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Chapter 5

Sorption Properties of Clay and Pectin-Containing Hydrogels

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Additional information is available at the end of the chapter

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Abstract

As is known, polymeric polyelectrolyte hydrogels are superabsorbents that are capable of absorbing moisture in amounts many times greater than their own mass. Numerous studies have shown that besides water absorption and retention, they can also be effectively used as sorbents to purify water from heavy metals. In many works, attempts are made to improve the sorption properties of polyelectrolyte hydrogels by creating polymer composites based on them. Organic/inorganic composite materials frequently exhibited desired hybrid performance superior to their individual components and cost-efficient characteristics. The composites derived from natural polysaccharides and inorganic clay minerals are of special interest by virtue of their unique commercial and environmental advantages, which means that the design and development of environmentally friendly superabsorbents, introducing natural ingredients, have long been necessary. In this paper, we consider polymer hydrogels based on a copolymer of acrylic acid and acrylamide filled with pectin and bentonite. The aim of this study is to investigate the influence of chemical conditions on hydrogels and their composites, kinetic, and absorption behavior toward metal ions in the presence of the chelating agent. In this chapter, an investigation of the kinetic patterns of swelling, deswelling, and sorption of the hydrogels and their composites will be presented.

Keywords: hydrogel, semi-interpenetrating networks, bentonite, pectin

1. Introduction

The term "hydrogel" is ambiguous, and it must first be clarified. We will call gel, a polymer network swollen in a solvent—a set of a large number of polymer chains chemically

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(or physically) sewn together. More strictly, the polymer gel is a system consisting of at least two components, one of which is a mesh polymer and the other is a liquid present in a palpable amount.

Polymer gels can almost completely (by 99% or more) consist of a liquid and be very soft materials. Despite this, they have the inherent ability of solid bodies to maintain their shape. This is due to the fact that the polymer mesh that forms part of the gel plays the role of a framework that provides rigidity (elasticity) of the entire system, i.e., it does not allow it to flow under the action of a deforming force (if the force is not too great and does not last too long).

1.1. Composite polymer hydrogels

The combination of the properties of hydrogels inherent in solids predetermines a wide range of applications from technical spheres (sorbents, gas separating, and ion exchange membranes [1–3]) to the food industry and medicine (food structure, drug carriers, artificial substitutes for biological tissues, materials for soft and intraocular lenses, etc. [4–6]). The emergence of new fields of application of polymer hydrogels puts forward new requirements to their properties.

These goals can be achieved by obtaining fundamentally new materials—composite hydrogels containing at least two components, each of which performs certain functions. It is obvious that the characteristics of the composite hydrogel are due not only to the physicochemical properties of the individual components, but also to the structure of the material. Given the limited thermodynamic compatibility of the polymers, a variety of hydrogel structures are possible, from complete stratification of the polymer phases to the formation of matrix-nanoscale structures or the formation of structures in which both polymer phases are continuous.

In most cases, composite hydrogels are biphasic systems. The interphase boundary in such materials is not always clearly expressed. It can be a transition layer in which a gradual change in properties occurs (transition from the properties of phase 1 to the properties of phase 2). At least one of phases must be a polymer hydrogel. The hydrogel can be either a synthetic or a natural polymer. The second phase can be a synthetic hydrogel of synthetic or natural origin, a hydrophobic polymer and an inorganic substance. In accordance with the foregoing, it is possible to propose a classification that divides composite hydrogels into three groups [7]:

1. Hydrogels consisting of two hydrophilic polymers, each of which is capable of forming an individual polymer hydrogel.
2. Hydrogel, including hydrophilic and hydrophobic polymers.
3. A polymeric hydrogel containing an inorganic phase.

The nature of the interactions between the components may be due to covalent bonds in the block and graft copolymers, the formation of interpolymer complexes due to the formation

of hydrogen bonds, donor-acceptor, ionic and hydrophobic interactions of functional groups, and the engagement of macromolecular chains in interpenetrating and semi-interpenetrating polymer networks.

The compositional polymeric materials, consisting of hydrophilic polymers, have most application in last time. The presence of charged polar groups in hydrophilic polymers lids to communication with solution particles at help of the formation of intermolecular hydrogen and ionic bonds between molecules. Under conditions of corresponding implementation of functional groups, covalent bonds can exist in composite hydrogels. The hydrogels form by the type of interpenetrating and semi-interpenetrating polymer networks usually. In this case, the intermolecular bonds are caused by physical interactions between polar groups.

Inorganic components in composition hydrogels are introduced either to modify the properties of conventional polymer hydrogels (changing mechanical properties, increasing the sensitivity of hydrogels to thermal effects, changing pH, etc.) or to impart new properties not typical for hydrogels (magnetic characteristics and antibacterial properties). Oxides, various clays, carbon materials, water-insoluble inorganic salts, and metals are most often used in organo-inorganic composite hydrogels.

Methods for the preparation of organo-inorganic hydrogels can be divided into two groups:

1. Mixing of inorganic additives in the form of nano- or microparticles with a solution of a water-soluble polymer or monomers, followed by their polymerization. In such cases, the filler particles often serve as physical crosslinking centers.
2. Formation of the inorganic phase as a result of sol-gel process, which involves the introduction of monomers or polymer, precursors of the inorganic component into the solution, and its subsequent conversion in the course of various chemical reactions into solid water-insoluble particles. The final step is the polymerization of the monomers or, if required, crosslinking of the polymer.

1.2. Swelling and collapse of polyelectrolyte gels

Polymer gel, placed in a solvent, changes its volume, i.e., swells or contracts, appropriately absorbing or releasing the solvent, until it reaches an equilibrium swelling. The equilibrium degree of swelling of the gel, determined by the amount of solvent in it, depends both on the properties of the gel and on the properties of the solvent. The nature of this relationship was established for the first time in theoretical studies carried out by Flory and Rener [8, 9] and Kachalsky [10, 11]. According to Flori-Rener's postulate, the equilibrium of free swelling of the polymer network is determined by the balance between the mesh expanding the osmotic pressure and the elastic stress that arises in it. In 1977, Peppas and Merrill modified the Flory-Rehner theory in application to the production of hydrogels from polymer solutions. Due to elastic forces, the presence of water affects the change in the chemical potential within the system [12].

Of all polymer gels, the most interesting are gels based on chains containing charged units, polyelectrolyte gels. Since the macroscopic sample of the gel must be electrically neutral, the charge of the polymer chains of the gel must be compensated by the opposite charge of the low molecular weight counterions floating in the solvent in which the gel swells. When the gel swells in a large volume of water, the counterions should be advantageous to leave the gel and go to the external solution, which would lead to a significant gain in their translational entropy. However, this does not occur, since this leads to a violation of the electroneutrality condition of the gel sample. Counterions are forced to stay inside the gel and create there a bursting osmotic pressure. This osmotic pressure is responsible for the two most important effects associated with polyelectrolyte gels swelling in water.

