



## BEHAVIOR OF EUROPIUM, STRONTIUM AND CESIUM ON ION EXCHANGERS PREPARED FROM POLYVINYL ALCOHOL GRAFTED WITH SUCCINIC OR CITRIC ACID USING GAMMA RADIATION

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The behavior of europium, strontium and cesium on ion exchange resins prepared from polyvinyl alcohol grafted with citric or succinic acid was investigated using gamma spectroscopy in three different media (HNO<sub>3</sub>, HCl, and H<sub>2</sub>SO<sub>4</sub>). The investigation shows that adsorption of the studied elements depends on the concentration of grafted succinic or citric acid and the concentration of the used acidic media. The time needed to reach the adsorption equilibrium is relatively short. The resins were prepared by irradiation of ternary mixtures of PVA / citric or succinic acid / water by gamma irradiation dose of 25 kGy in air and at ambient temperature. The maximum swelling and gel fraction of the prepared resins were investigated. Swelling and gelation decrease with increasing the concentration of citric acid. The decrease in the maximum swelling is due to increased hydrogen bonding between the carboxyl groups of the bonded/trapped citric or succinic molecules and the hydroxyl groups of the polymer. The decrease in the gel fraction can be explained by the presence of the acid that leads to other reactions in the mixture and not preferably to building cross links between the polymer chains.

### INTRODUCTION

Ion-exchange resins are widely used chemicals in separation, purification, and decontamination processes: water softening, removal of toxic metals from water in the environment, wastewater treatment, hydrometallurgy, sensors, chromatography, and bimolecular separations.<sup>1-4</sup> Ion-exchange resins are divided in two groups: organic and inorganic resins. Some organic ion exchange resins consist usually of polymers with a carboxyl function group for cation exchange resins. The required active groups can be introduced after polymerization, or substituted monomers can be used. Radiation synthesis of membranes, hydrogels and adsorbents for various purposes is a wide field of important applications of the radiation technology.

Radiation processing techniques have been widely applied for the synthesis of new materials with specific functional features for various applications such as: hydrogel dressings,<sup>5-8</sup> and membranes for separation.<sup>9-11</sup>

There are a number of works in literature about modification of PVA by means of radiation-induced graft copolymerization of monomers.<sup>12-22</sup> In all this works, with the exception of the work of Yan 2003, only the uptake capacity of the resin for various elements was determined. In this work the behavior of europium, cesium and strontium on ion exchange resin, prepared from polyvinyl alcohol, grafted with citric or succinic acid, was studied. The effect on the sorption of the concentration and nature of acidic external solutions and the effect of contact time were investigated.

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## EXPERIMENTAL

### 1. Preparation of the resin

Polyvinyl alcohol was used for the preparation of the cross-linked resin. 10 g PVA (Merck, MW = 72000) was dissolved in 90 mL distilled water and heated. Then different amounts of grafting acid (0.8 – 15 g) were dissolved in the 10% (w/w) PVA solutions, heated and placed into PVC straws. Before irradiation they were degassed in an ultrasonic bath. They were irradiated in air at ambient temperature in a Co-60 Gamma cell at a dose rate of 3.5 kGy/h, to a dose of 25 kGy. The long cylindrical hydrogels obtained were cut into pieces of 2-3 mm in length and dried in air, and then in a vacuum oven ( $W_o$ ).

### 2. Gel fraction

The samples were dried after irradiation ( $W_o$ ), and then soaked in distilled water for 3 days at room temperature, to achieve the equilibrium of swelling  $W_s$  in order to remove the soluble and unreacted species. The gels were then dried again in air and in a vacuum oven ( $W_E$ ) at 50 °C until constant weight. The gel fraction was calculated according to the following equation:

$$\text{gel - fraction } [\%] = \frac{W_E}{W_o} \times 100 \quad (1)$$

where  $W_o$  is the weight of dried gel after irradiation, and  $W_E$  is the dried weight of the sample after extraction of soluble and unreacted species.

### 3. Maximum swelling

After the soaking and washing procedures, maximum swelling ( $S_{\max}$ %) was calculated using the following equation:

$$S_{\max} \% = \frac{W_s - W_o}{W_o} \times 100 \quad (2)$$

where  $W_s$  is the weight of gel at swelling equilibrium (after three days of soaking in water), and  $W_o$  is the weight of dried gel after irradiation.

