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CATION EXCHANGE PROPERTIES OF ANTIMICROBIAL POLYMERS WITH IMMOBILIZED N-CHLOROSULFONAMIDE GROUPS

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Deterioration of water quality requires the new ways for its purification, especially in field conditions. Various polymers are widely used in modern water treatment. A separate direction of this industry is the development of ion exchange resins, which are designed for water softening and removal of heavy metals. In this work, the cation exchange properties of granular styrene-divinylbenzene polymers with immobilized N-chlorosulfonamide groups, which were synthesized from the cation exchanger Purolite C100, were investigated. It is shown that the working exchange capacity of polymers with functional groups $-SO_2NClNa$ with respect to the Mg^{2+} cation is approximately 7.11 mg-eq/g, which is on average 20% higher than that of the initial Purolite C100. The exchange properties of the material are due to both chlorine-active groups and residual sulfo groups $-SO_3H$. An experiment in a flow system showed that the ion exchange rate in Purolite C100 significantly exceeds that for the modified polymer. Treatment of the working solution with such a chlorine-active polymer does not lead to a significant change in its pH and the release of active chlorine. Increasing the pH of the working solution contributes to the acceleration of ion exchange. The presence of ammonia buffer increases the rate of Mg^{2+} adsorption, but reduces the exchange capacity. Polymers with immobilized groups $-SO_2NH_2$, $-SO_2NClH$ and $-SO_2NCl_2$ are less effective, although not critically inferior to Purolite C100. The pronounced ion-exchange properties of the studied polymers, together with their previously proven disinfection activity, make them promising as components for express water purification systems.

Keywords: ion exchange resins, cation exchange capacity, active chlorine, antimicrobial polymers, water treatment.

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Introduction

Water treatment technologies are one of the most pressing and rapidly developing areas, driven by the deteriorating water quality trend and increasing water consumption [1]. The need to implement new, effective water treatment methods exists both for the technical needs of large industrial enterprises and for household consumption [2]. At the same time, tightening environmental regulations are forcing the search for new approaches to these measures, for example, by eliminating the use of traditional chemical reagents.

A promising solution to water quality issues is the use of various functional polymers and composites [3]. Such materials offer a variety of physical forms, a wide range of mechanical characteristics, controlled chemical properties, and are often biodegradable or reusable. They are widely used as filter materials, sorbents, coagulants, transport systems for chemical

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agents, etc. In order to simplify the technological design of water treatment systems, preference is given to multifunctional materials [4].

An integral procedure in water treatment is the removal of undesirable ions. In particular, in industry, it is important to remove hardness salts (formed by calcium and magnesium ions), which contribute to the formation of mineral deposits on the internal surfaces of pipelines, accelerate corrosion, and lead to equipment malfunction [5]. The presence of such salts also reduces the effectiveness of detergents, affects the organoleptic properties of water, and can lead to skin and other diseases, so water softening is also important in household use [6]. In addition to hardness ions, the removal of heavy metal ions from drinking water is important. Due to its ease of operation, cost-effectiveness, minimal dependence on complex infrastructure, and the absence of toxic by-products, adsorption is considered the preferred technology for this process. Selective adsorption, which is achieved using polymer ion exchangers, is optimal [7]. To date, numerous cation exchangers have been developed, among which the most studied and widespread are granular styrene-divinylbenzene polymers with grafted sulfonic acid groups, such as Purolyte C100 [8]. The advantage of such products is a relatively simple and inexpensive production technology, high exchange capacity, and a long service life, which is why they are produced in large quantities worldwide and used in both industry and household appliances.

We have previously described polymeric materials with immobilized N-chlorosulfonamide groups, the synthesis of which is possible from cation exchangers such of Purolite C100 type [9]. A distinctive feature of such polymers is their ability to controllably release active chlorine into the environment, which determines their powerful antimicrobial properties. We have studied their microbiocidal activity [10,11], and have proven the possibility of obtaining high-purity antiseptic solutions [12] and disinfecting water [13] with their use. At the same time, the presence of both residual free sulfo- and N-chlorosulfonamide groups themselves suggests their specific cation exchange capacity, which has not been studied. This allows considering them as multifunctional active components of water purification systems that combine disinfecting and softening properties. In this paper, the processes of sorption of cations by polymers of different structures under various hydrodynamic conditions have been studied in order to determine the prospects for their applications in water treatment.