First, a simple theory shows [13, 14] that the effect of the expanding osmotic pressure is very strong, it leads to a significant swelling of the gel in the water. Therefore, polyelectrolyte gels are used as superabsorbents of water.

Second, the superstrong swelling of polyelectrolyte gels in water leads to the fact that their concentration decreases extremely sharply with a deterioration in the quality of the solvent. The volume of the gel may decrease by a factor of thousands. This phenomenon, called the collapse of gels, was first predicted theoretically in [15] and was experimentally found in [16]. It is associated with the transition of the tangle-globule in the chains constituting the polymer gel. As a result, the gel sample collapses as a whole. In this case, the higher the degree of gel charge, the more sharply the collapse occurs [13]. The theory of collapse of gels developed in [13, 17, 18] shows that this is due to the fact that the collapsed phase is stabilized by the forces of attraction of uncharged links and the volume of the gel in this case depends little on the degree of charge, whereas the volume of the swollen gel is substantially increases with an increase in the degree of charge due to the expanding osmotic pressure of the counterions.

As discussed earlier in the works [19, 20], the equilibrium swelling of ionic hydrogels depends on the network structure, degree of crosslinking, hydrophilicity, and ionization of the functional groups. The major factor contributing to the swelling of ionic networks is the ionization of the network.

2. Experimental

In this chapter, the sorption properties of two different types of hydrogel composites will be compared. The first type is a clay-containing hydrogel composite—a copolymer of acrylic acid and acrylamide, filled with bentonite. The second type is a hydrogel filled with polysaccharide—pectin. Pectin is a naturally occurring biopolymer that is finding increasing applications in the pharmaceutical and biotechnology industry. The combination of the hydrophilic acrylic polymer properties with the biodegradable character of pectin-based blends, can lead to interesting hydrogels with potential applications as biomaterials exhibiting different properties depending on the composition and on the type of interactions within the network, attending to chemical crosslinking and hydrogen bonding interactions. In addition, a

hydrogel composite based on a copolymer of acrylic acid and acrylamide, filled with such a polysaccharide as pectin, is a hydrogel with a semi-interpenetrating network.

2.1. Material

Pectin (chemical grade, M_W 50,000) was purchased from Merck Chemical Co. (Germany). N,N′-methylene-bis-acrylamide (MBA), sodium hydroxide, ammonium persulfate, and bentonite were supplied by Sigma-Aldrich and were used without any further purification. Acrylic acid was distilled under reduced pressure before use. Acrylic acid (AAc) and acrylamide (AAm) were from Merck and were used without any further purification. All agents were of analytical grade quality.

2.2. Preparation of superabsorbent composites

Crosslinked acrylamide-sodium acrylate hydrogel and its composites were synthesized by free radical solution polymerization of AAm and AAc monomers in aqueous solution. A series of hydrogels were prepared by the following procedure.

Polymerization is carried out with constant stirring with a magnetic stirrer at a speed of 500 rev/min. According to the procedure, 10 ml of AAc monomer were dissolved in 3.5 ml distilled water. Acrylic acid was neutralized with 14 N aqueous solution of potassium hydroxide. The degree of neutralization is 0.8. Then 3 g of acrylamide monomer was added. To increase the crosslink density was added 0.001 g N,N-methylenebisacrylamide crosslinking agent. To initiate radical polymerization process a redox system consisting of 4 ml of a 2% ammonium persulfate aqueous solution and 4 ml of a 0.5% solution of TEMED are used. The polymerization was carried out at 35°C (**Figure 1**).

For the preparation of poly(AAm-co-AAc)/bentonite composite hydrogels, 1, 2, 3, or 4 mas.% bentonite was added into solution of sodium acrylate (AAcNa), AAm, and MBA, and was stirred for 10 min. Then, an oxidation–reduction system was added.

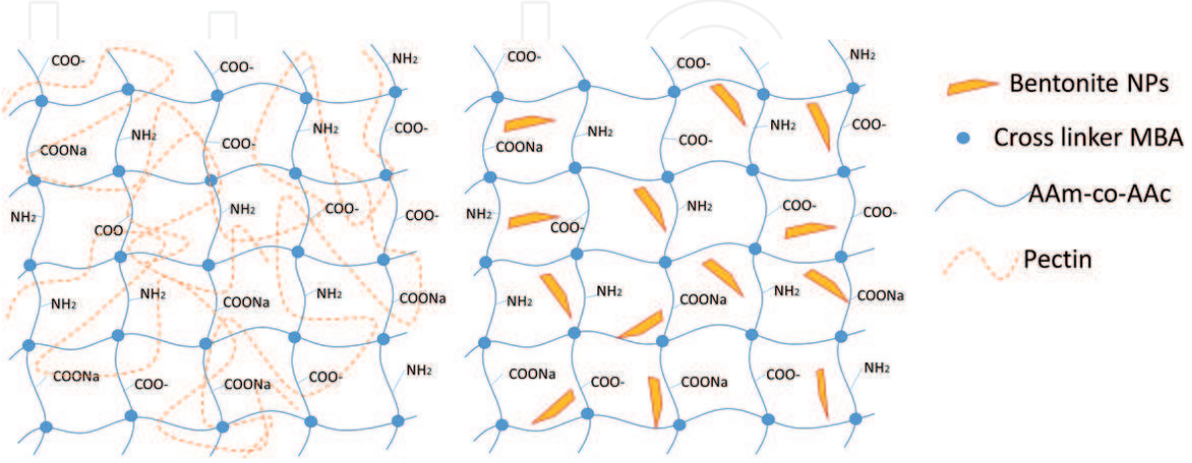


Figure 1. Schematic representation of a hydrogel with semi-interpenetrating networks—poly(AAm-co-AAc)/pectin and a dispersion-filled hydrogel composite—poly(AAm-co-AAc)/bentonite.

Poly(AAm-co-AAc)/pectin composite semi-IPNs were prepared using the same preparation method. However, the pectin powder was dissolved in a solution of sodium acrylate, stirred with a magnetic stirrer for 10 min, then acrylamide, a crosslinking agent and a redox system were added. To prepare highly swollen poly(AAm-co-AAc)/pectin (containing different contents of pectin) semi-IPNs, same method was used as mentioned above with the addition of 1, 2, 3, or 4 mas.% of pectin to solution of sodium acrylate.

