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COMPARATIVE CHARACTERISTICS OF SORPTION PROPERTIES OF POLY-4-VINILPYRIDINE AND POLY-2-METHYL-5-VINILPYRIDINE IN RELATION TO RARE-EARTH ELEMENTS IONS

Abstract. The rare-earthelements (lanthanum, cerium, neodymium, and samarium) ions sorption by individual hydrogels of poly-4-vinylpyridine (gP4VP) and poly-2-methyl-5-vinylpyridine (gP2M5VP) was studied.

The maximum values of the extraction degree by gP4VP were observed after 48 hours, while the degree of extraction was 66.05%; 56.67%; 54.60%; 62.89% respectively for lanthanum, cerium, neodymium, samarium ions.The final polymer chain binding degree values by poly-4-vinylpyridine hydrogel were 55.00%; 47.00%; 45.60%; 52.10% for the La, Ce, Nd, Sm ions, respectivelyand was achieved after 48 hours of the starting contact of the polymer hydrogel with thenitrates solutions.The maximum effective dynamic exchange capacitieswere 4.95; 3.78; 3.67; 4.30 mmol/g for the La, Ce, Nd, Sm ions, respectively,andwere observed at 48 hours of the interaction.

The maximum values of the extraction degree were 63.65%; 50.00%; 48.60%; 57.60% for La, Ce, Nd, Sm ions, respectivelyby gP2M5VP and were observed after 48 hours.The final values of the polymer chain binding degree 53.00%; 41.47%; 38.80%; 48.40%for lanthanum, cerium, neodymium, and samarium ions, respectively, were reached after 48 hours.At 24 hours of interaction, the exchange capacity was 4.47; 2.71; 2.56; 3.13 mmol/g. Further P2M5VP hydrogel ionization was very weak, which indicated the approached equilibrium state. The maximum effective dynamic exchange capacities were 4.77; 3.33; 3.07; 4.17 mmol/g were observed for the La, Ce, Nd, Sm ions, respectively at 48 hours.

The obtained results indicate the possibility of creating and improving the selective systems for lanthanum, cerium, neodymium, and samarium ions sorption technologies.

Key words: hydrogels, poly-4-vinylpyridine, poly-2-methyl-5-vinylpyridine, rare-earth elements, ions, sorption.

Introduction. Rare-earth elements are used in various industries: instrument making, radio electronics, machine building, nuclear engineering, metallurgy, chemical industry, etc. Lanthanum, cerium, praseodymium, neodymium are widely used in the glass industry in the form of oxides and other compounds [1]. These elements increase the translucence of the glass. Rare-earth elements are part of special-purpose glasses that transmit infrared rays and absorb ultraviolet rays, and heat-resistant glass [2].

These rare earth elements and their compounds are widely distributed in the chemical industry, for example, in the production of pigments, varnishes and paints. In addition, these rare-earth elements being used in the production of certain explosives, special steels and alloys, as degasifiers [3]. Single-crystal compounds of rare-earth elements (and also glasses) are used to create laser and other

optically active and nonlinear elements in optoelectronics [4]. Some lanthanum compounds, for example, chlorides and oxides are components of various catalysts used in particular for oil cracking [5].

Lanthanum is a soft, silvery-white, ductile and malleable metal. It is the first member of the Lanthanoid Group (Rare Earths) of the Periodic Table and is the 28th most abundant element within the Earth's crust. It is soft enough to be cut with a knife and when exposed to air will tarnish rapidly. When ignited, it will burn easily. Lanthanum is one of the most reactive elements within this group and will react even with water to give off hydrogen gas [6]. Lanthanum metal has no commercial uses. However, its alloys have a variety of uses. A lanthanum-nickel alloy is used to store hydrogen gas for use in hydrogen-powered vehicles. Lanthanum is also found in the anode of nickel metal hydride batteries used in hybrid cars. It is an important component of mischmetal alloy (about 20%). The best-known use for this alloy is in «flints» for cigarette lighters.

