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THE INFLUENCE OF WATER QUALITY ON PROPERTIES OF HYDROGEL MEMBRANES PREPARED BY IONIZING RADIATION

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ABSTRACT

Insoluble hydrogels are crosslinked polymeric materials which have ability to absorb significant amounts of water in their three-dimensional polymeric matrix.

Ionizing radiation has been used in hydrogels preparation allowing the structure formation and sterilization simultaneously in only one step without necessity to add any initiators crosslinkers. These advantages make irradiation an useful method for synthesis of hydrogels, especially for biomedical use.

There are numerous applications of hydrogels such as contact lenses, drug delivery devices, wound dressings, etc.

Poly(N-vinyl-2-pyrrolidone) (PVP) is a water soluble polymer, which exhibits a series of interactions in aqueous solutions. The aim of this work is to investigate the effect of ions present in distillated water to prepare PVP hydrogels because Hofmeister series ions have the capacity to change the water structure that represents the largest fraction of the system. Another reason is that the use of high purity water can be costly in large industrial production of these materials.

Hydrogels with 12% and 20% of PVP were prepared using distillated and ultrapure water. The polymerization was induced by gamma radiation at 25kGy. For the investigation of the distillated water effect, the ions present as impurities were identified by ion chromatography. Physical-chemical properties such as degree of crosslinking of hydrogels was determined using gel fraction methodology and swelling kinetic was studied in the prepared hydrogels.

1. INTRODUCTION

Hydrogels are more often defined as two-component system. The first one is a hydrophilic polymer insoluble in water due the existing three-dimensional network joining its chains. The second one is water.

Hydrogels have found a wide range of biomedical applications including controlled drug delivery systems as well as transdermal systems, replacement of blood vessels, wound dressing, dental materials, ophthalmic applications, contact lenses, and a variety of other related and potential uses. Hydrogels closely resemble living tissues in their physical properties because of their relatively high water content and soft and rubbery consistency. The biocompatibility to tissue and blood coupled to water content is similar to tissue[1].

Ionizing radiation has long been recognized as a suitable process for the formation of hydrogels. Ionizing radiation presents many advantages such as easy process control, possibility of joining hydrogel formation and sterilization in one technological step, no necessity to add any initiators, crosslinkers, etc., minimal waste production, and relatively low cost running[2]. These advantages make irradiation a method of choice in the synthesis of hydrogels, especially for biomedical use[1].

Poly(*N*-vinyl-2-pyrrolidone) (PVP) is a water soluble polymer, which exhibits a series of interactions with dissolved small molecules and ions in aqueous solutions[3]. Fundamental relationship exists between the swelling of a crosslinked polymer in a solvent and the nature of polymer and solvent. Swelling of the three-dimensional network structure in a suitable solvent is the most important parameter for swelling process studies [4].

Ions of the Hofmeister series have a significant effect on the solubility of macromolecular substances and on the stability of their respective secondary, tertiary and quaternary structures[5]. Ionic effects are ubiquitous in aqueous systems of both synthetic and natural polymer gels. These effects have significant influence on the swelling behavior and play an important role in industrial applications and in bioscience. Generally, inorganic ions act as salting-out agents in polymer/water systems and lead to deswelling of hydrogels. Ionic effects on the swelling of gels from poly(vinylpyrrolidone) were found to agree with Hofmeister series. The deswelling degree usually follows the Hofmeister series, i.e., $SO_4^{2-} > F^- > Cl^- > Br^- > I^-$ and $Mg^{2+} > Li^+ > Na^+ > K^+$ for anions and cations, respectively[6]. Depending on ion's chemical nature, it may either destabilize or stabilize the dissolved chains. There is a delicate balance between hydrogen bond, entropy, and hydrophobic interactions. Traditionally, the Hofmeister series were related to the way in which an ion modifies the local arrangement of water[5].

