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Analysis of the process of pharmaceutical substances removal from aquatic solution using membranes modified with calcium carbonate

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ABSTRACT

One of the biggest problems related to water management is water pollution with pharmaceutical substances. The diversity of these substances makes conventional wastewater treatment methods ineffective. For this reason, there is a need to develop new, more efficient methods. A solution that can improve the efficiency of removing pharmaceutical substances from water is an integrated filtration–adsorption process. For this purpose, polyvinylidene fluoride (PVDF) ultrafiltration membranes were modified with calcium carbonate particles, which have adsorption properties. The modification process was carried out by dip coating method, in which a layer-forming solution consisting of dissolved PVDF polymer and $CaCO_3$ particles was applied to the membrane surface. In the conducted tests, the ability to remove pharmaceutical substances from the aqueous solution was determined. The influence of such parameters as pH, NaCl salt concentration, $FeCl_2$ salt concentration and surface tension on the filtration–adsorption process was also examined. The filtration–adsorption process was carried out in a classic flow system used for the microfiltration process. The tested pharmaceutical substances were tetracycline and sulfadiazine. Based on the conducted tests, it was found that the process of removing the tested substances occurs intensively only at specific pH range, 6.5–10 for tetracycline and 4.5–6.5 for sulfadiazine. Below and above this range, there is a significant decrease in the efficiency of the process. On the other hand, in the presence of salt ions, their low concentration does not adversely affect the efficiency of the process, but above a certain concentration, the amount of removed pharmaceutical substance decreases (from 40 to 20 mg/m^2 for NaCl and from 80 to 5 mg/m^2 for $FeCl_2$). The presence of substances reducing the value of surface tension has a similar effect as salts.

Keywords: Membrane filtration; Filtration–adsorption process; Pharmaceutical substances; Calcium carbonate

1. Introduction

In recent years, more and more attention has been paid to the threats related to the presence of synthetic and natural chemical compounds in the aquatic environment, the production of which has increased significantly over the last century due to the development of technology. Such compounds are called “emerging contaminants”. Many of these substances are not yet monitored, but they are believed to have a negative impact on the environment. Sources of such harmful substances include municipal and industrial sewage, agriculture and transport. One of the groups of such substances are PPCPs (pharmaceuticals and personal care products), which include bioactive chemical compounds used in medicine, veterinary medicine and pharmaceuticals (drugs, excipients, supplements, surfactants, hormones), as well as cosmetics (soaps, personal care products, cleaning products). Although their concentration oscillates at

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the level of nano- or micrograms per liter, their continuous accumulation in the environment is a serious threat to the natural environment, as well as to human health [1].

One of the groups of pharmaceutical substances whose removal efficiency will be analyzed in the following work are antibiotics. It has been shown that many antibiotics administered to humans and animals, after being metabolized, are released into the environment unchanged or in the form of metabolites, which are often even more active and toxic than the original form of the drug [2]. The presence of antibiotics in the aquatic environment also affects the development of antibiotic-resistant bacteria, making antibiotics less and less effective in treating human and animal diseases. In addition, antibiotics and the products of their chemical transformations accumulate in the waters and tissues of organisms, which affects the quality of human food and drinking water [3]. Based on the literature, it can be concluded that antibiotics and antibiotic-resistant bacteria have already been discovered in water reservoirs around the world. Pharmaceutical compounds belonging to β-lactams have been detected in lakes and rivers throughout Asia [4]. Antibiotics, including amoxicillin, tetracycline, sulfadiazine and erythromycin, are present in the waters of Europe, North America and Africa [5–7]. Antibiotic-resistant bacteria have been detected not only in water reservoirs, but also in drinking water and bottled water [8].

