

POLYMER ION-EXCHANGER MODIFIED WITH ZIRCONIUM HYDROPHOSPHATE FOR REMOVAL OF URANIUM(VI) FROM WATER

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Introduction

Significant uranium content in water sources is due to the ingress of mine water, wastes of nuclear power plants, mining and mineral processing plants. The content of this element in water is strictly limited (0.015 mg dm^{-3} or less) due to its toxicity. Adsorption and ion exchange are the most suitable methods to reduce U(VI) content in water down to required level. Organic-inorganic resins containing zirconium hydrophosphate (ZHP) were proposed for removal of toxic ions from water [1, 2]. The purpose of this work is to establish the interrelation between structure of the ZHP-containing composites and sorption of U(VI) ions. Another tasks are to ascertain a possibility to remove U(VI) compounds from water and to use the ion-exchangers many times. Method of standard contact porosimetry [3, 4] was applied to investigations.

Experiments

Such strongly acidic cation-exchanger as Dowex HCR-S (*Dow Chemical*) containing $\approx 8\%$ DVB was used for modification with ZHP. Preliminarily the resin was immersed with acetone, the CR sample was obtained by this manner. The resin was modified with ZHP one (*CR-ZHP-1*) and seven (*CR-ZHP-3*) times, additionally sorbed electrolyte (ZrOCl_2) was removed as much as possible before ZHP deposition. The sample modified one time without ZrOCl_2 removal was also obtained (*CR-ZHP-2*). Individual amorphous ZHP was also researched for a comparison. Kinetics of UO_2^{2+} sorption from the solution containing both U(VI) ($2 \times 10^{-4} \text{ M}$) and HCl (0.02 M) was investigated under batch conditions. A number of cycles of sorption-regeneration (using a $1 \text{ M H}_2\text{SO}_4$ solution) was carried out. Sorption of UO_2^{2+} in ion exchange column from the similar solution containing additionally hardness ions was researched.

Results and Discussion

Both single ZHP nanoparticles and their aggregates, which are located in voids between gel fields, have been found for the *CR-ZHP-1* and *CR-ZHP-3* samples. The *CR-ZHP-2* ion-exchanger contains also dendritic particles of micron size in structure defects of the polymer (Fig. 1).

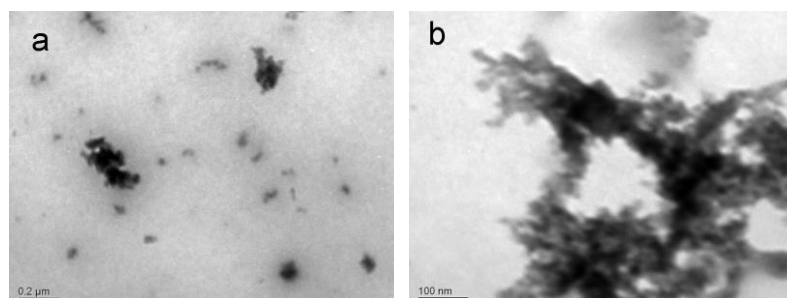


Figure 1. Inorganic constituent in voids between gel fields (*CR-ZHP-1*, a) and in structure defects (*CR-ZHP-3*, b).

Isotherms of water adsorption (Fig. 2a) are related to the polymer constituent according to thermal pretreatment before the measurements (353 K). A change of the swelling pressure (defined according to Gregor model [5]) can be estimated qualitatively by a comparison of the P/P_s ratios

at similar $A_{\text{H}_2\text{O}}$ values (Table 1). The particles in voids between gel fields reduce swelling pressure in the polymer (*CR-ZHP-1*, *CR-ZHP-3*). Large particles in structure defects increase swelling pressure (*CR-ZHP-2*). Regarding CR, build-ups at $\log r = 0.46$ (nm) and 0.63 (nm) of pore size distributions are attributed to clusters and voids between gel fields respectively (Fig.