The aim of the present study is to investigate the influence of water quality used to prepare PVP hydrogels by gama-irradiation in the swelling properties. One may consider, however, that the use of water of the high purity quality increases the production costs of industrial hydrogels.

2. METHODS

2.1. Materials

To prepare the hydrogels poly(vinyl pyrrolidone) PVP K90 was purchased from BASF, poly(ethylene glycol) PEG 300 from Oxiteno, agar from Oxoid. All these raw material were medical grade. Distilled and ultrapure water (Barnstead, Inc.) were used along the study.

2.3. Water Characterization

Water conductivity and pH determination were carried out at 26°C using pHmeter, Quimis model G400AS. The anions were determinate in Dionex DX-120 Ion Chromatograph, using Ion Pac AS14 column.

2.2. Hydrogels Preparation

Four hydrogels were prepared for this study: two samples A (12% PVP) and two samples B (20% PVP), by weight, dissolved in distilled water and ultrapure water. The hydrogels solutions were prepared dissolving the PVP in water and then removing oxygen gas bubbling nitrogen gas. The solutions were poured in poly(ethylene terephthalate) molds and sealed. The next step were the irradiation with gamma rays generated in a ^{60}Co source at dose of 25 kGy.

2.4. Hydrogels Characterization

2.4.1. Gel fraction

Hydrogel samples were dried in stove at 60°C until constant weight. The dried samples were weighed and extracted in Soxhlet apparatus with distilled water as solvent during 40 hours. The gels were dried again until constant weight. The gel fraction was calculated as Eq.(1), using initial weight of dry gel (W_d) and weight of extracted dry gel (W_f).

$$\text{Gel}(\%) = \frac{Wf}{Wd} x100 \qquad (1)$$

2.4.2. Swelling

Distilled and ultrapure water were used for investigation of swelling properties of the hydrogels at room temperature. At a given time, each sample was removed from water and placed on the sieve net where it was carefully wiped using filter papers and then weight. This procedure was repeated several times until a constant weight was reached for each sample. The swelling percentages of hydrogels were calculated as Eq. 2, from the difference between the initial and the final weight of the sample divided by the initial weight. Where: Ws is the weight of the swollen gels and Wd is the gel weight before immersion.

$$\text{Swelling}(\%) = \frac{Ws - Wi}{Wi} x100 \qquad (2)$$

3. RESULTS AND DISCUSSION

3.1. Water Characterization

3.1.1. Conductivity and pH

The values of pH and conductivity obtained in distilled water and ultrapure water are showed in Table 1. Distilled water presented an acidic behaviour and ultrapure water a neutral equilibrium. The conductivity values showed a higher presence of impurities in distilled water if compared to ultrapure water. The negative value to ultrapure water conductivity is due to low conductivity and out of calibration range.

Table 1. Results observed in distilled and ultrapure water

Water used in Hidrogel	pH	Conductivity Mv
Distilled	6,0	54
Ultrapure	7,1	-9

3.1.2. Ion Chromatography

The chromatograms of waters used to prepare and investigate of swelling properties of the hydrogels, Figure 1 and 2, show the presence of F^- in ultrapure water, Cl^- in distilled water and NO_3^- and SO_4^{2-} in both. However, the amount of ions in distilled water is so small as in ultrapure water, Table 2.