«Rare earth» compounds containing lanthanum are used extensively in carbon lighting applications, such as studio lighting and cinema projection. They increase the brightness and give an emission spectrum similar to sunlight. Lanthanum (III) oxide is used in making special optical glasses, as it improves the optical properties and alkali resistance of the glass. Lanthanum salts are used in catalysts for petroleum refining.The ion La^{3+} is used as a biological tracer for Ca^{2+}, and radioactive lanthanum has been tested for use in treating cancer [7].

The goal of this work was to study the sorption ability of poly-4-vinylpyridine and poly-2-methyl-5-vinylpyridine individual hydrogels in relation to lanthanum, cerium, neodymium, samarium ions.

EXPERIMENTAL PART

Equipment. The conductivity meter Mark 603 (Russia) was used to measure conductivity, the pH of the solutions was determined by a Metrohm 827 pH – meter (Switzerland). The mass of swollen samples of hydrogels for the subsequent calculation of swelling degree (α) was determined by weighing on an electronic analytical balance SHIMADZU AY220 (Japan). The optical density of lanthanum, cerium, neodymium and samarium nitrates solutions was determined for the subsequent calculation of the concentration of lanthanum ions and cerium ions using a Jenway 6305 spectrophotometer (SC) and an ARCOS Simultaneous ICP Spectrometer atomic emission spectrometer (ICP-AES) (Germany).

Experiment. Experiments were performed at room temperature. The study of electrochemical, volume-gravimetric and sorption properties of individual polymer hydrogels was carried out as follows:

1) The estimated amount of each hydrogel (poly-4-vinylpyridine, poly-2-methyl-5-vinylpyridine) in dry form was placed in a glass beaker.

2) For 2 days, electrochemical properties (pH, conductivity) of aqueous solutions and the mass of polymer samples of hydrogels were measured. Measurement of electrical conductivity and pH was carried out in the absence of

hydrogels in an aqueous medium. The degree of swelling was calculated using the following the formula:

$$\alpha = \frac{m_2 - m_1}{m_1}, \quad (1)$$

where m_1 – the weight of the dry hydrogel, m_2 – the weight of the swollen hydrogel.

Methodology of rare-earth elements ions determination. The method for rare-earth elementsions determination in solution was based on the formation of a colored complex compound of the organic analytic reagent arsenazo (III) with lanthanum ions [2].

Extraction (sorption) degree (η) was calculated by the following equation:

$$\eta = \frac{C_{initial} - C_{residual}}{C_{initial}} * 100\%, \quad (2)$$

where $C_{initial}$ is the initial concentration of rare-earth elementsin solution, g/L; $C_{residue}$ is the residual concentration of rare-earth elements in solution, g/L.

Polymer chain binding degree (θ) was determined by calculations in accordance with the following equation:

$$\theta = \frac{\nu_{sorbed}}{\nu} * 100\%, \quad (3)$$

where ν_{sorbed} – the quantity of polymer links with sorbed rare-earth elements, mol; ν – the total quantity of polymer links (if there are two hydrogels in solution, it is calculated as sum of each polymer hydrogel links), mol.

The effective dynamic sorption capacity (Q) was calculated by the following equation:

$$Q = \frac{\nu_{sorb}}{m_{sorbent(s)}}, \quad (4)$$

where ν_{sorb} is the amount of sorbed metal, mole; $m_{absorbent}$ - the mass of the sorbent (if there are two hydrogels in solution, it is calculated as the sum of the two hydrogels masses), g.

RESULTS AND DISCUSSION

The study of the P4VP hydrogel sorption properties. Figure 1 represents the dependence of the ions extraction degree of lanthanum, cerium, neodymium, samarium by P4VP hydrogel on time. A sharp increase in the extraction degree was observed for 6 hours, the degree of La, Ce, Nd, Sm ions extraction was 38.43%; 30.00%; 28.30%; 36.59%, respectively. After that, there was a further increase in the degree of extraction. The maximum values of the extraction degree were observed after 48 hours, while the degree of extraction was 66.05%; 56.67%; 54.60%; 62.89% respectively for lanthanum, cerium, neodymium, samarium ions.