2b). Volumes of these pores are approximately equal. A volume of pores, which correspond to plateau, is $0.06 \text{ cm}^3 \text{ g}^{-1}$ at $\log r = 0.6-2$ (nm). The voids between gel fields are available for ZHP particles during modification, clusters and channels are free from the inorganic constituent. ZHP in voids between gel fields (*CR-ZHP-1* and *CR-ZHP-3*) causes a shift of the curves to the region of lower $\log r$ values (0.17 and 0.38 (nm) for clusters and void between gel fields respectively). A volume of the last type of pores is higher in a comparison with clusters. In the case of *CR-ZHP-2*, a volume of structure defects is higher than that for other samples, a size of these pores becomes also larger.

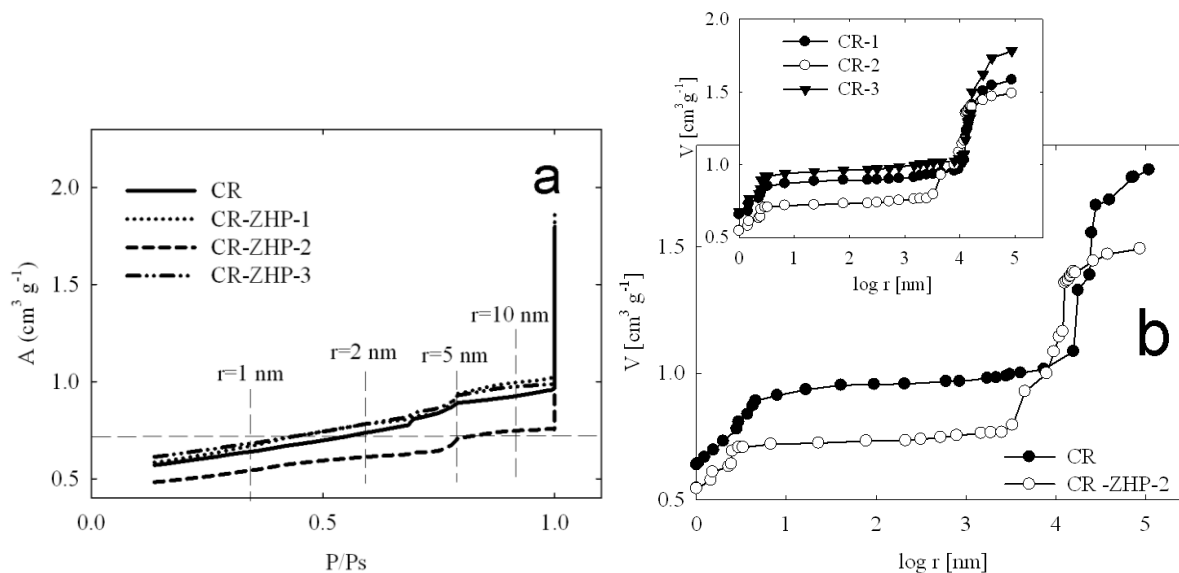


Figure 2. Isotherms of water adsorption (a) and integral pore size distributions (b).

Based on adsorption isotherms, we can calculate a number of water molecules (n) in a hydration shell of the counter-ions (H^+) of $-\text{SO}_3$ groups of the polymer as $n = \frac{A_{\text{H}_2\text{O}}}{A_p V_{\text{H}_2\text{O}} (1-m)}$

(here A_p is the polymer capacity, $V_{\text{H}_2\text{O}}$ is the molar volume of water, m is the mass fraction of ZHP), Increasing in ZHP content results in a growth of the n value due to squeezing of transport pores of the polymer (increase of a distance between groups due to unwinding of macromolecule coil). Some clusters and channels are free from water (decrease of swelling pressure). In the case of *CR-ZHP-2*, ZHP in structure defects provides own swelling pressure, the resulting value is higher in a comparison with the unmodified resin.