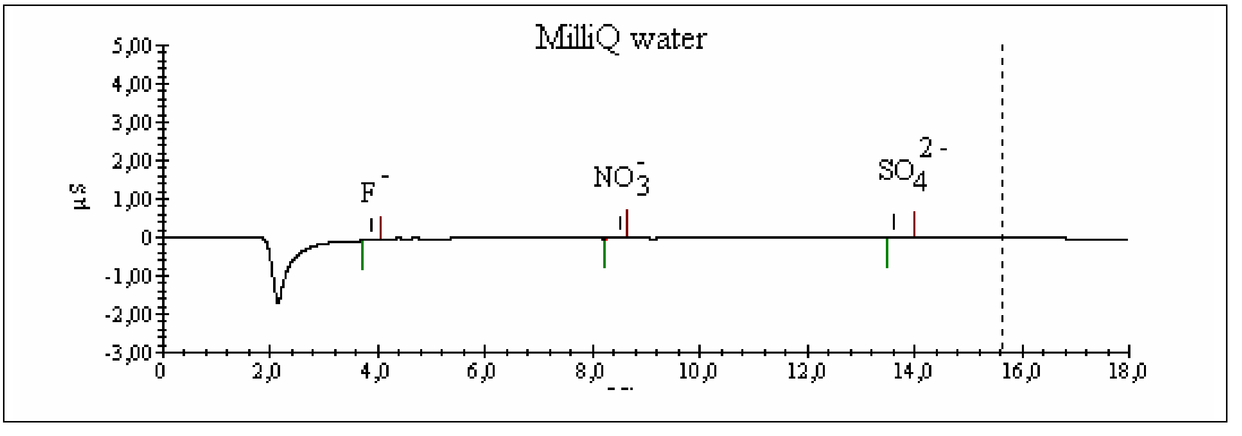

Fig. 1 Chromatogram of ultrapure water used to prepare hydrogels and swelling analyses

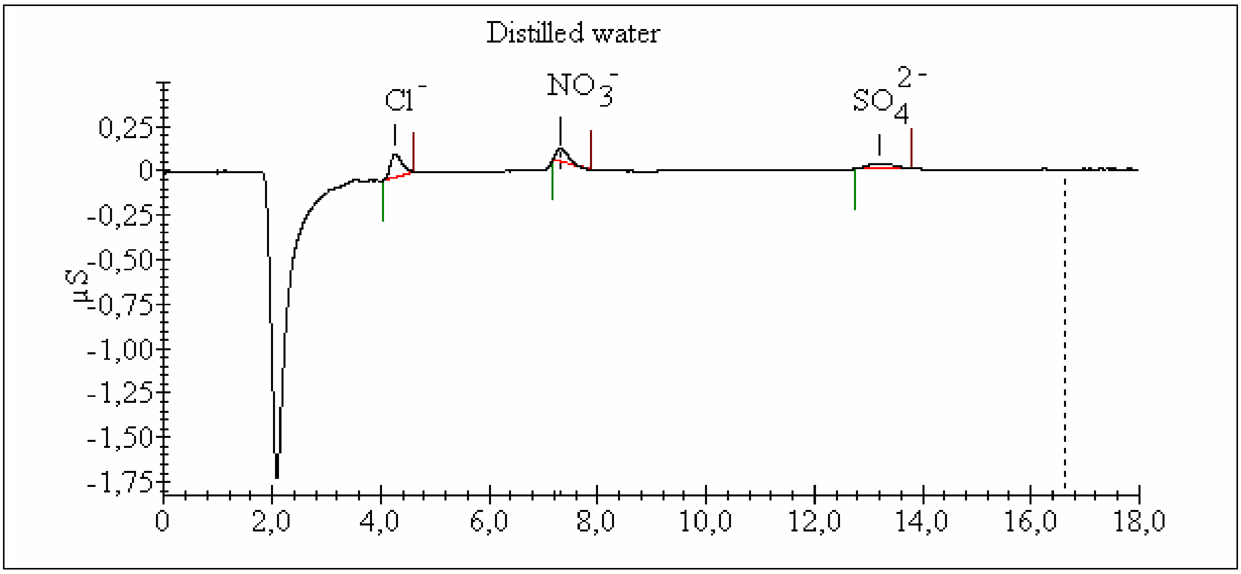

Fig. 2 Chromatogram of distilled water used to prepare hydrogels and swelling analyses

The results showed small amount of anions in distilled water. If considering the conductivity, others ions can be present, but not determined for this study.