Due to the great diversity in the chemical structure of pharmaceutical compounds and their low concentration in water, many works are devoted to the study of the effectiveness of existing methods of water purification or the development of new technologies. The need to develop new technologies results from the fact that conventional, individual processes are not effective or their use is not economically justified in this case. One of the conventional processes is membrane filtration, which allows the removal of pharmaceutical compounds at the level of 80%–90% or even higher in some cases [9–12]. However, the disadvantage of using membrane filtration is the formation of a retentate stream, that is, a concentrated solution of pharmaceutical substances, which requires further management. Another group of processes that also enable obtaining a high degree of removal of pharmaceutical substances are oxidation processes [13–16]. However, the disadvantages of these methods are the high energy demand and the possibility of formation of oxidation reaction products that are more harmful than degraded pharmaceutical substances. The adsorption process also has a high potential in pharmaceutical substances removal [17–19]. However, the disadvantages of this process include the formation of a worn bed and the need to design an additional process step enabling the removal of adsorbent particles from water. In order to improve the efficiency of pharmaceutical substances removal, the development of new technologies is based on both the implementation of new processes, most often integrated or hybrid processes [20–24], and the search for new materials with adsorption [25–30] or photocatalytic properties [31–33].

The solution proposed in this paper, which can increase the efficiency of pharmaceutical substances removal from water, is the integrated filtration and adsorption process. In this process the adsorption process takes place on the surface of the membrane. In order to impart adsorption properties, the membrane is modified by covering its surface with particles with adsorption properties. Such a solution has a number of advantages. Placing particles with adsorption properties on the surface of the membrane prevents them from entering the treated water stream. In addition, the removed substances accumulate on the surface of the membrane, and thus their concentration in the retentate decreases significantly. It should be noted here that the tubular membrane was modified on its outer part. Since the membrane was fed with feed into the tube, the modified side of the membrane was on the permeate side. Therefore, the liquid flowing to the modified part of the membrane was pre-cleaned of solids, undissolved salts and complexes, the presence of which may significantly reduce the sorption capacity of the adsorbent.

In the presented work, calcium carbonate ($CaCO_3$) nanoparticles were used as particles with adsorption properties placed on the membrane surface. Based on literature data, it can be concluded that this compound has the ability to adsorb heavy metal ions [34–36], dyes [37], surfactants [38], organic vapors [39] and organic compounds [40–42] including pharmaceutical substances [43]. $CaCO_3$ also has a number of advantages, including a large specific surface area, a relatively simple method of production, low cost of production and non-toxicity [38,44,45].

The aim of the research was to better understand the possibility of using $CaCO_3$ to remove pharmaceutical compounds from water in the filtration and adsorption process, the following study examined the impact of water physico-chemical parameters, that is, pH, salt concentration (NaCl, $FeCl_2$) and surface tension on the efficiency of removing two antibiotics - tetracycline and sulfadiazine.

2. Experimental set-up

The research was carried out in two stages. In the first stage of the research, the impact of the above-mentioned parameters on the effectiveness of the removal of the tested antibiotics in the stationary system was determined. In the second stage, tests were carried out in a flow system on model wastewater with different pH, salts concentration and surface tension, on the basis of which the degree of antibiotics removal and changes in the permeate flux value during the process were determined.

2.1. Materials and methods

Tubular ultrafiltration membranes made of polyvinylidene fluoride (PVDF) with a cut-off value of 20 kDa (PCI Membranes, UK) were used in the study. The membranes were modified with the dip-coating method using our own methodology [46]. Calcium carbonate ($CaCO_3$), produced according to the procedure developed by team members [47], was used as particles with adsorbing properties. The content of $CaCO_3$ in the modifying layer was 10% by mass. The tests were carried out on an unmodified membrane and a modified membranes.

Tetracycline (Pol-Aura, Poland) and sulfadiazine (Sigma-Aldrich, Poland) were used to test the effectiveness of antibiotic removal using $CaCO_3$. This substances were chosen as representatives of antibiotics present in the aquatic environment.

Formic acid (HCOOH) 85% pure (Chempur, Poland), sodium hydroxide (NaOH) 0.1 mol/dm^3 (Chempur, Poland), ethyl alcohol 96% (C_2H_5OH) pure (Stanlab, Poland) and salts: sodium chloride (NaCl) (Sigma-Aldrich, Poland) and $FeCl_2$ (Sigma-Aldrich, Poland) were used for the preparation of aquatic solution.