Materials and methods

Polymers used in the study

Granular styrene-divinylbenzene polymers with immobilized N-chlorosulfonamide groups of various structures were used in the study. Materials were synthesized from the commercially available sulfonic acid cation-exchange resin Purolite C100 in the Na-form (Ecolab, USA) according to the methods described earlier [9]. All samples were dried under vacuum over sulfuric acid, then in a drying oven not exceeding 70^0C, and stored in an air-dry state. In the experiments, the initial Purolite C100 polymer in commercial form, as well as Purolite C100 granules in the H-form, which were obtained by rinsing the original raw with hydrochloric acid and then drying to an air-dry state, were used as a comparison samples. To minimize the influence of granule size on ion exchange, all materials were sieved through a sieve system, and only the 700–800 μm fraction, most characteristic of the initial Purolite C100, was used. General characteristics of all studied samples are presented in Table 1.

Determination of the working exchange capacity of polymer samples

The working solution was prepared by dissolving an accurately weighed portion of approximately 0.5 g of magnesium nitrate hexahydrate $Mg(NO_3)_2{\cdot}6H_2O$ in 1.0 liter of distilled water. The initial pH of this solution was 5.7–5.9. Then accurately weighed sample of approx. 0.12 g of the polymer (in terms of absolutely dry substance) was added to 200 ml of a working solution. The mixture was stirred for 6 hours on a shaker at 150 rpm, which was sufficient in all cases to achieve adsorption equilibrium. The solution was decanted, its acidity was measured, and its total

Table 1

Key characteristics of the polymers samples used

Sample number	Functional group	Air-dried product moisture content, %	Active chlorine content in air-dried product, %
1	$-SO_3-Na$	46	–
2	$-SO_3-H$	37	–
3	$-SO_2-NH_2$	12	–
4	$-SO_2-NClNa$	18	10.7±0.8
5	$-SO_2-NClH$	15	8.7±0.6
6	$-SO_2-NCl_2$	11	16.4±1.3

chlorine content (the sum of free and combined chlorine) was determined colorimetrically using an eXact Micro 20 photometer and the corresponding reagents (standard DPD method). Next, 10 ml of ammonia buffer (pH 10.0) was added to 50 ml of the treated solution, and the concentration of Mg^{2+} ions was measured using the standard method for determining water hardness by titrating with EDTA in the presence of the Eriochrome Black T [14]. The exchange capacity of the polymer was calculated from the difference between the concentration of Mg^{2+} ions in the initial and treated solutions, using the equation:

$$WCEC = \frac{(V_0 - V) \cdot C}{V_{al} \cdot M} \cdot 1000,$$

where *WCEC* is the working cation exchange capacity (mEq/g); V_0 and V are the volumes of EDTA used for titration of the working solution before and after polymer treatment, correspondingly (ml); C is the normal concentration of EDTA solution (eq/l); V_{al} is the aliquot volume (ml); and M is the mass of the polymer sample in terms of dry matter (g).

It should be noted that the generally accepted industrial method for determining the exchange capacity of cation exchangers [14] includes a mandatory step of converting all exchange groups to the H-form by rinsing with concentrated HCl. In the case of immobilized

N-chlorosulfonamides, this step will lead to structural changes and hydrolysis of the functional groups, and therefore cannot be applied. Accordingly, the WCEC value in our method cannot be considered the total exchange capacity, but specifically the working exchange capacity under given conditions. However, from an applied perspective, this characteristic is nevertheless important, because under real-world conditions, adsorption never reaches the experimentally determined total exchange capacity.

Study of cation exchange in a flow system

An accurately weighed sample of approximately 0.12 g (in terms of dry substance) of the polymer was placed in a glass 25 mlburetteequipped with a bottom tap, a ceramic membrane located close to it to prevent the passage of sample granules, and an upper nozzle with a hose outlet. Then, 200 ml of a working solution of approximately 0.5 g/l $Mg(NO_3)_2 \cdot 6H_2O$ was pumped through the burette from the bottom up using a peristaltic pump at a rate of 100 ml/min in recirculation mode. The flask with the working solution was constantly stirred with a magnetic stirrer, and its pH was monitored. An aliquot 2 ml of the solution was periodically withdrawn from the flask, mixed with 1 mL of ammonia buffer (pH 10.0) and 7 mL of distilled water, and the Mg^{2+} and total chlorine contents were determined colorimetrically using an eXact Micro 20 photometer and the corresponding reagents. In separate experiments, the polymer, pre-swollen in distilled water for 2 hours, was analyzed using the same technique. The ion exchange process was also studied under these conditions at a constant pH. For this purpose, the initial working solution was buffered with different buffers before circulation. The experiment was conducted until the equilibrium concentration of Mg^{2+} ions in the solution was established (in most cases, within 2 hours).