3. Results and discussions

3.1. Characterization of hydrogels

IR spectra confirm the formation of a copolymer of acrylamide and acrylic acid, as seen from the bands that appeared in the range of 3100–3500 cm^{-1} (O—H and N—H stretching) (**Figure 2**). Absorption bands located in the region 3350–3330 and 3200–3185 cm^{-1} corresponds to the asymmetrical and symmetrical stretching —NH_2 of acrylamide [21].

On the other hand, the broad absorption band of 3400–2950 cm^{-1} may be attributed to the —OH of the carboxyl group. Absorption bands in the regions of 2950–2940 and 2915–2900 cm^{-1} correspond to asymmetric and symmetric stretching of the —CH_2 groups. In addition, the absorption band at 2790–2770 cm^{-1} is characteristic stretching —CH group of the polymer chain. The stretching of the —C= group of acrylamide and acrylic acid in the frequency of 1653–1645 cm^{-1} appear in all spectra of the hydrogel composites. The typical band, which

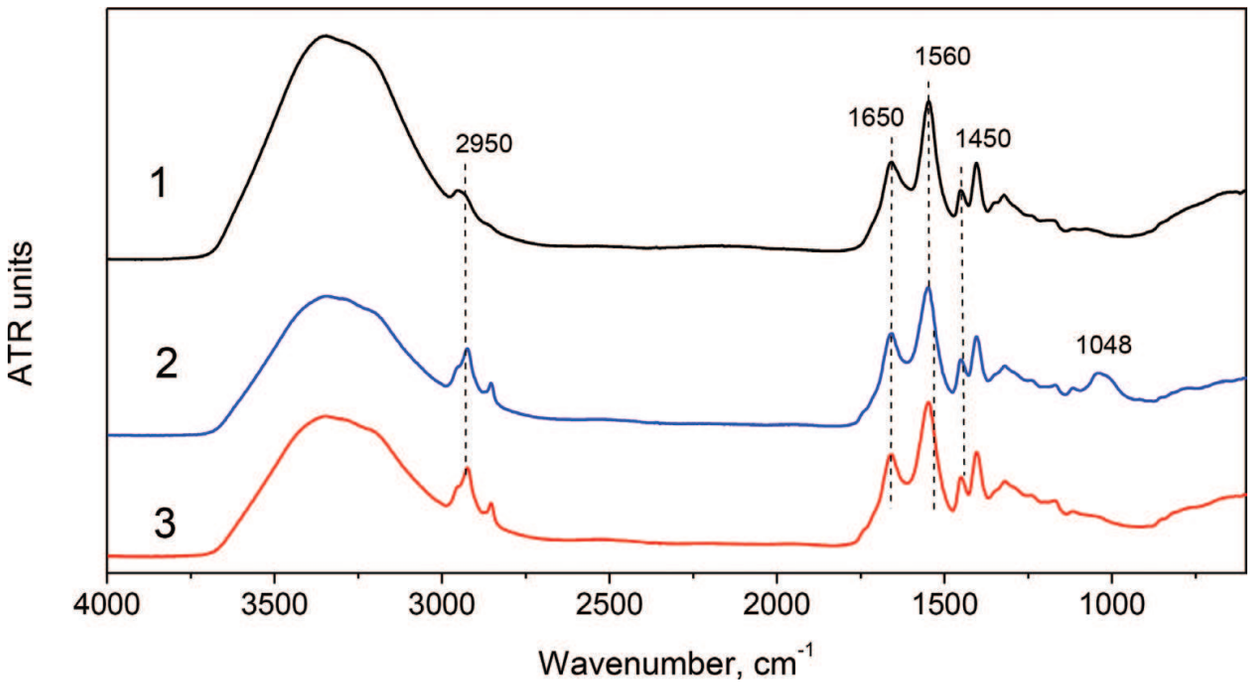


Figure 2. ATR FTIR spectra of poly(AAm-co-AAc)/pectin (1), poly(AAm-co-AAc)/bentonite composites (2), and poly(AAm-co-AAc) hydrogel (3).

appeared in the range of 1620–1600 cm^{-1}, results to deformation vibrations group —NH_2 acrylamide. The absorption band in the 1455–1445 cm^{-1} belongs to the stretching vibrations group —CH_2. The absorption band, which is located in the region 1450–1410 cm^{-1}, is a characteristic for the C—H stretching. The absorption bands at 1560 and 1406–1410 cm^{-1} results to the symmetric and asymmetric stretching of —COO-acrylate (acrylic acid neutralized with NaOH). The presence of absorbed water can be seen through the band at 3300 cm^{-1} in all spectra of the samples.

The absorption band 987 cm^{-1} of Si—O—Si of bentonite in the spectra composites is shifted from the frequency of 1048 cm^{-1}. This indicates that the composite components interact with each other by complexation to form homogeneous gels. From the FTIR it is clear that there is no significant shift in major peaks, which indicates that there is no chemical interaction between the polymer and the pectin used.

As can be seen from the SEM image (**Figure 3**), pectin is evenly distributed throughout the volume of the hydrogel. The structure of composite existing pectinate scaffold resulted in a double network architecture, where filamentous polyAA-co-AAm networks penetrated through pores of the pectin network.

3.2. Study of water absorption properties

3.2.1. Measurement of swelling

Swelling kinetic experiments were carried out by immersing a known amount of the dried hydrogels with 100 mL of distilled water in a constant temperature at 25°C. Gravimetrical measurement method was used to measure the swelling rate of the hydrogels. The water absorption amount Q (g/g) was calculated as follows:

$$Q = \frac{m - m_0(1-\gamma)}{m_0(1-\gamma)}, \tag{1}$$

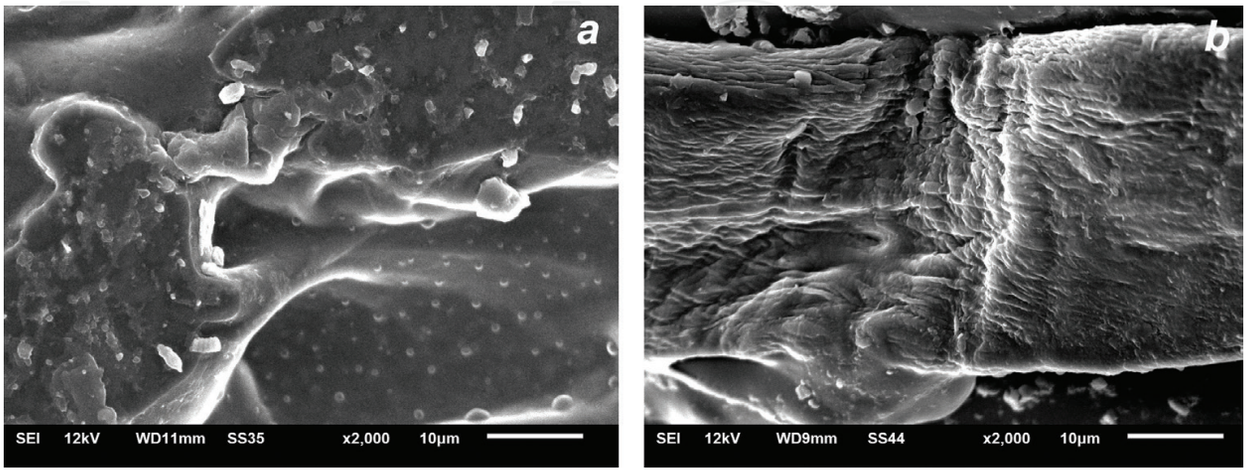


Figure 3. SEM image at 20.0 kV, showing surface structures of poly(AAm-co-AAc)/bentonite 3% (a) and poly(AAm-co-AAc)/pectin 3% (b).

where m_0 and m (g) are the weights of the dry and swollen sample, respectively, and γ is the water content of the hydrogel. Q was calculated as grams of water per gram of dry sample.

The hydrophilic properties of poly(AAm-co-AAc) and its composites hydrogels filled with bentonite and pectin were investigated by measuring their water uptake. Water uptake values were obtained by the mass ratio of the swollen hydrogel to dried hydrogel. **Figure 4** shows the dependences of water uptake as a function of the immersion time of the hydrogels swelled in distilled water.

Polymer hydrogel swells when it is brought into contact with a distilled water and salt aqueous solution. Swelling of the polymer hydrogel continues until the forces due to swelling of the polymer balance the osmotic pressure, driving the solvent into the swollen polymer. The swelling process of hydrogels is a complicated phenomenon and involves three successive steps: (i) the diffusion of water molecules into the polymer network, (ii) the relaxation of hydrated polymer chains, and (iii) the expansion of the polymer network into the surrounding aqueous solution [22].

Figure 4 presents the dynamic swelling data for poly(AAm-co-AAc)/pectin and poly(AAm-co-AAc)/bentonite in distilled water.

For each samples, the swelling ratio increases with time until a certain point, when it becomes constant, i.e., the equilibrium state is reached. At the beginning, the swelling is very fast. Besides, all hydrogels exhibit a salt-responsive swelling. Values of Q_{eq} decrease with increasing salt concentration. Moreover, the results clearly reveal that all hydrogels undergo drastic mass and/or volume change in the definite concentration range.

Poly(AAm-co-AAc)/pectin and poly(AAm-co-AAc)/bentonite hydrogel composites differ in their molecular structure (hydrogel containing dispersed filler particles and a mixture of linear and crosslinked polymers—semi-interpenetrating networks), however, the degree of crosslinking, the content of ionizable groups, and the supramolecular structure (degree of crystallinity)

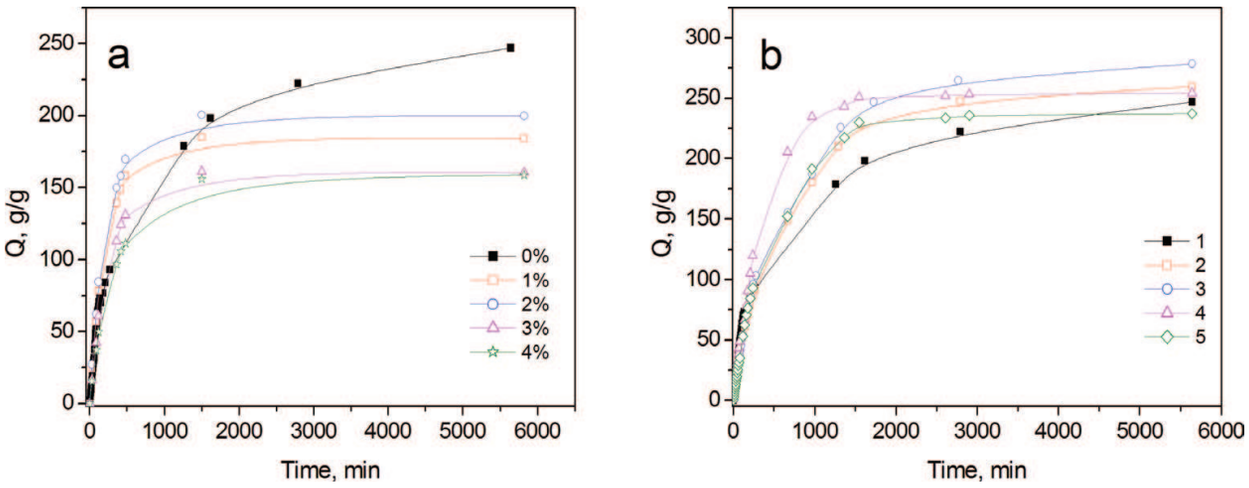


Figure 4. Swelling curves of poly(AAm-co-AAc)/pectin semi-IPN hydrogels (a) with 0% (1), 1% (2), 2% (3), 3% (4), 4% (5) pectin and poly(AAm-co-AAc)/bentonite (b) with 0% (1), 1% (2), 2% (3), 3% (4), 4% (5), 5% (6) bentonite in water.

are the same. Bearing in mind these differences in molecular and supermolecular structure of dispersed composite and semi-IPN and all factors affecting the swelling of ionic hydrogels, we could look for some differences in poly(AAm-co-AAc)/pectin and poly(AAm-co-AAc)/bentonite swelling behavior.

It was shown that there was a decrease in the equilibrium swelling (Q_{eq}) of the semi-IPN systems when pectin was added to the hydrogel systems. Incorporation of pectin into the copolymer network leads to lower degrees of swelling. The reason of this is the polymeric structure of pectin. Here, it could be said that chains of pectin were placed in the crosslinked polymeric systems, instead of crosslinked AAm and AAc molecules. So, it was seen that there was a decrease in the value of the Q_{eq}, because of the decrease in the hydrophilic character at crosslinked polymeric systems. But there was generally an increase in the Q_{eq} of the hydrogel systems when bentonite was added to the hydrogel systems. It was seen that there was an increase in the value of the Q_{eq}, because of the increase in the hydrophilic character at crosslinked polymeric systems. However, an increase in the percentage of filling bentonite in the hydrogel composite leads to a deterioration in the swelling properties, since at high filler concentrations it acts as an additional crosslinking agent.