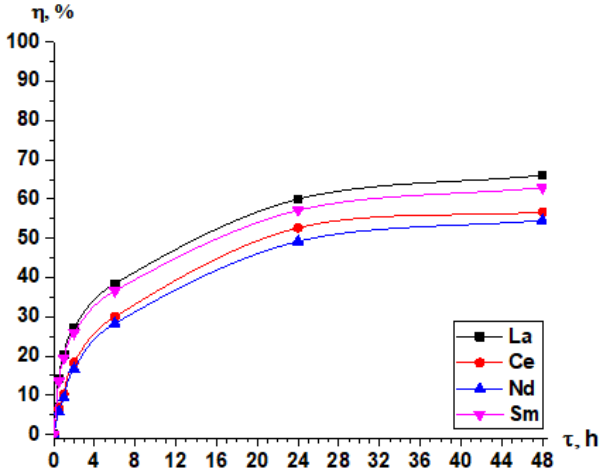

Figure 1 – The dependence of the ions extraction degrees of P4VP hydrogel with respect to lanthanum, cerium, neodymium, samarium ions on time

Figure 2 shows the dependence of the degree of the polymer chain binding (with respect to lanthanum, cerium, neodymium, samarium) of P4VP hydrogel on time. As can be seen from the figure 2, over time, the degree of binding increases. The obtained results indicate that the most intensive binding of lanthanum, cerium, neodymium, samarium with P4VP polymer hydrogel occurs within 6 hours, at which time the polymer interacts with the solutions of rare earth metal salts the degree of binding of the polymer chain reaches 32.00%; 24.88%; 22.60%; 27.50% with respect to lanthanum, cerium, neodymium, samarium ions.

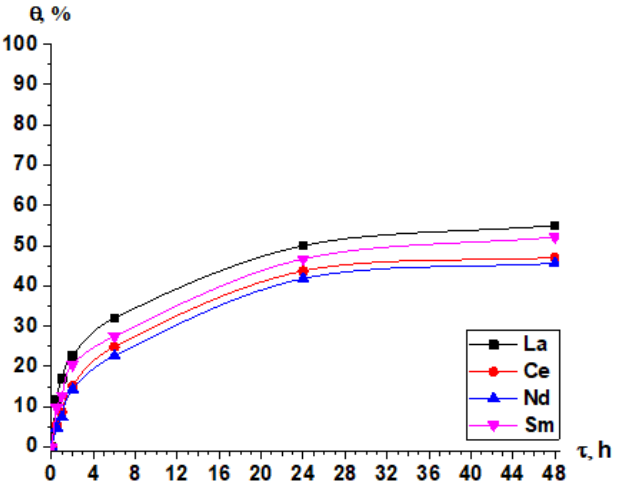

Figure 2 – Dependence of the polymer chain binding degree of P4VP hydrogel with respect to lanthanum, cerium, neodymium, samarium ions on time

After this, a further increase in binding was observed, after 24 hours 49.99% (lanthanum), 43.69% (cerium), 41.80% (neodymium), 46.70% (samarium) were bound. It should be noted that the further binding of metal ions by a polybase occurs very weakly, the final values of the polymer chain binding degree bypoly-4-vinylpyridine hydrogel (55.00%; 47.00%; 45.60%; 52.10% with respect to the La, Ce, Nd, Sm ions, respectively) was achieved after 48 hours of the starting contact of the polymer hydrogel with thenitrates solutions.