2.1.1. Solutions of model wastewaters

In order to determine the impact of changes in physico-chemical parameters characterizing aquatic solutions on the filtration and adsorption process, stationary and flow tests were performed. Aquatic solutions of antibiotics with a concentration of 40 mg/dm^3 were used to carry out the tests. This initial concentration value was determined based on literature data [48–50]. The concentration of antibiotics in the solutions was measured by UV-vis spectrophotometry (Gensys 10S UV-Vis, Thermo Fisher Scientific, Waltham, MA, USA).

Demineralized water with pH = 6.5, conductivity 35 μS/cm and surface tension 72 mN/m was used to prepare the solutions. In order to achieve the required level of pH, conductivity and surface tension of the prepared laboratory solutions, measured amounts of formic acid or sodium hydroxide, NaCl and $FeCl_2$ and ethyl alcohol were added in turn.

For tests in the stationary system, drug solutions with different values of physico-chemical parameters characterizing aquatic solutions, that is, pH, conductivity and surface tension, were prepared. At this stage of the research, drug solutions with only one changed physico-chemical parameter were prepared. The other parameters correspond to the parameters of the RO water used in the tests. The values of the parameters characterizing the prepared solutions are presented in Table 1.

Based on the tests carried out in the stationary system and data on the composition of water occurring in natural conditions, 4 aquatic solutions were prepared. At this research stage, wastewater with more than one changed physico-chemical parameter in relation to the used RO water was produced. The physico-chemical parameters characterizing the prepared model wastewater are presented in Table 2.

2.2. Membrane adsorption properties (stationary system)

The influence of changes in the examined physico-chemical parameters characterizing aqueous solutions on the adsorption properties of membranes modified with $CaCO_3$ particles was carried out in a stationary system. For this purpose, a 7 cm long capillary membrane sample was placed in 50 cm^3 of the solution. Then, after the specified time has elapsed, the drug concentration in the solution was tested. Based on the obtained values and Eq. (1), it was possible to determine the mass of the adsorbed antibiotic by the membrane in the stationary system q_{istat} (g/m^2).

$$q_{\text{istat}} = \frac{\left(C_0 - C_t\right)}{S} \cdot V_s \tag{1}$$

where c_0 is the initial concentration of the antibiotic (g/dm^3), c_t is the drug concentration in time t (namely 90 min) (g/dm^3), V_s is the volume of the drug solution (0.05 dm^3) (dm^3), and S is the membrane area (0.003 m^2) (m^2).

2.3. Filtration–adsorption setup (flow system)

A typical installation for the ultrafiltration process and own membrane modules with a filtration area of 0.077 m^2 (4 membranes 0.47 m long) were used to carry out the tests in the flow system. The process was carried out in a closed system with continuous permeate recycling. The volume of the solution was 7.5 dm^3. The process was carried out at a pressure of 1 bar with a retentate flow of 400 dm^3/h.

Table 1
Physico-chemical parameters of the tested solutions

Antibiotic concentration (mg/L)	pH	Conductivity (NaCl) (μS/cm)	Conductivity ($FeCl_2$) (μS/cm)	Surface tension (mN/m)
40	2, 2.5, 4.5, 6.5, 10, 12	35 (as a two-salt solution)		72
40	6.5	0, 100, 400, 600	–	72
40	6.5	–	0, 30, 60, 140	72
40	6.5	35 (as a two-salt solution)		72, 65, 58

Table 2
Physico-chemical parameters of the model wastewater

Type of model wastewater	Antibiotic concentration (mg/L)	pH (–)	Conductivity (NaCl) (μS/cm)	Conductivity ($FeCl_2$) (μS/cm)	Surface tension (mN/m)
I	40	6.5	35 (as a two-salt solution)		72
II	40	7	180	–	65
III	40	8	180	–	65
IV	40	5.5	220 (as a two-salt solution)		65

During the process, the permeate volumetric flow and the concentration of the antibiotic in the feed and permeate were measured. Measurements were made after the specified time has elapsed from the start of the process. Based on the obtained values of changes in the concentration of the antibiotic in the feed during the process and Eq. (2), it was possible to determine the mass of the antibiotic removed from the feed in the flow system q_{flow} (g/m^2).

$$q_{\text{flow}} = \frac{\left(C_0 - C_t\right)}{S} \cdot V_s \tag{2}$$

where c_0 is the initial concentration of antibiotic (g/dm^3), c_t is the drug concentration after time t (g/dm^3), V_s is the volume of the drug solution (7.5 dm^3) (dm^3), and S is the membrane area (0.077 m^2) (m^2).