All experiments were performed in at least three replicates. Mathematical processing of obtained data included calculations of arithmetic means (M) and standard deviations (M±SD).

Results and discussion

Working exchange capacity of the studied polymers

The results of determining the working exchange capacity of polymer samples under the described conditions are given in Table 2.

As seen, during treatment with samples 2, 3, 5, and 6, the pH of working $Mg(NO_3)_2$ solutions shifts significantly toward the acidic region. For sample 2, this is due to the release of a proton during ion exchange. This may also be partially true for polymer 5, but the decrease in pH is more pronounced in this case. The acidification of the solution in the case of samples 3 and, especially, 6, which does not have a mobile proton in the N-chlorosulfonamide fragment, cannot be explained by this phenomenon. For samples 5 and 6, this effect is likely associated with the synthesis method of these polymers, which involves treating the Na-form of N-chlorosulfonamide with a solution of acetic or hydrochloric acid [9]. Sample 3 is rinsed with a weak solution of hydrochloric acid at the final stage of synthesis and may also contain its residues. Apparently, even repeated rinsing of the resulting granules with water and subsequent drying does not ensure the complete removal of residual acids, which in current experiment are released during sample swelling. This is confirmed by the rapid decrease in the pH of the $Mg(NO_3)_2$ solution: within 10 minutes of the experiment, it reaches 4.1–4.3 and 4.5–4.8 for samples 6 and 3, respectively, and is highly dependent on the polymer sample weight for the same solution volume. Furthermore, approximately the same pH values are achieved when the polymer is added to distilled water. The presence of acid residues, combined with the moisture content of the granules, leads to a sharp decrease in the stability of the functional groups in granules 5 and 6: the amount of immobilized active chlorine decreases by 52% and 68%, respectively, within 1 month, in contrast to Na-form 4, in which it remains virtually constant. However, complete removal of water from such polymers, which could impede hydrolysis during storage, is impossible due to the destruction of chlorine-active groups at high temperatures and the economic impracticality of vacuum drying. Furthermore, as Table 2 shows, an acidic environment promotes the release of active chlorine into the treated solution due to accelerated hydrolysis of N−Cl-bonds. Free sulfo groups $-SO_3H$, which, as will be shown below, are present in all sulfonamides and, in the case of 3, 5, and 6, are in the H-form, also affect the pH of the solutions. No significant change in acidity of working solutions is observed when using granules 1 and 4. The slight increase in pH in case 4 is likely due to the admixture of sodium hydroxide, which is a component of NaOCl solution used in the synthesis of this polymer. In the absence of organic impurities, active chlorine is not transferred to the aqueous phase in this case.

The total exchange capacity of the initial Purolite C100, as shown in Table 2, corresponds to that stated in the manufacturer's certificate (at least 4.0 mEq/g). However, when the functional group is converted to the H-form, it decreases slightly (by an average of 12%), which may be due to less effective swelling as polarity of the molecule is reduced. Sample 4 proved to be the most effective of all tested. Its WCEC exceeds that of Purolite C100 by an average of 20%. This result may be due to a combination of several factors. Firstly, the $-SO_2-NClNa$ functional groups are obviously capable of effective ion exchange; accordingly, the exchange capacity does not decrease with the conversion of the initial $-SO_3H$ moieties. Secondly, the first step in the synthesis of polymer 4 involves treating Purolite C100 with chlorosulfonic acid. This may lead not only to the conversion of existing $-SO_3H$ (sulfo) groups to $-SO_2Cl$ (sulfochloride) groups but also to the incorporation of additional $-SO_2Cl$ groups into the aromatic fragment of the chain. Thus, the final concentration of desired $-SO_2-NClNa$ groups may be higher than that calculated based on the initial $-SO_3H$ group content in the raw. Also, due to these additional groups, which are hydrolyzed during further processing, the concentration of sulfo groups in polymer 4 may be increased compared to the initial cation exchanger. Finally, functionalization likely increases the pore size of the polymer granule, making the adsorption sites more accessible for ion exchange. At the same time, the exchange capacity of samples 3, 5, and 4 was virtually the same and significantly lower than that of the Na-form 4, indicating that their functional groups do not participate in cation adsorption. However, it is not critically inferior to that of the H-form of Purolite C100, indicating the presence of a large number of free $-SO_3H$ groups, in which ion exchange, however, is less intensedue to the lower surface hydrophilicity and steric hindrance. Thus, the previously noted inability to produce granules with an active chlorine concentration above 10% using the developed method [9] is most likely due to the hydrolysis of the intermediate polymeric sulfochloride during the amidation stage. Unfortunately, the obtained results do not allow an accurate determination of the degree of conversion of the sulfo groups of the initial ion exchange resin and do not correlate with the content of immobilized active chlorine.