To characterize the effect of the swelling medium on the kinetics of water uptake of poly(AAm-co-AAc)/bentonite and poly(AAm-co-AAc)/pectin hydrogel composites, kinetic modeling was conducted on the basis of the Fickian diffusion law.

3.2.2. Diffusion water

Many mathematical models have been proposed to describe the kinetics of hydrogel swelling. Most dynamic hydrogel swelling models are based in some way on Fick's laws of diffusion. To determine the type of diffusion of water into hydrogels the simple and commonly used method, based on the power-law expression (Eq. (3)) was applied [23]:

$$\frac{Q_t}{Q_{eq}} = kt^n \tag{2}$$

where Q_t and Q_{eq} represent the amount of solvent diffused into the gel at time t and at infinite time (equilibrium state), respectively, k is a constant related to the structure of the network, and the exponent n is a number that determines the type of diffusion. This equation can be applied only to the initial stages of swelling, i.e., to a 60% increase in the mass of hydrogel ($Q_t/Q_{eq} \leq 0.6$; $\log(Q_t/Q_{eq}) \leq -0.22$).

The phenomenon of water sorption by hydrogels depends on the diffusion of water molecules into the gel matrix and subsequent relaxation of macromolecular chains of the hydrogel. The mechanism of water transport in a swelling hydrogel is greatly affected by many factors, such as equilibrium water content, chemical composition of the hydrogel, swelling rate, etc. [24]. In general, three models are used to describe transport phenomena into polymer networks [25].

According to the relative rates of diffusion (R_{diff}) and polymer relaxation (R_{relax}), three classes of diffusion can be distinguished. For a planar geometry, the value of (i) n = 0.5 indicates a Fickian diffusion mechanism (Case I) in which the rate of diffusion is much smaller than the

rate of relaxation ($R_{diff} \ll R_{relax}$, system controlled by diffusion), (ii) n = 1.0 indicates Case II, where the diffusion process is much faster than the relaxation process ($R_{diff} \gg R_{relax}$, system controlled by relaxation), (iii) $0.5 < n < 1.0$ indicates non-Fickian (anomalous) diffusion mechanism, which describes those cases where the diffusion and relaxation rates are comparable ($R_{diff} \approx R_{relax}$). Occasionally, values of $n > 1$ have been observed, which are regarded as Super Case II kinetics. When the water penetration rate is much below the polymer chain relaxation rate, it is possible to record the n values below 0.5. This situation, which is classified also as Fickian diffusion, is called as "Less Fickian" behavior.

Calculation of the exponent n and constant k was achieved by plotting the data in log-log plots, according to Eq. (3) and estimating the obtained curves by linear functions

$$log\frac{Q_t}{Q_{eq}} = log k + n \, log t \tag{3}$$

The study of diffusion phenomena of water in hydrogels is of value in that it clarifies polymer behavior. **Table 1** shows that the number determining the type of diffusion (n) is over 0.50. Hence, the diffusion of water into the hydrogel systems is generally found to have a non-Fickian character. When the diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. Thus, both diffusion and polymer relaxation control the overall rate of water uptake. However, poly(AAm-co-AAc) has the values of $n > 1$, which means a Super Case II kinetics, where the diffusion process is much faster than the relaxation process ($R_{diff} \gg R_{relax}$, system controlled by relaxation). Thus, the addition of bentonite and pectin to the hydrogel increases the rate of diffusion of water into the hydrogel composite, due to the increased hydrophilic properties of this composite. Moreover, pectin increases the rate of diffusion of water into the hydrogel to a greater extent.

3.2.3. Swelling kinetics

To describe the swelling kinetics of different hydrogel, three empirical models, namely, Peleg's, first-order, and Schott's second-order absorption kinetic model, are used.

Hydrogel	k (min^{-1})	n	Mechanism
Poly(AAm-co-AAc)	0.4449	1.0507	Super Case II transport
Poly(AAm-co-AAc)/bentonite 1%	0.0038	0.8480	Non-Fickian (anomalous) diffusion
Poly(AAm-co-AAc)/bentonite 2%	0.0029	0.8757	Non-Fickian diffusion
Poly(AAm-co-AAc)/bentonite 3%	0.0031	0.9217	Non-Fickian diffusion
Poly(AAm-co-AAc)/bentonite 4%	0.0025	0.9325	Non-Fickian diffusion
Poly(AAm-co-AAc)/pectin 1%	0.0078	0.8277	Non-Fickian diffusion
Poly(AAm-co-AAc)/pectin 2%	0.0088	0.8008	Non-Fickian diffusion
Poly(AAm-co-AAc)/pectin 3%	0.0044	0.9211	Non-Fickian diffusion
Poly(AAm-co-AAc)/pectin 4%	0.0057	0.8321	Non-Fickian diffusion

Table 1. Some diffusion parameters of hydrogel systems.

Peleg proposed a two-parameter model to describe water absorption by hydrogels [26]:

$$Q_t = Q_0 \pm \frac{t}{k_1 + k_2 t}, \tag{4}$$

where Q_0 is the swelling content at $Q = 0$ (g/g d.b.), Q_t is the swelling content at any time (g/g d.b.), t is the swelling time (s), k_1 is the kinetic constant of the model (h(g d.b.)/g), and k_2 is a characteristic constant of the model (g d.b.)/g). In Eq. (4), "±" becomes "+" if the process is absorption or adsorption and "−" if the process is drying or desorption.

This section examines the possibility that diffusion-controlled swelling follows fist-order kinetics, as is frequently assumed. According to first-order kinetics, the rate of swelling at any given time (t) is directly proportional to the uptake of swelling medium that has yet to occur before the maximum or equilibrium uptake (Q_{eq}) has been reached. If Q is the uptake at time t, $Q_{eq} - Q$ is the unrealized uptake of swelling medium. If k is the proportionality constant between the rate of swelling and the unrealized swelling capacity, then [27]:

$$\frac{dQ}{dt} = k_1\left(Q_{eq} - Q_t\right), \tag{5}$$

which integrates to:

$$ln\left(\frac{Q_{eq}}{Q_{eq} - Q_t}\right) = k_1 t. \tag{6}$$

The Schott's second-order equation for swelling is [27]:

$$\frac{dQ}{dt} = k_2\left(Q_{eq} - Q_t\right)^2, \tag{7}$$

where Q_{eq} is the equilibrium water swelling ratio, Q_t is the water swelling ratio at time t, k_2 is the swelling rate constant, respectively. After definite integration between the limits $Q = 0$ at t = 0 and Q = Q at t = t and rearrangement, Eq. (7) can be rewritten as follows:

$$\frac{t}{Q_t} = \frac{1}{Q_{eq}^2 k_2} + \frac{1}{Q_{eq}} t. \tag{8}$$

To test the all kinetics models described above, $ln\left(\frac{Q_{eq}}{Q_{eq} - Q}\right)$ vs. t, t/Q vs. t, and 1/Q vs. 1/t graphs were plotted for analyzed hydrogel composites. Values of swelling rate constant and equilibrium swelling ratio, which were calculated from the slope and the intersection of the lines, respectively, are presented in **Table 2**.