3. Results and discussion

In the first part of the research, the impact of changes in individual physico-chemical parameters characterizing aqueous solutions on the effectiveness of the adsorption process on membranes modified with calcium carbonate was determined. These studies were carried out in a stationary system. It should also be noted that the mass of adsorbed tetracycline and sulfadiazine (solution based on demineralized water) for the unmodified membrane is 8.31 and 2.77 mg/m^2, respectively. Such small amounts make it possible to conclude that the adsorption capacity of the unmodified membrane itself may be considered statistically insignificant in further considerations.

3.1. Impact of pH

The results of the mass of adsorbed tetracycline and sulfadiazine after 90 min of the process for different pH values are presented in Figs. 1 and 2.

Based on the results presented in Figs. 1 and 2, it can be stated that there is a specific pH range for which the adsorption of both antibiotics is relatively most effective. Outside this range, the mass of the adsorbed substance decreases significantly. This is due to the effect of the pH of the solution on both the zeta potential of the surface of the calcium carbonate particles and the ionic forms of the antibiotic particles. The zeta potential on the surface of calcium carbonate is positive for acidic, neutral and alkaline

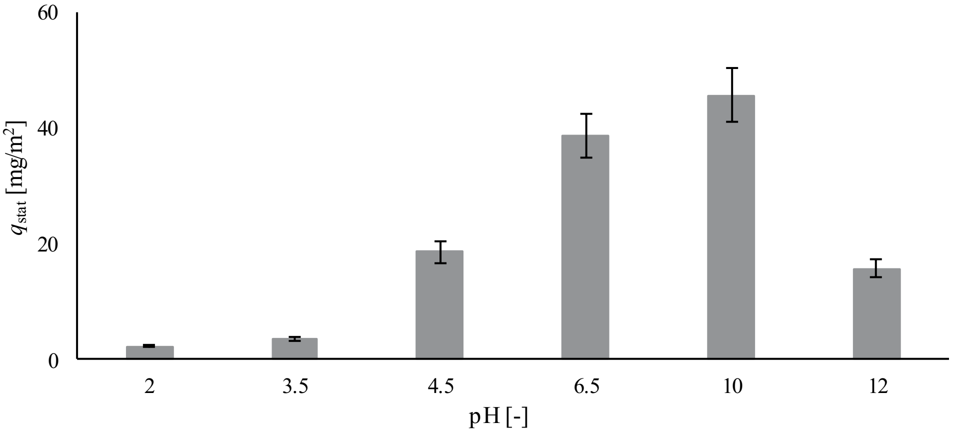

Fig. 1. Mass of adsorbed tetracycline for different pH values.

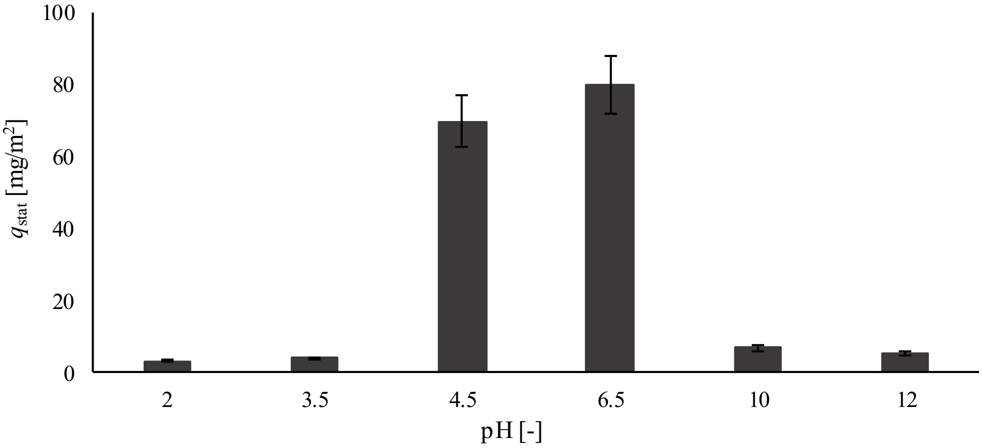

Fig. 2. Mass of adsorbed sulfadiazine for different pH values.