To summarize, the obtained data indicate that, in terms of cation exchange, a polymer with immobilized N-chlorosulfonamide groups in the Na-form is optimal for use in water treatment systems. This is due to its greater stability and higher exchange capacity compared to other chlorine-active resins studied, as well as the absence of a sharp change in the pH of the treated solution. An additional advantage is its simpler and more reproducible synthesis method, which is accompanied by less granule degradation compared to the corresponding H-form and N,N-dichlorosulfonamide.

Table 2

Results of determining the cation exchange capacity of polymer samples

Sample number	Functional group	WCEC, mEq/g	Total chlorine content in the treated working solution, mg/l	pH of the treated working solution, pH units
1	$-SO_3-Na$	5.89±0.45	–	5.8–6.2
2	$-SO_3-H$	5.18±0.28	–	3.1–3.4
3	$-SO_2-NH_2$	4.36±0.19	–	3.4–3.7
4	$-SO_2-NClNa$	7.11±0.85	–	6.2–6.4
5	$-SO_2-NClH$	4.83±0.56	0.11±0.03	2.4–2.7
6	$-SO_2-NCl_2$	4.54±0.48	0.16±0.03	2.6–2.9

Study of cation exchange in a flow system

The most promising application for the studied chlorine-active polymers is in point-of-use water purification systems. Such systems are considered an effective solution for resource-limited areas, as well as in emergency situations and during military operations, as demonstrated particularly by the experience of Ukraine, which lost a significant part of its centralized water treatment systems during the current conflict [15]. Modern point-of-use systems most often combine coarse and fine filters, as well as adsorbents, including ion exchangers, to remove organic and inorganic contaminants. However, they do not provide complete disinfection, so tablets containing chlorine-active compounds and, less commonly, UV irradiation are additionally used to prevent waterborne diseases. Water softeners containing a mixture of ion exchangers, widely used in households, often become a source of microbial contamination, and the water passed through them requires additional disinfection as well. We have previously shown that polymeric N-chlorosulfonamides, when added to microbiologically contaminated water, release active chlorine in an amount proportional to the microbial count, and neutralize pathogens. This makes them promising additives to existing point-of-use systems as a compact and regenerable antimicrobial component. From the standpoint of efficiency and technological design, systems that pass water through filters/adsorbents in recirculation mode to achieve a specified degree of purity after a certain number of cycles are advisable. Therefore, in this study, we investigated the cation-exchange properties of chlorine-active polymers under such conditions.

Taking into account the results obtained in determining the WCEC, only polymeric sodium N-chlorosulfonamide (Table 2, sample 4) was tested in the flow system in comparison with the initial Purolite C100 (sample 1).

In the first stage, the working characteristics of sample 4 were determined in comparison with sample 1, using the sameworkingsolution approx. 0.5 g/l $Mg(NO_3)_2·6H_2O$ with initial pH 5.75. It was necessary to take into account that the Purolite C100 resin is supplied in a swollen state, in which it operates most effectively. At the same time, chlorine-active polymer 4 must be stored in an air-dry state to prevent hydrolysis of the functional groups. Therefore, we studied the exchange process for an air-dry sample and a sample pre-swollen in water for 2 hours. The polymer weights were approx. 0.23 g calculated on an absolutely dry matter, and coincided to thousandths of a gram for each sample. The results are shown in Fig. 1.