### 4. Sorption of the investigated elements on the resin

To study the sorption behavior of the elements from different acidic media ( $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{H}_2\text{SO}_4$ ) on the prepared resins a certain activity of the isotopes ( $^{152}\text{Eu}$ ,  $^{137}\text{Cs}$ ,  $^{85}\text{Sr}$ ) is injected in solutions of various acids with various concentrations (0.001, 0.01, 0.1, 1, 3, and 5 mol/L). These liquid phases were brought in contact with the resins. After a certain time, the phases were separated and measured using  $\gamma$ -spectrometry. An experiment series was done to determine the equilibrium time. Because of the short equilibrium time (less than 3 hours in all cases) a contact time of 24 hours was taken in all following experiments. The weight of the solid phase was 0.2 g, the volume of the liquid 5 mL, and the concentration of the investigated elements 0.1 mol/L in all experiments.

The prepared resin was used in a first experiment series without any conditioning. It was only washed with distilled

water for 48 hours to reach the maximal possible swelling. The results show that the adsorption of all three elements is less than 5%.

The reported results in this work were obtained after soaking the resin in distilled water for 48 hours to reach the maximum possible swelling. The resin was then washed with various concentrations of hydrochloric acid for 24 hours, and finally with distilled water.

As mentioned before, the element ratios of Eu, Sr, and Cs were determined using  $\gamma$ -spectrometry (HPGe-Detector, 60% Eff., FWHM=0.998 at 122 keV and 1.88 at 1332 keV, Canberra 35 plus). The uncertainties of all  $\gamma$ -measurements were estimated of about 5%.  $^{137}\text{Cs}$  was taken from an IAEA-standard.  $^{152}\text{Eu}$  and  $^{85}\text{Sr}$  were produced in the Syrian MNSR-reactor by irradiation of their nitrates with a neutron flux of  $10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ .

The element fraction in the aqueous phase was calculated according to the following equations:

$$F_w = \{[C_w]/[C_o]\} * 100 = A_w/A_o * 100 \quad (3)$$

where  $F_w$  is the element fraction in the aqueous phase,  $[C_w]$  is the element concentration in the aqueous phase after phase separation,  $[C_o]$  is the initial element concentration,  $A_w$  is the activity of the aqueous phase after phase separation, and  $A_o$  is the initial activity.

## RESULTS AND DISCUSSION

### 1. Gel fraction

When polymer solutions are irradiated with high-energy radiations, macroradicals are generally produced as a result of indirect effect of radiation. These macroradicals disappear later either through the formation of crosslinks between the polymer chains, or stabilize themselves by intramolecular linking or by chain scission.

Fig. 1 represents the gel fraction of PVA with respect to the amounts of citric or succinic acid, whereas the samples were exposed to a constant irradiation dose of 25 kGy. It can be observed that the gel fraction becomes lower as the acid concentration increases. One explanation for this behavior might be that the formed macromolecule radicals would react with the acid molecules; therefore, the polymer backbone becomes busy at these positions for crosslinking reactions. Another explanation could be that the formed acid radicals would react with the polymer radicals. In this case the polymer backbone will be blocked at these locations for crosslinking reactions.