environments in the initial alkaline pH range, and decreases with increasing pH value. For pH > 11, the zeta potential value is negative [36]. In turn, tetracycline is characterized by three dissociation constants, that is, pK_a = 3.3, 7.7 and 9.6 [51]. Thus, in a strongly acidic environment, tetracycline exists mainly in the cationic form. Then, as the pH increases, the tetracycline becomes anionic. Above pH = 7.8, tetracycline exists mainly in one of the two anionic forms. For this reason, in an acidic environment in which tetracycline has a cationic form and the surface of calcium carbonate is positively charged, the intensity of the adsorption process decreases significantly. With increasing pH value, when the tetracycline is present in the anionic form, and the surface of the calcium carbonate is still positively charged, the adsorption process takes place. The intensity of this process increases until the tetracycline is in anionic form and the surface of the calcium carbonate is negatively charged. Both of these phenomena occur for pH > 11 and above this pH value the intensity of the adsorption process decreases significantly. In turn, sulfadiazine, like tetracycline, is also characterized by more than one dissociation constant (pK_a = 2 and 6.5) [52]. It takes a cationic form in a strongly acidic environment and, as in the case of tetracycline, the intensity of the adsorption process is low at low pH. In the range of pH = 4.5–6.5, when the observed adsorption of sulfadiazine was the highest, sulfadiazine is present in a neutral form. For higher pH values, the mass of adsorbed sulfadiazine decreases. Unlike tetracycline, the negatively charged sulfadiazine molecule does not adsorb significantly on the membrane. Such an effect may be related to specific surface or electrostatic interactions between sulfadiazine and calcium carbonate particles that appear in a solution with a pH value greater than 6.5. However, despite the lack of a clear cause, a decrease in the mass of adsorbed drugs with an increase in pH value is also described in the literature [53–55].

3.2. Impact of conductivity (NaCl)

The results of the mass of adsorbed tetracycline and sulfadiazine obtained after 90 min of the process taking place in solutions of different conductivity, related to the NaCl concentration, are presented in Figs. 3 and 4, respectively.

Based on the results obtained for tetracycline, it can be concluded that the mass of the adsorbed drug decreases with increasing conductivity of the solution. This is due to the electrostatics screening effect [56]. An increase in the concentration of Na^+ ions reduces the electrostatic

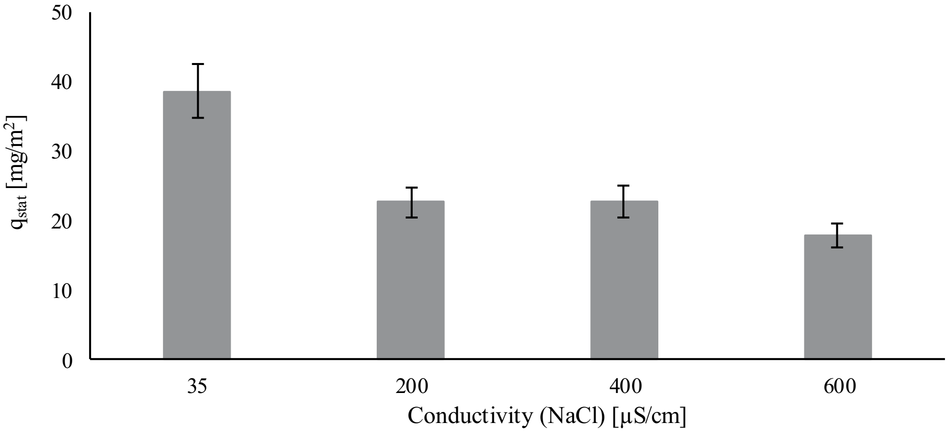

Fig. 3. Mass of adsorbed tetracycline for different conductivity (NaCl concentration).

