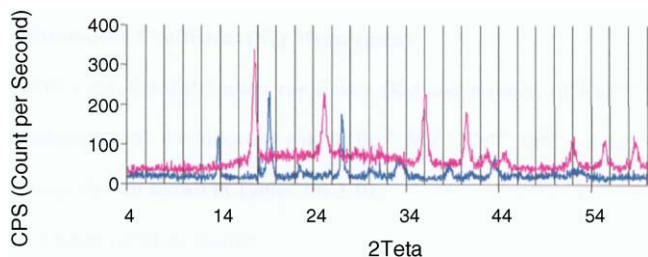


Fig. 3. XRD patterns for KCFC and KCFC-PAN absorbers.

Table 1

The distribution coefficient of various ion exchangers

Ion exchanger	Ions	Distribution coefficient, $K_d$ (mL/g)
KCFC	$\text{Be}^{2+}$	7440
KCFC	$\text{Mg}^{2+}$	5690
KCFC	$\text{Ca}^{2+}$	6540
KCFC	$\text{Sr}^{2+}$	10760
KCFC	$\text{Ba}^{2+}$	11350
KCFC	$^{99}\text{Mo}$	436
KCFC-PAN	$\text{Be}^{2+}$	$4.7 \times 10^7$
KCFC-PAN	$\text{Mg}^{2+}$	$6.0 \times 10^4$
KCFC-PAN	$\text{Ca}^{2+}$	$2.7 \times 10^5$
KCFC-PAN	$\text{Sr}^{2+}$	$2.7 \times 10^7$
KCFC-PAN	$\text{Ba}^{2+}$	$2.8 \times 10^7$
KCFC-PAN	$^{99}\text{Mo}$	722

Fig. 3 shows XRD patterns for KCFC and KCFC-PAN absorbers. The XRD pattern for both absorbers indicated a typical face-centered cubic (FCC) structure; however, the diffraction intensity is interrelated with the Co/Fe ratio [23], and with rather high ratio of 2.44 which was chosen in this study, a rather high crystallinity and narrow width of reflections which corresponds to the larger size of crystals are observed as shown in Photo 2. In XRD pattern of KCFC-PAN, there are sharp peaks corresponding to  $2\theta = 17.72, 25.24, 31.12, 36.08, 40.56, 42.8, 52.2$  and  $58.64^\circ$ . By comparing the data and XRD patterns of KCFC and KCFC-PAN absorbers, it was observed that the  $2\theta$  values at the peak points of KCFC-PAN are the same as those in KCFC, and their patterns almost match one another, and hence their crystalline structure is very similar.

The uptake behaviour of alkaline earth metals and molybdenum on KCFC and KCFC-PAN absorbers were examined by determining the distribution coefficients,  $K_d$ , as shown in Table 1. The distribution coefficient is often a proper quantity to express the distribution of an ion between the exchanger and the solution phase. This is especially true when the exchanging ion is present in the trace concentration, since the ionic composition does not practically change at macro levels in trace ion exchange. Its interesting to note that the  $K_d$  values tend to follow the same trend of increase for both sets of absorbers studied, i.e.  $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ , which closely resembles to the order of the size of the hydrated cations [24]. However, the  $K_d$  values show a significant increase for PAN based absorbers in comparison to KCFC absorbers.

Fig. 4 shows the effect of equilibration time on the uptake percentage of molybdenum on KCFC-PAN. The uptake rate increased with decreasing particle size of the sample, suggesting that the rate determining step of the adsorption of  $^{99}\text{Mo}$  would be governed by an intergranular diffusion through the tunnel in the FCC structure of KCFC-PAN.