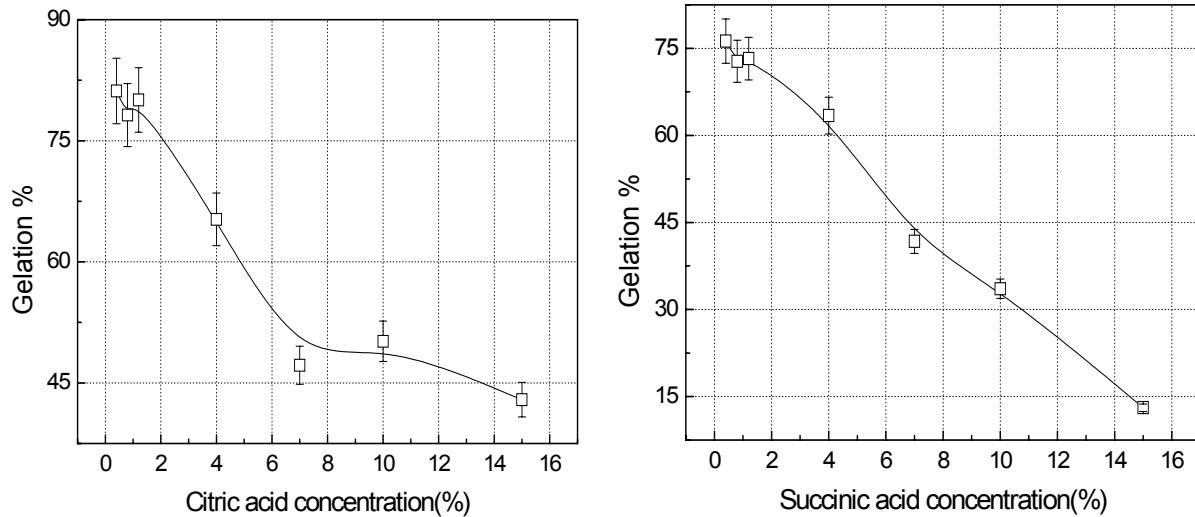


Fig. 1 – Gel fraction of PVA grafted with different citric and succinic acid concentrations.

## 2. Maximal swelling

The swelling of non-ionic hydrogels depends on the hydrophilicity of the base monomer or polymer, and the density of the intermolecular cross-links.<sup>23</sup> Fig. 2 shows the maximum swelling of the prepared resins versus the amounts of citric

or succinic acid. It can be seen that the maximum swelling decreases with increasing the acid concentration. This behavior can be explained with increased hydrogen bonds due to the increased acid groups bonded to the polymer chains.

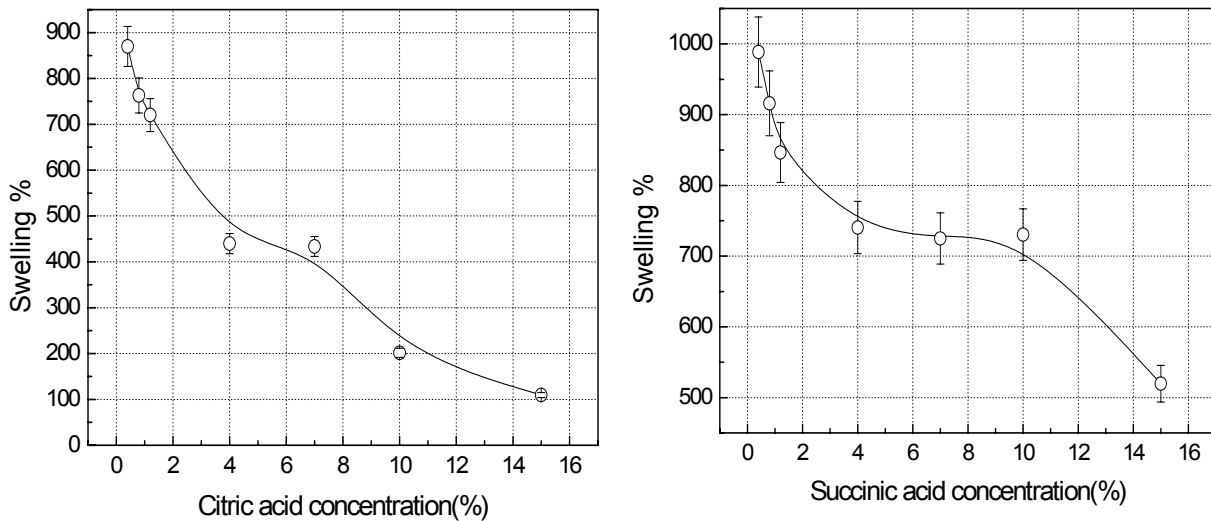


Fig. 2 – Maximal swelling of PVA grafted with different citric and succinic acid concentrations.

## 3. Sorption of the investigated Elements on the resin

Figs. 3, 4 and 5 show element ratios in the liquid phase in different acidic media for europium, cesium and strontium respectively (contact time of the phases 24 hours, weight of the

solid phase 0.2 g, volume of the liquid phase 5 ml, initial concentration 0.1 mol/L). The left panel of the figures show the results for PVA grafted with citric acid and the right panel the results for PVA grafted with succinic acid. Every curve represents a different concentration of grafted acid.