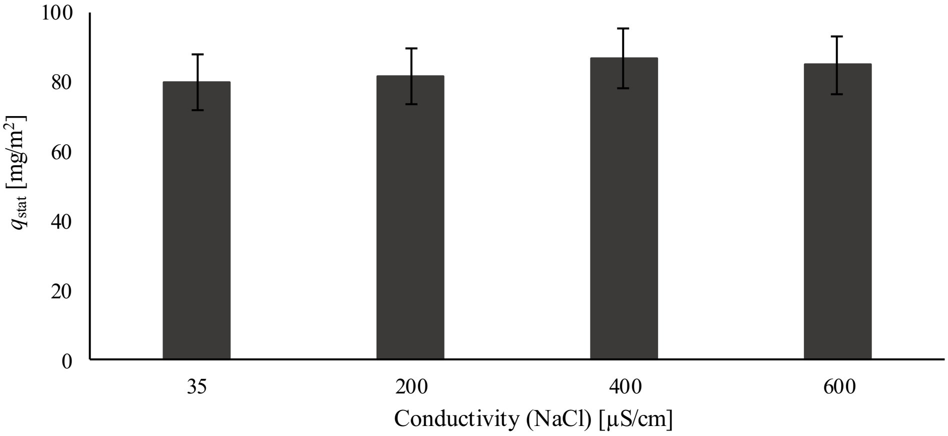

Fig. 4. Mass of adsorbed sulfadiazine for different conductivity (NaCl concentration).

interactions between tetracycline molecule and calcium carbonate particles, which leads to a decrease in adsorption intensity. In the literature, similar conclusions were presented regarding the study of the adsorption of antibiotics on carbon materials [54–58]. In turn, based on the results for sulfadiazine, it can be seen that the occurring changes in the mass of the adsorbed substance for different concentrations of NaCl are statistically insignificant. This effect may result from the fact that the interactions between sulfadiazine and calcium carbonate particles are so strong in a solution at pH = 6.5 that Na^+ and Cl^- ions do not compete with sulfadiazine [59]. It should be emphasized that the described phenomena apply only to the NaCl salt concentration range used in the work. Other phenomena may occur at higher salt concentrations [54,58].

3.3. Impact of conductivity ($FeCl_2$)

The results of the mass of adsorbed tetracycline and sulfadiazine obtained after 90 min of the process taking place in solutions of different conductivity, related to the $FeCl_2$ concentration, are presented in Figs. 5 and 6, respectively.

Based on the obtained results (Figs. 5 and 6), it can be concluded that only the increase in the adsorbed mass occurs for tetracycline removed from the solution with the lowest $FeCl_2$ concentration. It has been shown in the literature that the effect of divalent ions on the surface of calcium carbonate is opposite to that of monovalent ones - the potential of the calcium carbonate surface becomes more positive [59]. As a result, the adsorption intensity of tetracycline increases. Another possible reason may be the formation of a new tetracycline complex with Fe^{2+} ion with better affinity to the membrane surface. Such a phenomenon is described in literature studies in the case of magnesium or calcium ions, which retain chemical similarity to iron ions [60]. However, a further increase in the $FeCl_2$ concentration causes a decrease in the pH value of the solution, which reduces the intensity of tetracycline adsorption (Fig. 1). On the other hand, in the case of sulfadiazine, a decrease in the mass of the adsorbed substance can be observed with an increase in the conductivity of the solution. This is due to the fact that, as previously mentioned, the pH value of the solution decreases with the increase in $FeCl_2$ concentration, which in turn reduces the intensity of sulfadiazine adsorption. However, sulfadiazine, unlike tetracycline, does not form complexes with Fe^{2+} ions so intensively, which may increase the intensity of adsorption [51,61]. In addition, the literature indicates that divalent ions have a greater