Table 2. Concentration of ions present in distilled and ultrapure waters

Water	Ions (ppm)			
	Chloride	Fluoride	Nitrate	Sulphate
Distilled	0,03	-	0,08	0,07
Ultrapure	-	0,02	0,04	0,04

3.2. Hydrogels Characterization

3.2.1. Gel fraction

The values obtained in gel fraction analyses showed similar results for the crosslinking on hydrogels prepared, indicating the same level of crosslinking in samples with equal amount of PVP.

Table 3. Gel fraction of samples prepared with 12% and 20% PVP

Water used in Hydrogel	Gel Fraction (%)	
	Sample A (12% PVP)	Sample B (20% PVP)
Distilled	95,7 ± 4,2	96,3 ± 0,2
Ultrapure	96,7 ± 1,0	98, 4 ± 0,7

3.1. Swelling

Swelling curves of hydrogel with 12% and 20%, w/w, PVP were plotted and presented in Figures 3 and 4, respectively. To hydrogels prepared with distilled water, 12% PVP, the equilibrium state in the water were established at 99,2%. For samples prepared with ultrapure water, the equilibrium was established at 107,2%. With 20% PVP, the hydrogels reached the equilibrium state at 257,0% and at 290,9% with ultrapure and distilled water, respectively. Similar capabilities of equilibrium swelling were obtained.

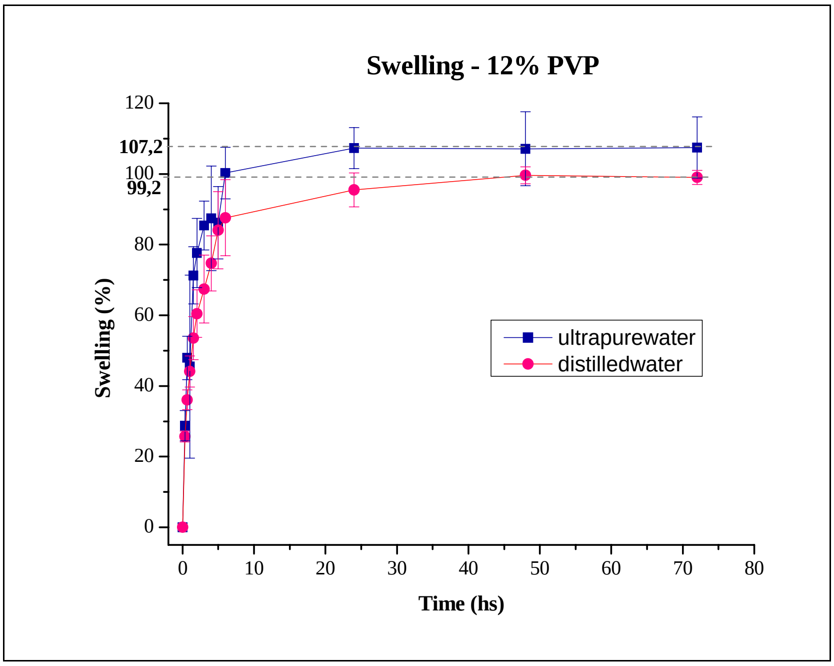

Fig. 3. swellilng kinetics of hydrogels prepared with 12% pvp plus distilled water and plus ultrapure water.