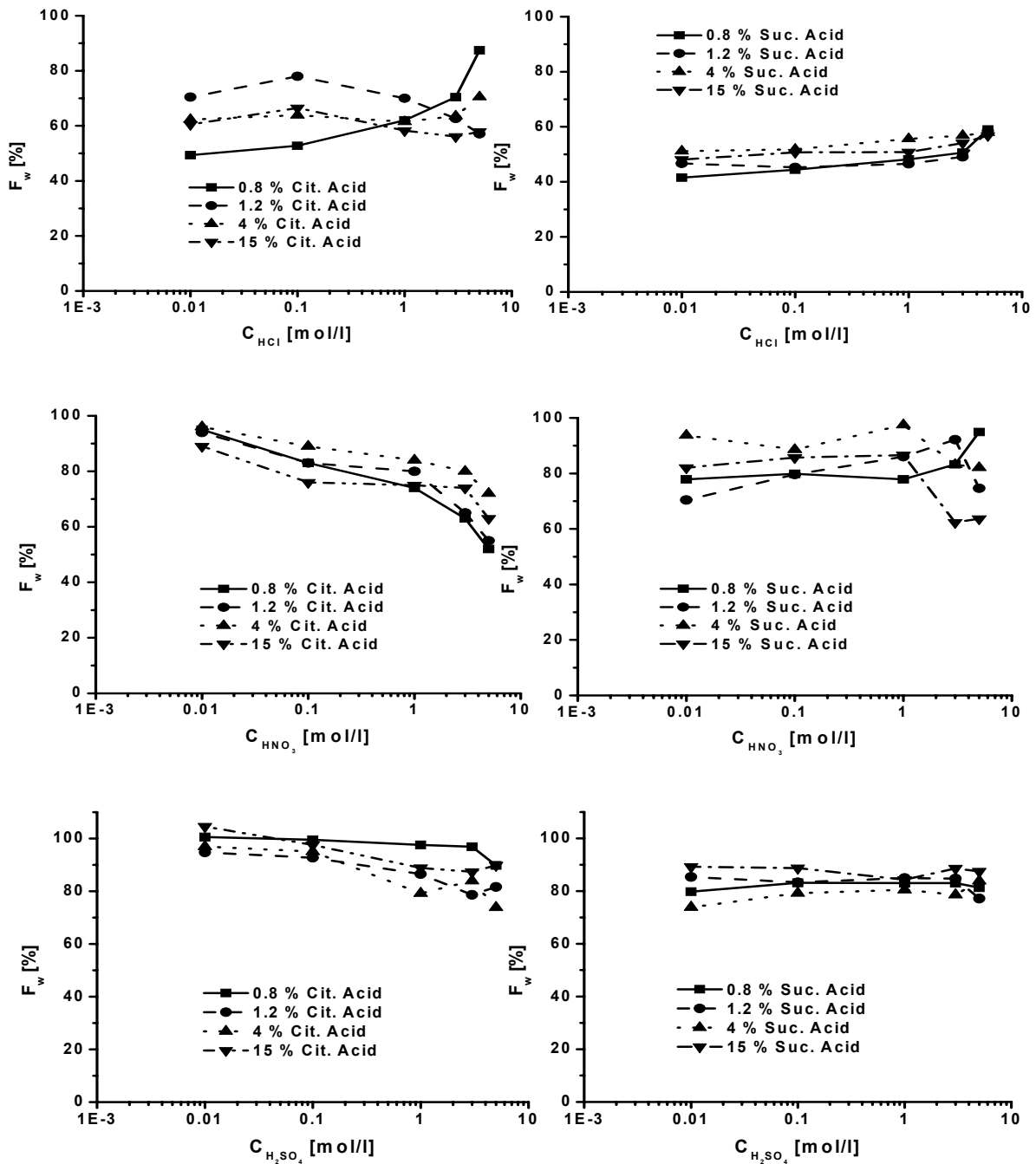


Fig. 3 – Europium ratios in the liquid phase in different acidic media  
( $t=24$  h, weight of the solid phase 0.2 g, volume of the liquid phase 5 ml).

The adsorption of europium on both resins in all concentrations of H<sub>2</sub>SO<sub>4</sub> is very weak (less than 4%) in all cases. Adsorption ratios of more than 60% are achieved in low HCl-concentration on the resin prepared in the presence of 0.8% succinic acid. The best adsorption ratio in HNO<sub>3</sub> is by the use of acid concentrations about 5 mol/L. By higher concentrations of HNO<sub>3</sub> the liquid phase

became brown, which gives indication about resin degradation.