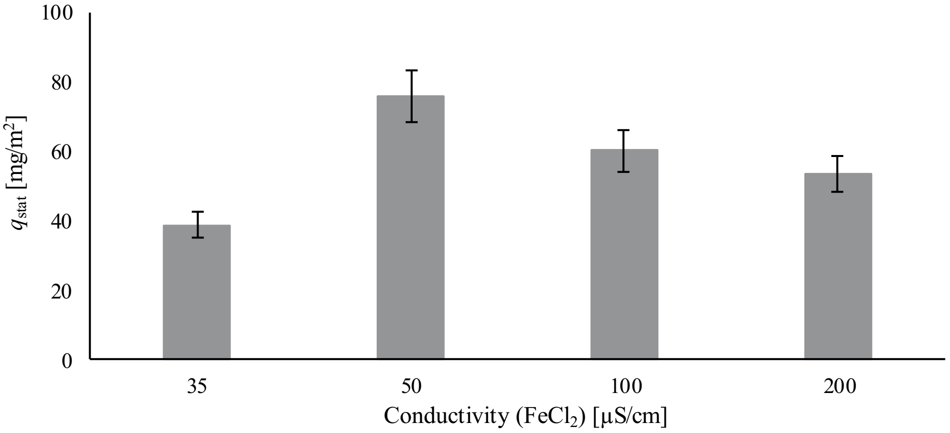

Fig. 5. Mass of adsorbed tetracycline for different conductivity ($FeCl_2$ concentration).

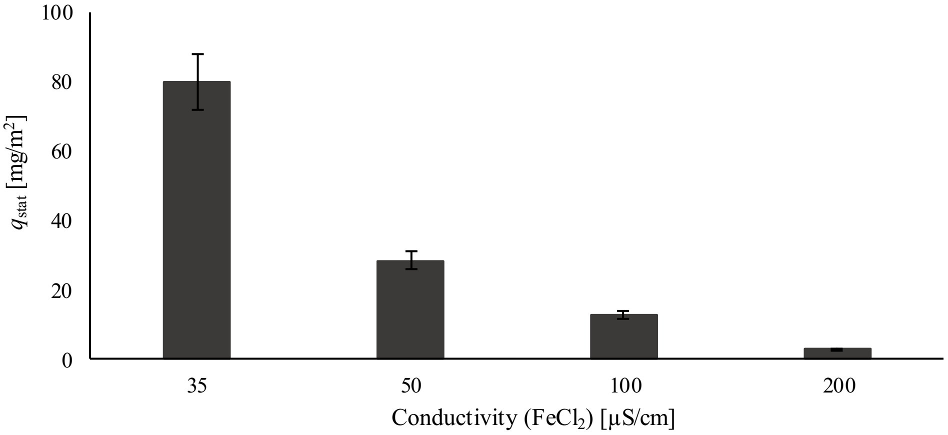

Fig. 6. Mass of adsorbed sulfadiazine for different conductivity ($FeCl_2$ concentration).

ionic strength than monovalent ions, which results in the electrostatics screening effect occurring more intensively. As a result, the intensity of the sulfadiazine adsorption process in the discussed system decreases [62].

3.4. Impact of surface tension

The results of the mass of adsorbed tetracycline and sulfadiazine obtained after 90 min of the process taking place in solutions of different surface tension are presented in Figs. 7 and 8, respectively.

Based on the obtained results (Figs. 7 and 8), it can be concluded that the mass of adsorbed antibiotics decreases with the decrease in the surface tension of the solution. This is because the ethanol molecules, being a surface-active substance, accumulate at the surface of the solid, that is, in this case on the surface of the calcium carbonate particles. Accumulating ethanol molecules occupy active sites on the surface of the adsorbent particles, reducing the intensity of the adsorption process of the remaining components. In addition, the increasing concentration of the surface-active substance at the surface of the solid makes it difficult to transport the remaining components of the solution to the surface [63].

3.5. Filtration–adsorption setup (flow system)

In the next stage of research, tests were carried out in a flow system using own made membrane modules and manufactured membranes modified with calcium carbonate. The tests were carried out for 4 laboratory wastewater (Table 2).

In the first part of the study, the mass of antibiotics removed from a solution containing only tetracycline or sulfadiazine (Waste I) was determined. The obtained values are shown in Fig. 9. In Fig. 9, for comparison purposes, the results obtained for the same solution in the stationary system are also presented.