As seen from Fig. 1, no significant difference in the adsorption efficiency of Mg^{2+} cations is observed between air-dry and swollen polymer 4, although the latter exhibits slightly higher values. Maximum adsorption is approximately the same for both polymers, achieved within the same time of about 90 min. Both chlorine-active samples exceed Purolite C100 in maximum adsorption by approximately 25%, which generally corresponds to the difference in their WCEC. However, the rate at which it is achieved is significantly higher for Purolite C100, reaching approximately 60 min. No

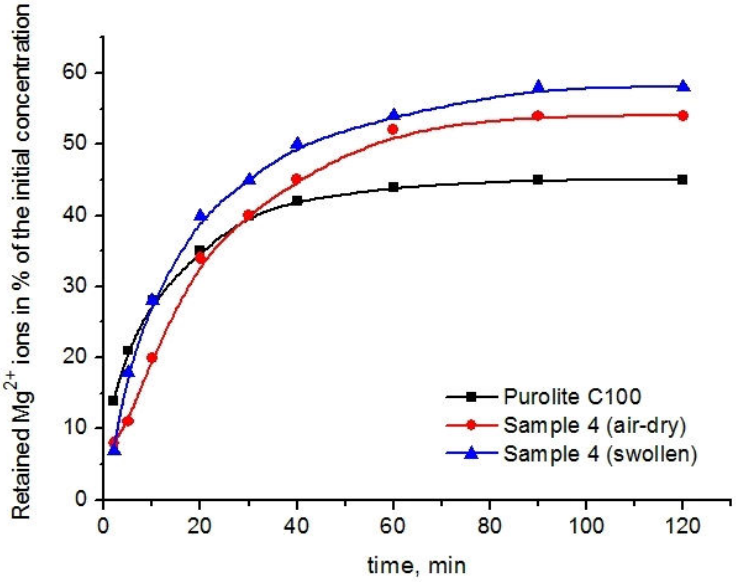

Fig. 1. Adsorption of Mg^{2+} cations in flow system from unbuffered working solution

active chlorine formation was observed in the solution, while its pH increased to 6.0–6.1 for Purolite C100 and to 6.3–6.4 for the chlorine-active samples.

It is known that the acidity of the medium has virtually no effect on the ion exchange characteristics of strongly acidic cation exchange resins, which include Purolite C100, but can significantly alter those of weakly acidic ones. Therefore, we additionally studied the treatment processes of the working solution with Purolite C100 and air-dried sample 4 at constant pH 10.0 (achieved by adding 5 ml of ammonia buffer to 200 ml of the solution) and pH 6.0 (achieved by adding 5 ml of acetate buffer to 200 ml of the solution). The results are shown in Fig. 2.

As is shown in Fig. 2a, no significant differences are observed at a constant pH 6.0 compared to the data obtained for unbuffered solution. However, in the presence of ammonia buffer (Fig. 2b), the chlorine-active polymer exhibits different properties, while the behavior of Purolite C100 remains unchanged. Under these conditions, sample 4 quickly, within 10 minutes, adsorbs the maximum amount of Mg^{2+} ions, which, however, is almost half that obtained at other pH values. The concentration of active chlorine in the solution gradually increases, reaching 75 mg/L by the end of the experiment. This is explained by the interaction of the polymer with the components of the ammonia buffer to form a mixture of chloramines, as described previously [13]. As a result, the immobilized $-SO_2-NClNa$ group is converted to the $-SO_2-NH_2$ group, which, as shown above, has a significantly lower WCEC. Thus, it can be assumed that under such conditions a more alkaline medium accelerates ion exchange, but at the same time deactivates the functional groups in this regard. To test this hypothesis, an additional experiment was conducted in which the working $Mg(NO_3)_2$ solution was adjusted to pH 10.0 using NaOH and maintained at this level by adding minimal (10–20 μl) amounts of NaOH directly during operation, while the acidity tended to decrease. This method was chosen because standard alkaline buffer systems (borate, phosphate, protein, etc.) are inapplicable to the electrolyte used due to the formation of complex or insoluble compounds that interfere with further analysis. The experimental results are presented in Fig. 3.