Initial conditions for optimum shaking time and pH for molybdenum adsorption on KCFC-PAN were investigated. In order to determine the optimum shaking time for the adsorption equilibrium of molybdenum between solid and liquid phases, a set of experiments was performed as a function of equilibration time in the range of 0.2–5 h. The effect of shaking time on the

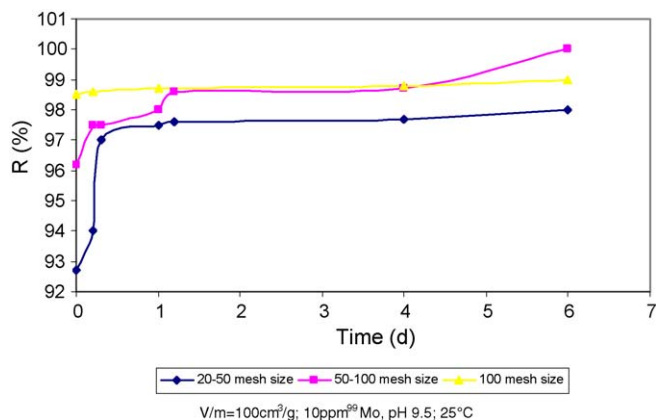


Fig. 4. Rate of <sup>99</sup>Mo uptake by KCFC-PAN with different particle sizes.

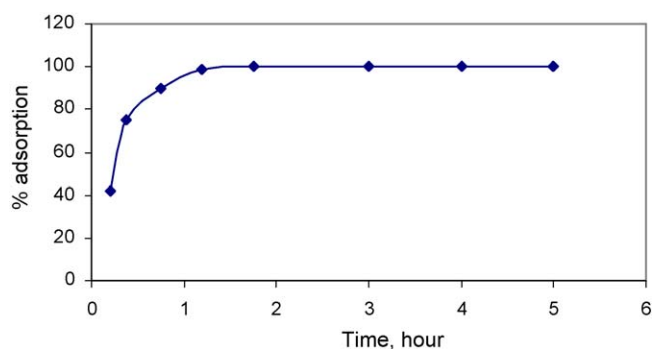


Fig. 5. Variation of percent adsorption of molybdenum with shaking time.

percent adsorption of cesium is given in Fig. 5, which shows that there is an increase in percent adsorption with increasing shaking time and equilibrium attained in about 2 h, showing the usual trend exhibited by ion exchangers: a fast initial adsorption followed by an almost constant value.

The variation of <sup>99</sup>Mo adsorption with the change in the pH of aqueous solution was examined from pH 1 to 12. The results are given in Fig. 6. This shows that the pH of aqueous solution has not any significant effect on molybdenum retention as the pH is increased from 1 to 12.

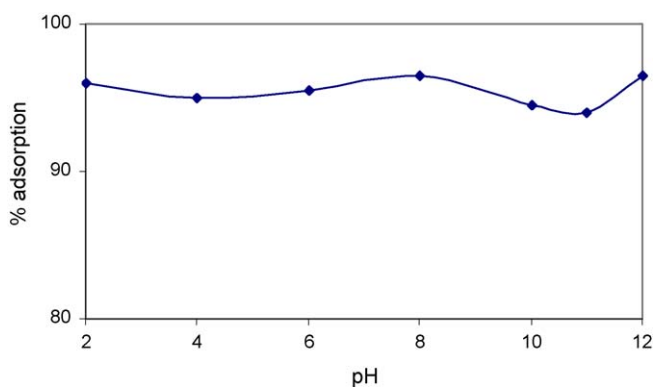


Fig. 6. Variation of percent adsorption of molybdenum with pH of the solution.

#### 4. Conclusion

The results obtained in this study showed that the high drying temperature of KCFC-PAN during preparation gave better surface properties which were due to an increase in the surface area, pore size and percentage capillary. The adsorption of molybdenum from aqueous solutions on KCFC-PAN was found to remain virtually unaltered with increase of pH values. The rate of adsorption of molybdenum increase with increase of shaking time and quickly reached equilibrium which is similar to other ion exchangers. Chemical stability of polyacrylonitrile as a binding matrix was considered and it was found that PAN has good resistance towards mineral acids and weak alkaline solutions. Furthermore, PAN based absorber increased the distribution coefficient values towards alkaline earth metals significantly in comparison to those of KCFC.

The use of PAN-based organic binding polymers has therefore a number of advantages related to the relative ease with which its physico-chemical properties (hydrophilicity, porosity and mechanical strength) are modified. These properties can be modified by the degree of polymer cross-linking, the use of suitable co-polymers or by the composition and temperature of the coagulation bath. Another advantage is the ability to prepare the composite ion exchangers directly in the aqueous solution, eliminating the necessity of introducing organic water immiscible solvents and oils, used frequently in other technologies that would require subsequent removal by washing.

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