Fig. 4 shows cesium ratios in the liquid phase in different acidic media. In spite of europium, the best adsorption ratio can be achieved by the use of H<sub>2</sub>SO<sub>4</sub> as a medium on the resin prepared in the presence of 10% succinic acid. Adsorption ratios of about 50% are achieved in 5 mol/L HCl on the resin prepared in the presence of 0.8% succinic

acid. The same ratio can also be achieved by the use of 5 mol/L HNO<sub>3</sub> on the resin prepared in the presence of 10% citric acid. By higher

concentrations of HNO<sub>3</sub> and HCl the liquid phase became brown, which gives indication about resin degradation.

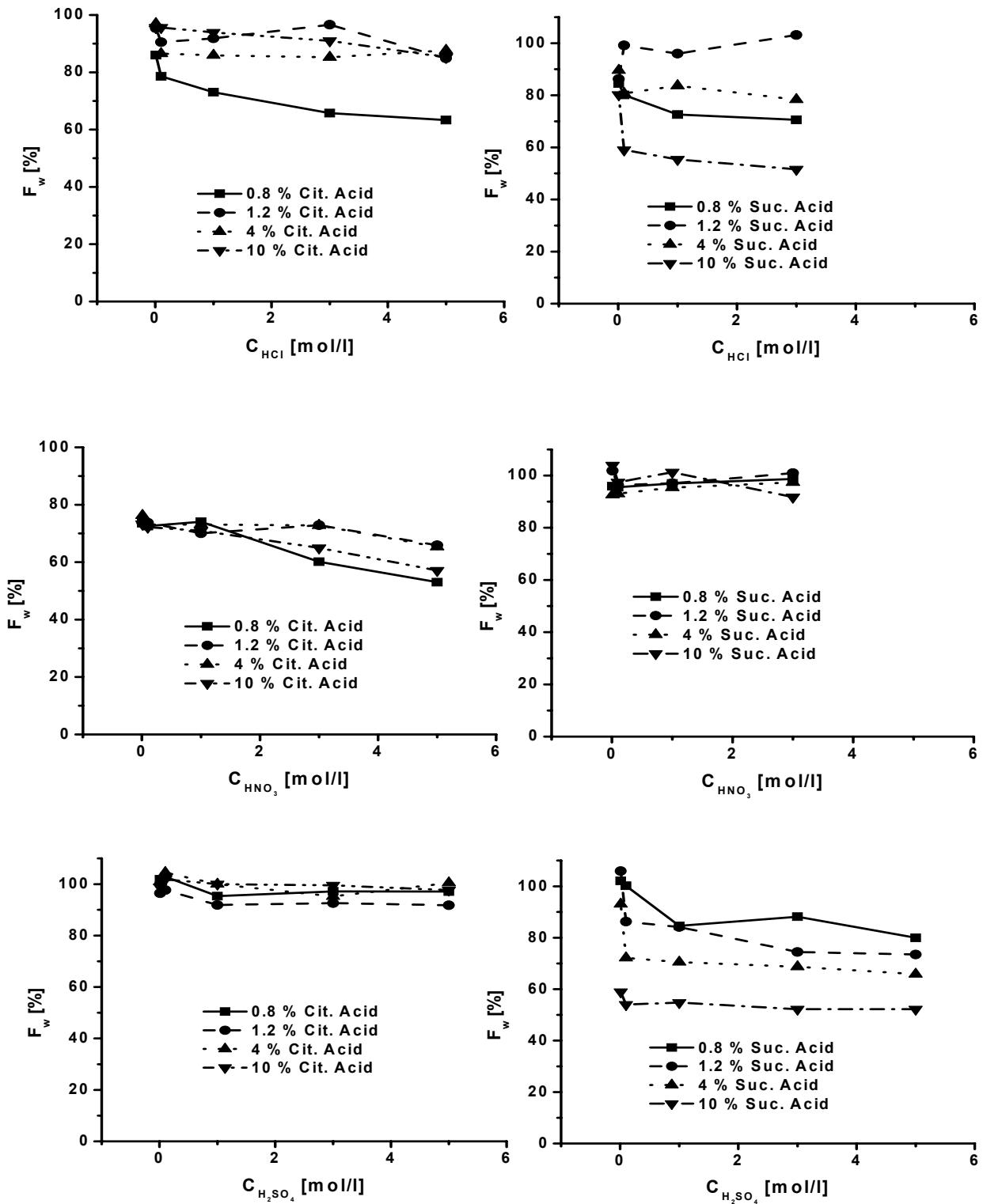


Fig. 4 – Cesium ratios in the liquid phase in different acidic media (t=24 h, weight of the solid phase 0.2 g, volume of the liquid phase 5 ml).