Figure 5 shows the comparison graphs of experimental data on the swelling kinetics in water with the three models described above. Many authors believe that the swelling kinetics behavior of ionic hydrogels (anionic and cationic hydrogels) is in good accordance with Schott's second-order diffusion kinetics [28, 29]. As can be seen from the **Table 2**, the most accurate process of swelling of hydrogel filled with bentonite describes the first-order kinetic model. Values of the calculated equilibrium degree of swelling $Q_{eq\ calc}$ are in good agreement with the experimental data. A second-order kinetic model also yields adequate results. For gels with pectin, all models give an acceptable result, although the most accurately nevertheless the kinetics of swelling describes a model of the first order.

	Content of bentonite in hydrogel composites (%)					Content of pectin in hydrogel composites (%)			
	0	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
Peleg's model									
k_1	2.1810	1.3559	1.4929	1.4593	1.7098	1.1032	0.9791	1.6753	1.7822
k_2	0.004	0.0069	0.0071	0.0036	0.0080	0.0044	0.0042	0.0044	0.0056
R^2	0.9989	0.9977	0.9973	0.9995	0.9938	0.9987	0.9988	0.9984	0.9994
Q_{exp}	247.0146	259.77287	278.517	254.182	237.26	185.447	200.764	161.373	158.642
Q_{calc}	276.749	140.4422	136.1533	259.1549	120.0033	216.941	226.848	210.621	170.177
First-order absorption kinetic model									
k_{R1}	0.0008	0.0012	0.0011	0.0020	0.0017	0.0047	0.0040	0.0042	0.0027
R^2	0.9808	0.9968	0.9957	0.9814	0.9920	0.9972	0.9995	0.9967	0.9995
Q_{calc}	244.305	259.474	277.954	254.178	237.243	185.447	200.764	161.373	158.642
Second-order absorption kinetic model									
k_{R2}	1.03E−5	0.93E−5	0.76E−5	1.23E−5	1.02E−5	3.89E−5	3.48E−5	3.50E−5	2.63E−5
R^2	0.9975	0.9960	0.9955	0.9961	0.9948	0.9995	0.9996	0.9992	0.9994
Q_{calc}	261.096	280.899	305.810	278.551	265.251	189.753	207.039	166.389	166.666

Table 2. Swelling kinetic parameters for poly(AAm-co-AAc)/bentonite and poly(AAm-co-AAc)/pectin hydrogel composites in distilled water.

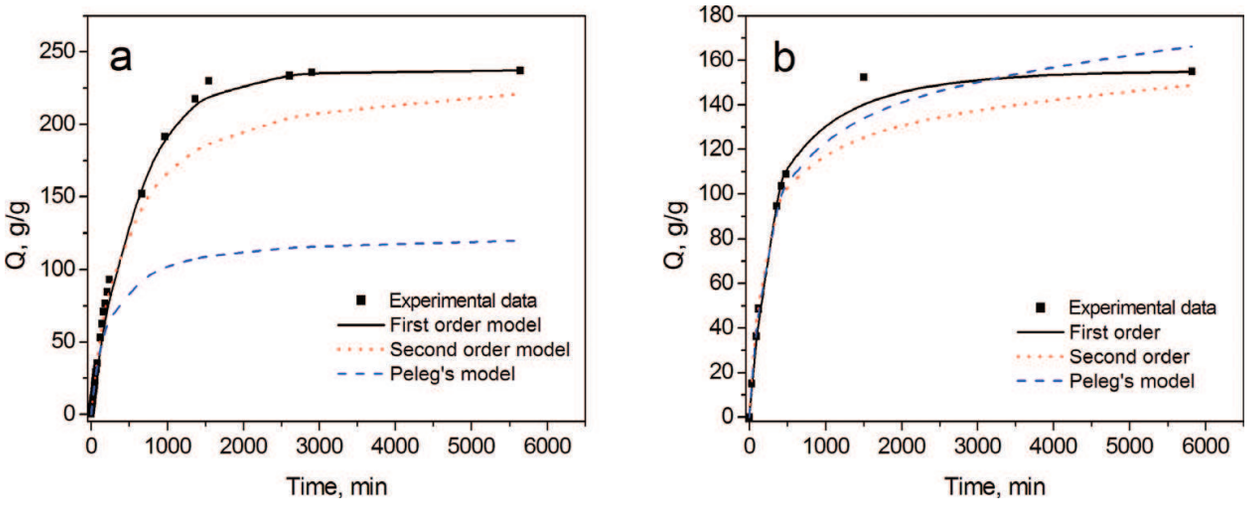


Figure 5. Comparison of the experimental swelling data with first-order, second-order kinetic models, and Peleg's model for a poly(AAm-co-AAc)/bentonite 4% (a) and poly(AAm-co-AAc)/pectin 4% (b).