As can be seen, the characteristics of Purolite C100 remained unchanged under these conditions. Chlorine-active sample indeed absorbed Mg^{2+} ions faster than in near-neutral media within first 30 min, with the same maximum adsorption, but these differences are insignificant. However, the rate at which this maximum was reached was significantly higher in ammonia buffer. These kinetic differences are likely explained by the rapid change in the structure of the electrical double layer near the surface of the polymer granule during the chlorination reactions of the ammonia buffer components. In general, the presence of amine impurities in treated water is undesirable both in terms of decreased disinfection efficiency due to the destruction of chlorinated groups, and of reduced cation adsorption.

Overall, the obtained data indicate that cation exchange resins such as Purolite C100, widely used in water treatment, could potentially be replaced with polymeric N-chlorosulfonamide without compromising water softening performance. This could also provide additional disinfection of the treated water, making the system more efficient. It should be noted that regeneration of ion exchange resins, typically achieved by rinsing with a concentrated NaCl solution, could theoretically be achieved in this case by replacing the latter with NaOCl. This would simultaneously restore both the exchange capacity and the content of immobilized active chlorine, which gradually decreases due to hydrolysis and transchlorination with amine

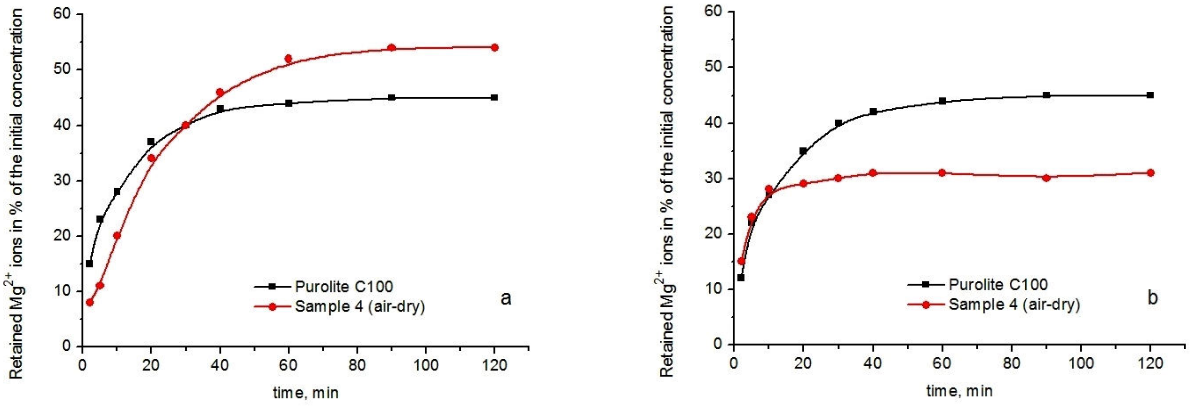

Fig. 2. Adsorption of Mg^{2+} cations in flow system from buffered working solutions with pH 6.0 (a) and pH 10.0 (b)

contaminants.

Conclusions

Granular styrene-divinylbenzene polymers with immobilized N-chlorosulfonamide groups exhibit cation exchange capacities comparable to those of industrially used sulfonic acid cation exchangers of Purolite C100 type. The polymer with $-SO_2-NClNa$ functional groups is most attractive in this regard. It effectively adsorbs Mg^{2+} cations, including in the flow, does not alter the acidity of the treated solution, does not release active chlorine into it in the absence of amine impurities, is more stable during storage, and is synthesized using a simpler technology. The combination of softening and disinfecting abilities makes this material attractive for point-of-use water treatment systems.

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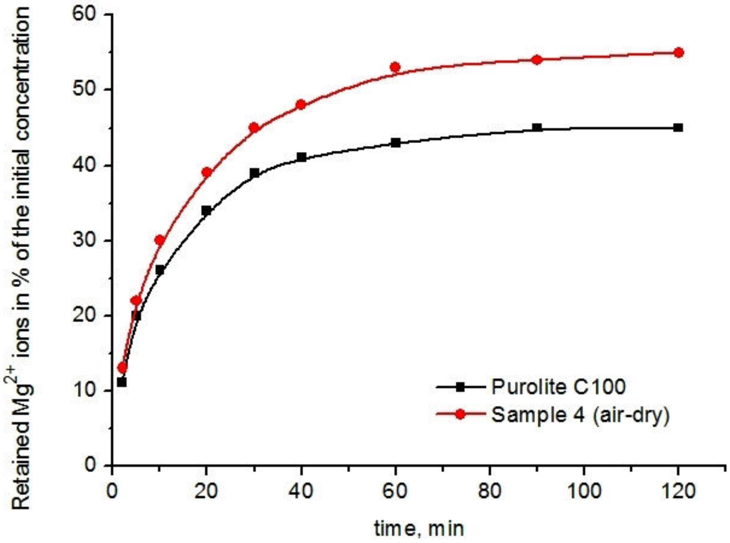