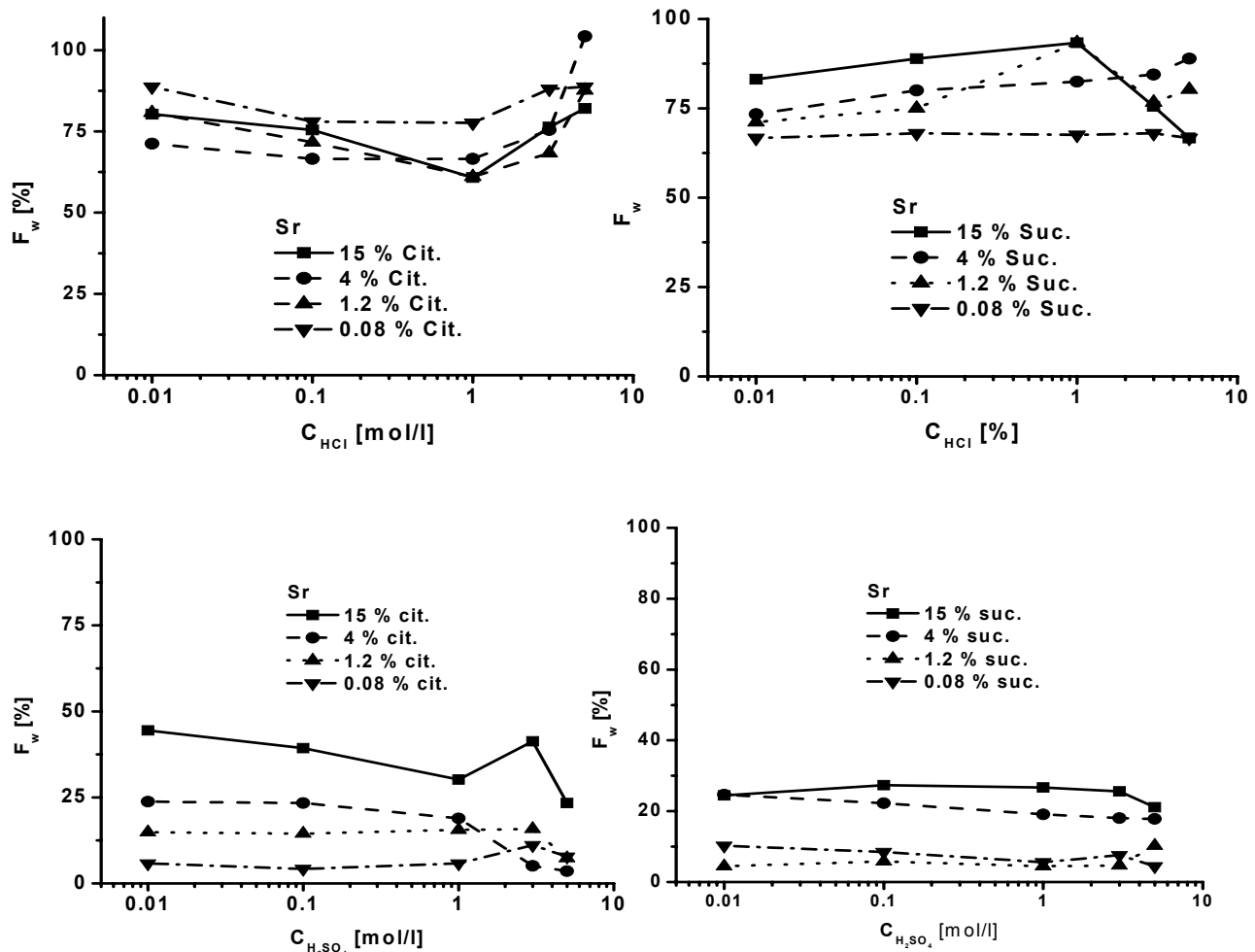


Fig. 5 – Strontium ratios in the liquid phase in different acidic media in equilibrium ( $t=24$  h, weight of the solid phase 0.2 g, volume of the liquid phase 5 ml).