Table 1. Characteristics of ion-exchangers

Sample	m	P/P_s ($A_{\text{H}_2\text{O}} = 0.75$ $\text{cm}^3 \text{ g}^{-1}$)	n	R^2 for models				$\bar{D} \times 10^{-12}$ ($\text{m}^2 \text{ s}^{-1}$)	Break-through capacity (mmol cm^{-3})
				I	II	III	IV		
CR	0	0.55	8.4	0.97	0.93	0.88	0.81	0.66	3.4×10^{-4}
CR-ZHP-1	10	0.43	9.8	0.99	0.97	0.98	0.93	1.01	7.12×10^{-4}
CR-ZHP-2	50	0.43	14.6	0.99	0.97	0.94	0.94	1.73	2.36×10^{-3}
CR-ZHP-3	15	0.82	10.9	0.99	0.99	0.95	0.91	0.98	3.93×10^{-3}
ZHP	100	-	-	0.99	0.96	0.96	0.98	0.03	-

I – particle diffusion, II – film diffusion or chemical reaction, III – reaction of pseudo-first order, IV – reaction of pseudo-second order.

The models of particle diffusion, film diffusion, chemical reaction, particularly reactions of pseudo-first and pseudo-second orders [5] were applied to kinetics of $\text{UO}_2^{2+} \rightarrow \text{H}^+$ exchange.

Sorption obeys particle diffusion model, since high correlation coefficients (R^2) have been found. The effective diffusion coefficient (\bar{D}), which corresponds to $\text{UO}_2^{2+} \rightarrow \text{H}^+$ exchange, was calculated as $0.03 \frac{r_g^2}{t_{1/2}}$ [15], where r_g is the grain size, $t_{1/2}$ is the half-time of exchange. The

highest \bar{D} value was found for the *CR-ZHP-2* sample, since it is characterized by the longest distance between $-\text{SO}_3$ groups of the polymer (the highest n parameter has been found for this ion-exchanger). The *CR-ZHP-3* sample and individual *ZHP* show film diffusion or chemical reaction. In owing to low \bar{D} values, chemical reaction (deposition of insoluble compounds or complex formation) is much more possible. The model of reaction of pseudo-first order can be applied to the *CR-ZHP-1* sample and *ZHP*. At last, kinetics can be described by the model of reaction of pseudo-second order only for *ZHP*. Thus, the rate of ion exchange is determined by the polymer constituent (*CR-ZHP-2*) or inorganic component (*CR-ZHP-1* and *CR-ZHP-3*). The effect of *ZHP* is possible due to partial exclusion of $-\text{SO}_3$ groups from ion exchange in owing to squeezing of transport pores. This effect is masked for the *CR-ZHP-2* sample due to maximal distance between functional groups of the polymer. The largest value of break-through capacity towards UO_2^{2+} species has been found for that ion-exchanger.

Since *ZHP* is related to weakly acidic ion-exchanger, increasing of its content in the polymer provides a reducing of a volume of the solution, which is necessary for UO_2^{2+} desorption. During 5 cycles of sorption-regeneration, UO_2^{2+} species were removed from the composites completely, providing high removal degree of these ions from the solution during the next sorption stage.

Conclusions

ZHP particles provide swelling pressure in the polymer pores, which are free from $-\text{SO}_3$ groups. The inorganic particles in structure defects increase swelling pressure, they can be formally considered as a cross-linking agent. However, the effective diffusion coefficient for $\text{UO}_2^{2+} \rightarrow \text{H}^+$ exchange is higher approximately in 3 times than that for unmodified resin due to an increase of a distance between functional groups of the polymer constituent, which is affected by *ZHP*. The *CR-ZHP-2* sample demonstrates the highest break-through capacity towards UO_2^{2+} species. In the case of *CR-ZHP-1* and *CR-ZHP-3* samples, which contain *ZHP* particles mainly in voids between gel fields, $\text{UO}_2^{2+} \rightarrow \text{H}^+$ exchange is complicated by chemical reaction similarly to the inorganic ion-exchanger. In other words, sorption is affected mainly by *ZHP*. This evidently caused by partial exclusion of $-\text{SO}_3$ groups from ion exchange due to squeezing of clusters and channels. In order to avoid this, the particles in transport pores are assumed to be necessary similarly to [1, 2].

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