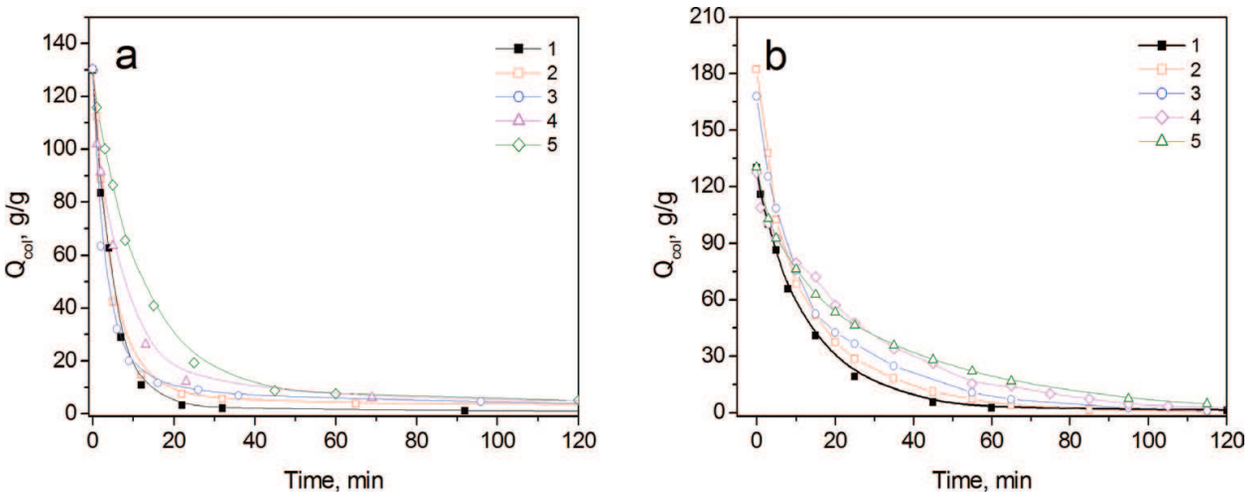


Figure 6. Collapse curves of poly(AAm-co-AAc)/bentonite composites and poly(AAm-co-AAc)/pectin composites filled with 0% (1), 1% (2), 2% (3), 3% (4), and 4% (5) bentonite (a) and pectin (b) in a 1 M solution of calcium chloride.

3.2.4. Collapse kinetics

Deswelling (or collapse) kinetic experiments were carried out by immersing a known amount of the fully swollen hydrogels at 25°C of the distilled water in various solutions with different ionic strength. At predetermined time intervals, the hydrogels were taken out and weighted. The percentage water retention was calculated using the following equation:

$$Q = \frac{m_2 - m_0}{m_0}, \tag{9}$$

where m_2 (g) and m_0 (g) are the weights of swollen hydrogel and of the original dry hydrogel in solution with different ionic strength.

Figure 6 shows the kinetic curves of collapse in a 1 M solution of calcium chloride. It can be seen from the figure that the collapse of composite gels occurs with both to bentonite, and to pectin. However, it can be noted that the presence of bentonite and pectin in polyelectrolyte hydrogel composites to some extent prevents collapse, reducing the rate of desorption of water into the solution. This effect is most typical for polymer hydrogels with higher filler content. **Figure 6** shows that the collapse curves have a high collapse rate at the initial section for an unfilled hydrogel than for a polymer composite with 5 wt.% bentonite and 4% pectin. A plausible explanation is that the spatial interactions between the bentonite plates exclude the further collapse of the gels. As can be seen from **Figure 6b**, a hydrogel with a semi-interpenetrating network has a lower collapse rate, which indicates large spatial interactions between the polymer network and the polysaccharide chains, as compared to bentonite particles.

The first-order collapse rate constants calculated from Eq. (6) are shown in **Table 3**. It can be seen from the table that the rate constants of collapse in various salts decrease with increasing percentage of bentonite and pectin filling in the polymer composite, which indicates a decrease the rate of collapse depending on the content of fillers.

Sample	**Percentage of filler in the composite (%)**					
		0	**1**	**2**	**3**	**4**
Peleg's model						
Poly(AAm-co-AAc)/bentonite	k_1	0.06488	0.04719	0.02848	0.02904	0.01437
	k_2	0.00764	0.00569	0.00706	0.00795	0.0077
	R^2	0.99596	0.98497	0.98842	0.99	0.99871
Poly(AAm-co-AAc)/pectin	k_1		0.02965	0.03337	0.08836	0.04875
	k_2		0.00274	0.00308	0.00806	0.01068
	R^2		0.98704	0.99775	0.99516	0.9369
First-order kinetic model						
Poly(AAm-co-AAc)/bentonite	k_1	0.029	0.04313	0.02999	0.03526	0.05486
	R^2	0.86309	0.86428	0.88308	0.8132	0.97665
	k_1^*	**0.08591**	**0.12385**	**0.14159**	**0.11425**	**0.07411**
	R^{2*}	**0.92486**	**0.97008**	**0.97526**	**0.99654**	**0.99946**
Poly(AAm-co-AAc)/pectin	k_1		0.06199	0.04873	0.03695	0.03544
	R^2		0.99515	0.98231	0.99362	0.99761
	k_1^*		**0.11433**	**0.08432**	**0.04918**	**0.0348**
	R^{2*}		**0.99147**	**0.99804**	**0.98799**	**0.96057**

*Kinetic constants are calculated at the initial stage of the collapse of hydrogels (0–50 min).

Table 3. The rate constants of the collapse, calculated from the Peleg's model and the first-order kinetic model.

Figure 7 compares the experimentally obtained dependence of Q on the time of the collapse process with the theoretical dependences obtained in the approximation of the experimental data to the dependences (6) and (4) corresponding to the kinetic models of the pseudo-first-order collapse and Peleg, respectively. As can be seen from the graph, the kinetics of the collapse of the poly(AAm-co-AAc)/bentonite hydrogel in salt solutions is most appropriately described by Peleg's model (**Figure 7a**). However, to describe the kinetics of the hydrogel collapse with a semi-interpenetrating network—poly(AAm-co-AAc)/pectin, the pseudo-first-order model is most suitable.

3.2.5. Equilibrium sorption studies

It is known that bentonite possesses good sorption properties and is used to purify water from pollutants. Articles [30, 31] cite data that bentonite is added to composite materials in order to increase the sorption properties of the material. It is also known that pectin is an enterosorbent [32]. Pectins have complex-forming ability based on the interaction of a molecule of pectin with ions of heavy metals and radionuclides. Due to the presence of a large number of free carboxyl groups in molecules, it is the low-esterified pectins that are most effective.

In the present work, the absorption properties of the synthesized polymer compositions in aqueous salt solutions of $Pb(NO_3)_2$ were to be studied. To observe the sorption of Pb^{2+} ions onto poly(AAm-co-AAc) hydrogel systems containing bentonite and pectin, the hydrogel systems were placed in aqueous solutions of $Pb(NO_3)_2$ and allowed to equilibrate for 1 day at 25°C. The concentration of sorbed ions was determined by the voltammetric method.

Equilibrium adsorption isotherms of poly(AAm-co-AAm), poly(AAm-co-AAc)/bentonite and poly(AAm-co-AAc)/pectin hydrogel systems are presented in **Figure 8**.