The strontium ratios in the liquid phase in HCl vary between 80 and 90 % and there are no special conditions or concentrations, which gives better results. Adsorption ratios more than 90% can be achieved on both resins in  $H_2SO_4$  (Fig. 5).

The low adsorption ratios on the resins indicate that transport mechanism is another one than ion exchange. It could be electrolyte sorption on the resin.

## CONCLUSION

Ion exchange resins have been prepared by grafting of polyvinyl alcohol with various concentrations of succinic and citric acid. The sorption of europium, cesium and strontium from different acidic media ( $HNO_3$ , HCl,  $H_2SO_4$  with various concentrations) on the prepared weak acid ion exchangers containing carboxyl and hydroxyl functional groups was investigated. The low

adsorption ratios on the prepared resins lead to the hypotheses that main mechanism of transport into the solid phase is electrolyte sorption instead of the ion exchange.

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## REFERENCES

1. O.Alhassanieh, A. Abdul-Hadi, M. Ghafar, and A. Aba, *Appl. Radiat. and Isot.*, **1999**, *51*, 493-498.
2. F. Helfferich, "Ion Exchange", Dover publication, New York, 1995.
3. M. Streat, "Applications of Ion Exchange in Hydrometallurgy, Hydrometallurgical Process Fundamentals"; Cambridge, 1984, p. 539-553.
4. J. B. Brower, R.L. Ryan, M. Pazirandeh, *Env. Sci. Tech.*, **1997**, *31*, 2910-2914.

5. J.M. Rosiak, A. Rucinska-Reybas, W. Pekala, US Patent No. 4, 490, 871 Method of Manufacturing of Hydrogel Dressings, 1989.
6. M.T. Razzak, D. Darwis, S. Zainuddin, *Rad. Phys. Chem.*, **2001**, 62, 107-113.
7. Z. Ajji, A.M. Ali, *Nucl. Inst. and Methods in Phys. Research B*, **2005**, 236, 580-586.
8. Z. Ajji, G. Mirjalili, A. Alkhatib, H. Dada, *Rad. Phys. and Chem.*, **2008**, 77, 200-202.
9. IAEA 2005, Radiation synthesis of stimuli-responsive membranes, hydrogels and adsorbents for separation purposes, IAEA, Vienna, IAEA-TecDoc-1465, 2005.
10. E. A. Hegazy, H. A. Abd El-Rehim, H. Kamal, K. A. Kandeel, *Nucl. Inst. and Methods in Phys. Research B*, **2001**, 185, 235-240.
11. A.M. Ali, Z. Ajji, *Rad. Phys. and Chem.*, **2009**, 78, 927-932.
12. M.G. Katz, T. Wydeven, *J. Appl. Polym. Sci.*, **1981**, 26, 2935-2943.
13. H.A. Abd El-Rehim, E.A. Hegazy, A.M. Ali, *J. Appl. Polym. Sci.*, **1999**, 74, 806-812.
14. H.A. Abd El-Rehim, E.A. Hegazy, A.M. Ali, *J. Appl. Polym. Sci.*, **2000**, 76, 125-129.
15. K. Burczak, T. Fujisato, M. Hatada, Y. Ikada, *Proc. Jpn. Acad. B*, **1991**, 67, 83-89.
16. V. Shantora, R.Y.M. Huang, *J. Appl. Polym. Sci.*, **1981**, 26, 3223-3229.
17. Z. Ajji, A.M. Ali, *Nucl. Inst. and Methods in Phys. Research B*, **2007**, 265, 362-365.
18. Z. Ajji, A.M. Ali, *J. of Hazardous Materials*, **2010**, 173, 71-74.
19. Y. Zhanhai, R. Lei, X. Jun, DOI cnki:SCN:31-1258.0.1997-02-000.
20. Y. Zhanhai, R. Lei, X. Jun, *J. of Appl. Polym. Sci.*, **1992**, 198, 683-687.
21. W. Yan, Z. Dong, T. Zhaoyi, L. Shunzhong, S. Zhenqing, Y. Anguo, F. Yijun, *Journal of The Chinese Rare Earth Society*, S1-007, DOI CNKI:SUN:XTXB.0.2003-S1-007.
22. N. Sahiner, N. Pekel, O. Güven, *Rad. Phys. Chem.*, **1998**, 52, 271-276.
23. O. Güven, M. Sen, E. Karadag, D. Saradin, *Rad. Phys. and Chem.* 56, **1998**, 381-386.