Figure 3 represents the time dependence of the effective dynamic exchange capacity of P4VP hydrogel (with respect to lanthanum, cerium, neodymium, samarium) ions. The most dramatic growth of this parameter was observed within 6 hours of the starting contact of the polymer hydrogel with thenitrates solutions. After this time, the exchange capacity was 2.89; 2.00; 1.92; 2.31 mmol/g. Further weak growth (after 24 hours) was directly related to the nature of the P4VP hydrogel - since the polybase is weak, it is weakly ionized and quickly reaches equilibrium in the salt solution. The maximum values of exchange capacity (4.95; 3.78; 3.67; 4.30 mmol/g) were observed at 48 hours of the interaction.

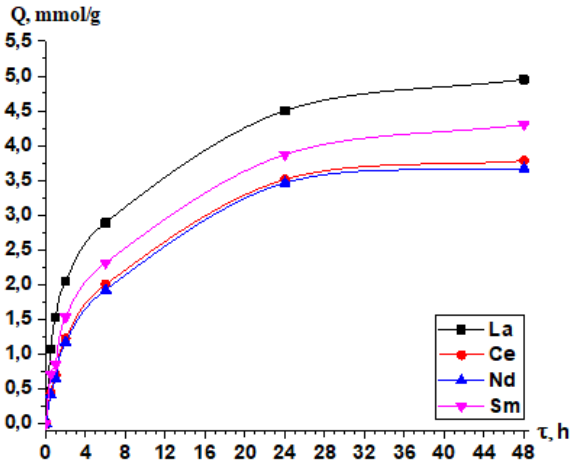

Figure 3 – Dependence of the effective dynamic exchange capacity of P4VP hydrogel with respect to lanthanum, cerium, neodymium, samarium ions on time

The study of the poly-2-methyl-5-vinylpyridine hydrogel sorption properties. Figure 4 shows the dependence of the P2M5VP hydrogel extraction degrees of lanthanum, cerium, neodymium, samarium ions on time. From the figure 4 we can see that with time the degree of these rare-earth metals ions extraction increases. After 6 hours, the extraction degree of La, Ce, Nd, Sm ions was 36.95%; 25.33%; 22.90%; 31.40%, respectively. After this point, there was a less sharp increase in sorption. At 24 hours, the recovery rate was 59.68%; 40.67%; 37.60%; 52.90%, respectively, and the maximum values 63.65%; 50.00%; 48.60%; 57.60% were observed after 48 hours.

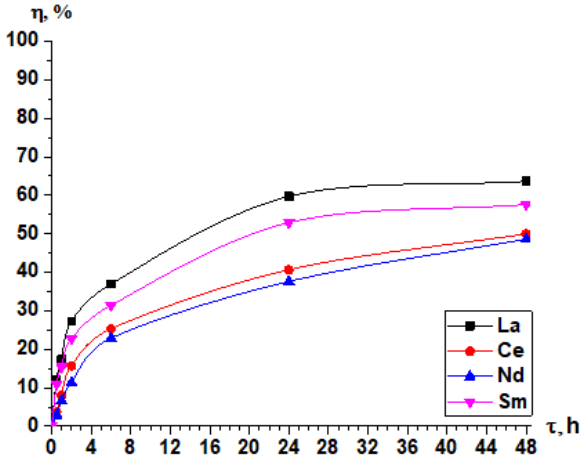

Figure 4 – The dependence of the P2M5VP extraction degrees of lanthanum, cerium, neodymium, samarium ions on time

Figure 5 represents the dependence of the polymer chain binding degree of the P2M5VP hydrogel (with respect to the ions of lanthanum, cerium, neodymium, samarium ions) on time. By analogy with the data on the degrees of lanthanum, cerium, neodymium, samarium ions extraction, (see figure 2) it can be seen that most of these metals are bound by the rarely crosslinked polymer during 6 hours, after this time, the polymer chain binding degree reaches 30.83%; 21.01%; 18.70%; 27.80% with respect to La, Ce, Nd, Sm ions. After that, a further increase in binding was observed, after 24 hours, 49.17% binds; 33.73%; 30.80%; 41.90% of these metals. Further increase in the polymer chain binding