Fig. 3. Adsorption of Mg^{2+} cations in flow system from working solution with pH 10.0, maintained with NaOH

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КАТІОНООБМІННІ ВЛАСТИВОСТІ АНТИМІКРОБНИХ ПОЛІМЕРІВ З ІММОБІЛІЗОВАНИМИ N-ХЛОРСУЛЬФОНАМІДНИМИ ГРУПАМИ

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Погіршення якості води вимагає нових способів її очищення, особливо в польових умовах. У сучасній водопідготовці широко використовуються різні полімери. Окремим напрямком цієї галузі є розробка іонообмінних смол, призначених для пом’якшення води та видалення важких металів. У цій роботі досліджено катіонообмінні властивості гранульних стирол-дивінілбензольних полімерів з іммобілізованими N-хлорсульфонамідними групами, синтезованих з катіоніту Purolite C100. Показано, що робоча обмінна ємність полімерів з функціональними групами $-SO_2NClNa$ по відношенню до катіона Mg^{2+} становить приблизно 7,11 мг-екв/г, що в середньому на 20% вище, ніж у вихідного Purolite C100. Обмінні властивості матеріалу зумовлені як хлорактивними групами, так і залишковими сульфогрупами $-SO_3H$. Експеримент у проточній системі показав, що швидкість іонного обміну при використанні Purolite C100 значно перевищує таку для модифікованого полімеру. Обробка робочого розчину таким хлорактивним полімером не призводить до суттєвої зміни його pH та виділення активного хлору. Наявність аміачного буфера збільшує швидкість адсорбції Mg^{2+}, але знижує обмінну ємність. Полімери з іммобілізованими групами $-SO_2NH_2$, $-SO_2NClH$ та $-SO_2NCl_2$ менш ефективні, хоча критично не поступаються Purolite C100. Виражені іонообмінні властивості досліджуваних полімерів разом з їх раніше доведеною дезінфекційною активністю роблять їх перспективними в якості компонентів експрес-систем очищення води.

Ключові слова: іонообмінні смоли, катіонообмінна ємність, активний хлор, антимікробні полімери, водопідготовка.

CATION EXCHANGE PROPERTIES OF ANTIMICROBIAL POLYMERS WITH IMMOBILIZED N-CHLOROSULFONAMIDE GROUPS

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Deterioration of water quality requires the new ways for its purification, especially in field conditions. Various polymers are widely used in modern water treatment. A separate direction of this industry is the development of ion exchange resins, which are designed for water softening and removal of heavy metals. In this work, the cation exchange properties of granular styrene-divinylbenzene polymers with immobilized N-chlorosulfonamide groups, which were synthesized from the cation exchanger Purolite C100, were investigated. It is shown that the working exchange capacity of polymers with functional groups $-SO_2NClNa$ with respect to the Mg^{2+} cation is approximately 7.11 mg-eq/g, which is on average 20% higher than that of the initial Purolite C100. The exchange properties of the material are due to both chlorine-active groups and residual sulfo groups $-SO_3H$. An experiment in a flow system showed that the ion exchange rate in Purolite C100 significantly exceeds that for the modified polymer. Treatment of the working solution with such a chlorine-active polymer does not lead to a significant change in its pH and the release of active chlorine. Increasing the pH of the working solution contributes to the acceleration of ion exchange. The presence of ammonia buffer increases the rate of Mg^{2+} adsorption, but reduces the exchange capacity. Polymers with immobilized groups $-SO_2NH_2$, $-SO_2NClH$ and $-SO_2NCl_2$ are less effective, although not critically inferior to Purolite C100. The pronounced ion-exchange properties of the studied polymers, together with their previously proven disinfection activity, make them promising as components for express water purification systems.

Keywords: ion exchange resins; cation exchange capacity; active chlorine; antimicrobial polymers; water treatment.

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