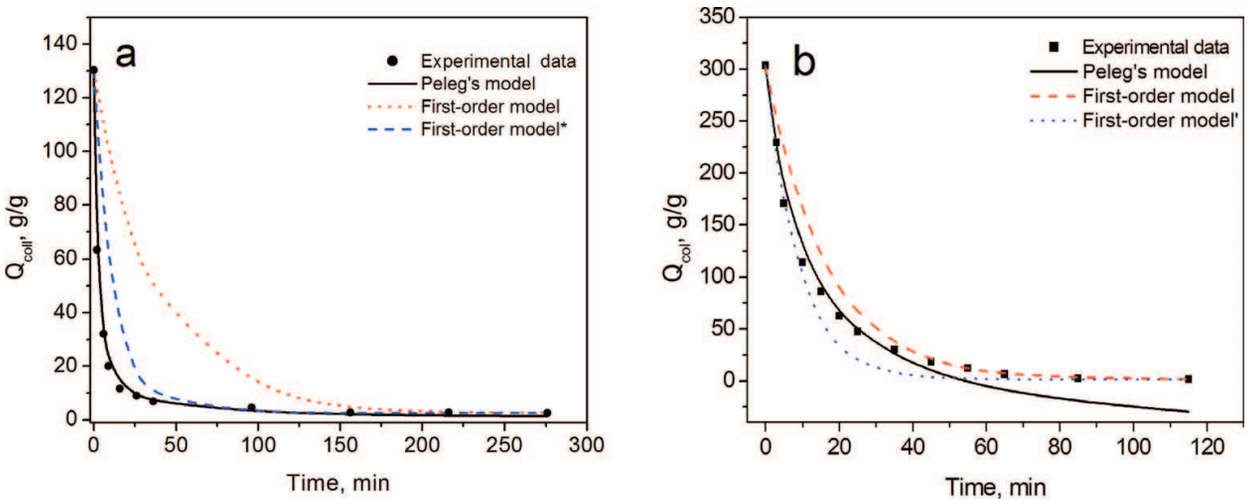


Figure 7. Experimental data and data obtained with first-order models and Peleg's model for poly(AAm-co-AAc)/bentonite 1% (a) and poly(AAm-co-AAc)/pectin 1% (b) hydrogel composites.

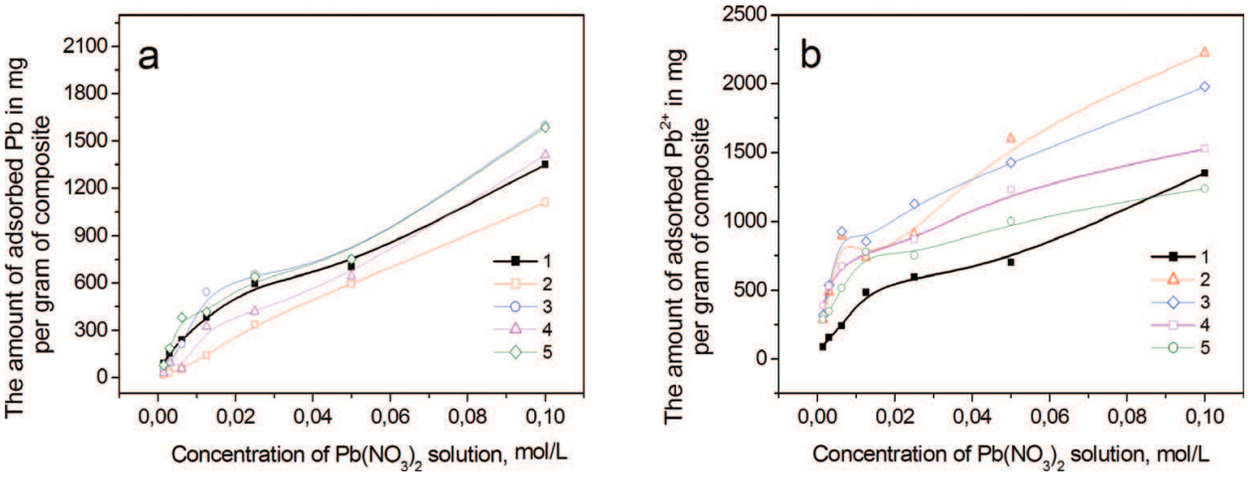


Figure 8. Sorption of lead ions from solutions of various concentrations of $Pb(NO_3)_2$ poly(AAm-co-AAc) hydrogel (1) and poly(AAm-co-AAc)/pectin (a) hydrogels with 1% (2), 2% (3), 3% (4), and 4% (5) pectin and poly(AAm-co-AAc)/bentonite (b) hydrogels with 1% (2), 2% (3), 3% (4), and 4% (5) bentonite.

In **Figure 8**, the heavy metal ions removal capacity (mg amount of sorption Pb^{2+} per unit mass) of the hydrogel systems is increased with the increasing concentration $Pb(NO_3)_2$ sorbed onto unit dry mass of the gel. Adsorption of heavy metal ions occurs due to ionic and coordination interactions with charged hydrogel groups (chemisorption).

At first, complexation takes place mainly on the surface of the hydrogel, as evidenced by the high initial rate of sorption of metal ions, possible to observe inhomogeneous distribution of ionic groups, which leads to uneven swelling of the hydrogel by volume. The experimental results show that the hydrogel-filled composites filled with pectin have greater sorption ability than the unfilled hydrogel (**Figure 8a**). The increase in the sorption of lead ions by pectin-containing hydrogels is via additional complex formation due to the presence of a large number of free carboxyl groups in the pectin molecules. Thus, from a solution with a concentration of 0.1 M lead nitrate, composites with 1 and 3% pectin are adsorbed by 20% of lead ions more than the uncharged hydrogel. However, as **Figure 8b** shows, hydrogels containing bentonite absorb a larger amount of lead ions. Moreover, the sorption capacity of bentonite-containing hydrogels is 25% higher than that of polysaccharide-containing hydrogels (as moisture absorbing properties).

4. Conclusion

Nowadays, there is a trend in development of multifunctional nanocomposites based on different types of hydrogels acting as a matrix for various nanomaterials. Crosslinked hydrophilic polymers are capable of absorbing large volumes of waters and salt solutions. Therefore, most of the modern work is devoted to the development of new composite materials based on hydrogels with improved sorption properties.

In the chapter of the book, two representatives of hydrogel composites are considered—a composite with dispersed filler and a composite with a semi-interpenetrating network and their sorption properties are compared.

Thus, incorporation of hydrophilic group containing chemicals, such as acrylic acid, polymers such as pectin, and clay such as bentonite in AAm hydrogels, can be obtained successively by the free radical solution polymerization method. Multifunctional crosslinkers such as MBA were used in the polymerization process. Poly(AAm-co-AAc)/bentonite and poly(AAm-co-AAc)/pectin hydrogel systems have showed high water absorbency. Some swelling and diffusion properties were discussed for different semi-IPNs and hydrogels prepared under various formulations. To determine the sorption characteristics of heavy metal ions such as Pb into the hydrogel systems, some sorption parameters have been calculated.

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