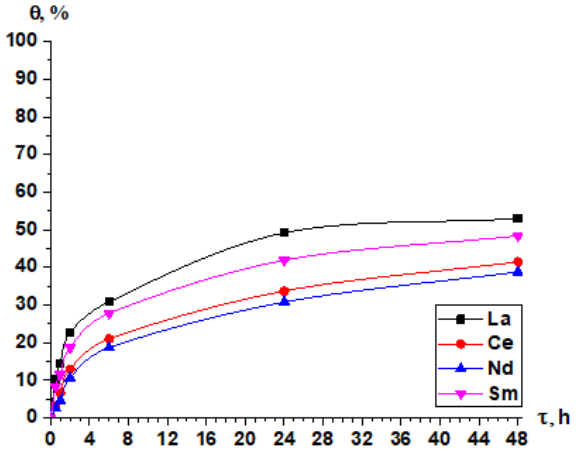

Figure 5 – Dependence of the polymer chain binding degree ofP2M5VP hydrogel (with respect to lanthanum, cerium, neodymium, samarium) on time

degree of the basic hydrogel of poly-2-methyl-5-vinylpyridine was very weak, indicating an approach of an equilibrium state. The final values of the polymer chain binding degree (53.00%; 41.47%; 38.80%; 48.40%) with respect to the ions of lanthanum, cerium, neodymium, samarium ions were reached after 48 hours.

The time dependence of the effective dynamic exchange capacity (with respect to lanthanum, cerium, neodymium, samarium ions) of P2M5VP hydrogel is shown in figure 6. The highest ionization rate of polybase was observed at 6 hours of P2M5VP hydrogel interaction with lanthanum, cerium, neodymium, samarium nitrates solutions. At this interaction time, this parameter reaches 2.77; 1.69; 1.43; 2.05 mmol/g, respectively. A further increase in the effective dynamic exchange capacity was not as intense. At 24 hours of interaction, the exchange capacity was 4.47; 2.71; 2.56; 3.13 mmol/g. Further P2M5VP hydrogel ionization was very weak, which indicated the approached equilibrium state. Maximum values (4.77; 3.33; 3.07; 4.17 mmol/g) of exchange capacity were observed at 48 hours.

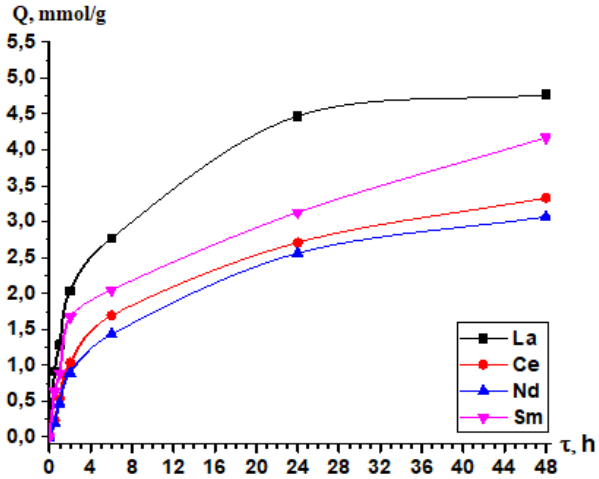

Figure 6 – Dependence of the effective dynamic exchange capacity of P2M5VP hydrogel with respect to lanthanum, cerium, neodymium, samarium ions on time

Conclusions. At the initial time, in the P4VP polybase ionization process, protons were intensively bound by nitrogen atoms, as evidenced sharp decrease in their concentration. Over time, the degree of their association decreases, as a result, a gradual increase in pH, reaching maximum values after 48 hours.

The protons formation occured in the solution during the P4VP polymer hydrogel entire interaction time with nitrate solutions, and a significant part was formed during the first 6 hours. Lanthanum, cerium, neodymium, and samarium ions sorption occurs due to the formationof heteroatoms coordination bonds with studied rare earth metal ions. Protonization of the polybase occured due to the addition of the formed hydrogen ions to P4VP heteroatoms, this shifted the equilibrium to the right, as a result, additional protons were released into the solution.