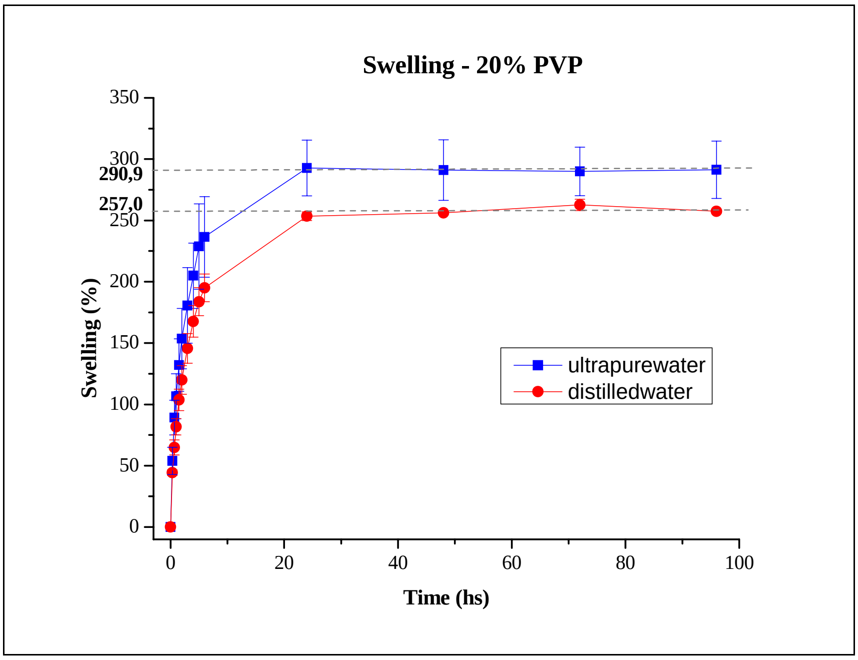

Fig. 4. Swelling kinetics of hydrogels prepared with 20% PVP plus distilled water and plus ultrapure water.

Both the membranes prepared with 12% PVP as those prepared with 20% PVP showed little difference between the swelling of which were used distilled water and ultrapure water, and the difference of 7% for the membranes with 12% PVP and 11.5% for membranes prepared with 20% PVP. In both cases the swelling of the membranes prepared with distilled water was lower than the water prepared with ultrapure.

4. CONCLUSIONS

- The quantity of anions found in the distilled water, used to prepare the hydrogels, was low. Although no cations determination were carried out, both waters showed enough quality to be used in these processes.
- Considering the swelling of the final products, no significant difference were observed even in the presence of small amount of anions. That mean distilled water can be used instead of ultrapure water lowing the production costs.
- If considering water quality parameters, conductivity, at least in this range of impurities presence, can not be used in identification of proper or improper water to be used in this process.

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REFERENCES

1. Sen, M.; Avcı, E. N. "Radiation synthesis of poly(*N*-vinyl-2-pyrrolidone)-K-carrageenan hydrogels and their use in wound dressing applications. I. Preliminary laboratory tests." http://www.interscience.wiley.com (2005).

2. El-Mohdy, H. L. A.; Hegazy, El-Sayed A. "Preparation of Polyvinyl Pyrrolidone-Based Hydrogels by Radiation-Induced Crosslinking with Potential Application as Wound Dressing". *Journal of Macromolecular Science* R, Part A: Pure and Applied Chemistry, **Volume45**, pp. 995–1002 (2008).

3. Kaplan, H; Ner, A.G. "Characterization and Determination of Swelling and Diffusion Characteristics of Poly(N-vinyl-2-pyrrolidone) Hydrogels in Water". *Journal of Applied Polymer Science*, **Volume 78**, pp. 994–1000 (2000).

4. Can, H. K.; Denizli, B. K.; Güner, A.; Rzaev, Z. M.O**. "**Effect of functional crosslinking agents on preparation and swelling properties of dextran hydrogels". *Carbohydrate Polymers* **Volume 59,** Issue 1, pp. 51-56 (2005).

5. Bünsow, J., Johannsmann, D. "Electrochemically produced responsive hydrogel films: Influence of added salt on thickness and morphology". *Journal of Colloid and Interface Science*, **Volume 326**, pp. 61–65 (2008).

6. Xu, L.; Watando, H.; Satoh, M. "Effects of chemical modifications on the swelling behaviors of poly(4-vinyl phenol) gel". *Colloid Polym Sci.* **Volume 284**, pp. 862–870 (2006).