Then,the sorption of lanthanum, cerium, neodymium, samarium by the coordination mechanism occured, as a result, protons were released into the solution.

During the time of P2M5VP hydrogel interaction with the nitrate solutions, hydrogen ions were released. This was due to the lanthanum, cerium, neodymium, and samarium ions sorption by polybase, as a result, the P4VP ionization occured due to the coordination bonds formation with metal ions. As in the case of the P4VP polymer hydrogel, a substantial release of hydrogen ions was observed within 6 hours after the starting contact of the polymer with the nitrate solutions. The process of hydrogen association by nitrogen atoms of a polybase led to an additional shift (to the right) of the equilibrium towards the protons formation. After 24 hours of the P2M5VP polymer hydrogel interaction with lanthanum,cerium, neodymium, and samarium nitrate solutions, the protons realising processinto the solution was so insignificant that it could be concluded that electrochemical equilibrium occured in the system.

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Резюме

Т. К. Джумадилов, Р. Г. Кондауров, А. М. Иманғазы

ПОЛИ-4-ВИНИЛПИРИДИН ЖӘНЕ ПОЛИ-2-МЕТИЛ-5-ВИНИЛПИРИДИН ГИДРОГЕЛЬДЕРІ МЕН СИРЕК ЖЕР ЭЛЕМЕНТТЕР ИОНДАРЫНЫҢ СОРБЦИЯЛЫҚ СИПАТТАМАЛАРЫ

Поли-2-метил-5-винилпиридин (П2М5ВП) және поли-4-винилпиридина (П4ВП) қышқылдарының жеке полимерлі гидрогельдерімен сирек жер металдардың, атап айтқанда лантан, церия, неодима, самария иондарының сорбциясы зерттелінді.

Лантан, церия, неодима, самария иондары мен П4ВП жеке гидрогелдерінің 48 сағат бойы араласып сорбциялық деңгейі максималды мәнге (сәйкесінше 66.05; 56.67; 54.60; 62.89 %) жеткендігі анықталынды. Сонымен қатар, лантан, церия, неодима, самария иондары мен П2М5ВП жеке гидрогельдерінің 48 сағат бойы араласып сорбциялық деңгейі мынадай максималды мәнге (сәйкесінше, 63.65; 50.00; 48.60; 57.60 %) жетті.

Түйін сөздер: гидрогельдер, поли-4-винилпиридин, поли-2-метил-5-винилпиридин, сирек жер элементтері, иондар, сорбция.

Резюме

Т. К. Джумадилов, Р. Г. Кондауров, А. М. Иманғазы

СРАВНИТЕЛЬНАЯ ХАРАКТЕРИСТИКА СОРБЦИОННЫХ СВОЙСТВ ПОЛИ-4-ВИНИЛПИРИДИНА И ПОЛИ-2-МЕТИЛ-5-ВИНИЛПИРИДИНА ПО ОТНОШЕНИЮ К ИОНАМ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ

Исследовано сорбционное извлечение ионов редкоземельных металлов, а именно, лантана, церия, неодима, самария, индивидуальными полимерными гидрогелями поли-4-винилпиридина (П4ВП) и поли-2-метил-5-винилпиридина (П2М5ВП).

Установлено, что степень сорбции ионов лантана, церия, неодима, самария индивидуальным гидрогелем П4ВП достигла максимальных значений (66.05; 56.67; 54.60; 62.89 % соответственно) по истечении 48 ч взаимодействия. Тогда как степень сорбции ионов лантана, церия, неодима, самария индивидуальным гидрогелем П2М5ВП достигло максимальных значений (63.65; 50.00; 48.60; 57.60 % соответственно) по истечении 48 часов взаимодействия.

Ключевые слова: гидрогели, поли-4-винилпиридин, поли-2-метил-5-винилпиридин, редкоземельные элементы, ионы, сорбция.