Based on the presented data (Fig. 9), it should be stated that conducting the process in the flow system increases the mass of tetracycline and sulfadiazine removed by about ten times, which results from several effects. Firstly, conducting the process in the flow system increases the intensity of the mass exchange process near the membrane surface. Secondly, the pressure of the feed allows the solution to penetrate the membrane pores more effectively, which makes the membrane surface on which the adsorption process can take place more effectively. Third, studies conducted on unmodified membranes show that tetracycline and sulfadiazine are partially retained by the membrane as a result

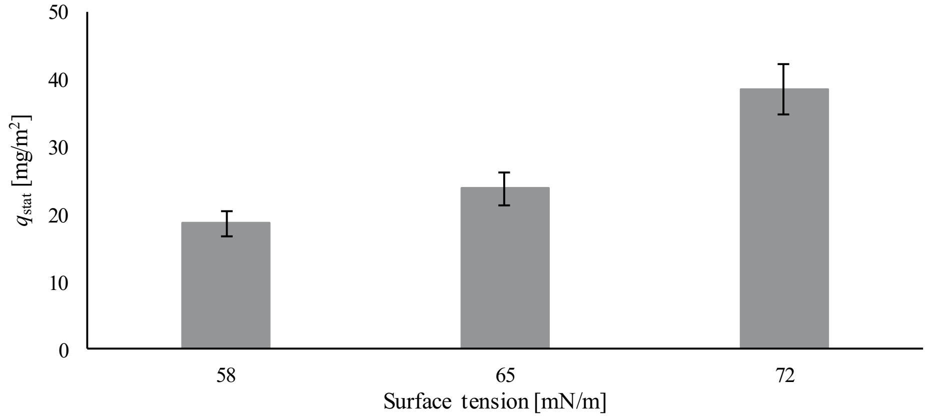

Fig. 7. Mass of adsorbed tetracycline for different values of wastewater surface tension.

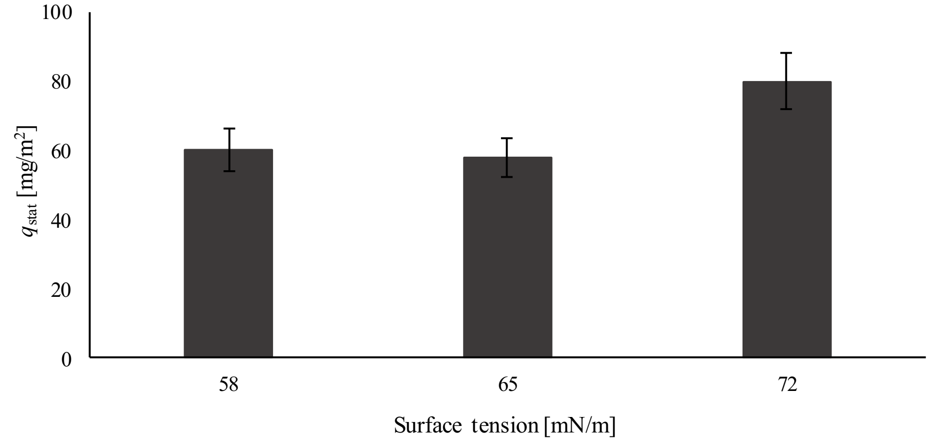

Fig. 8. Mass of adsorbed sulfadiazine for different values of wastewater surface tension

of the filtration process. The mass of tetracycline and sulfadiazine removed in the flow system on unmodified membranes is 215.09 and 413.54 mg/m^2, respectively.

In the next part of the research, the mass of tetracycline and sulfadiazine removed from various solutions of laboratory sewage was determined. The obtained results are shown in Figs. 10 and 11.

Based on the presented results (Figs. 10 and 11), it can be concluded that the mass of tetracycline and sulfadiazine removed from wastewater II (pH = 7, conductivity = 180 µS/cm as NaCl, surface tension 65 mN/m) is lower than for wastewater I. In the case of tetracycline, this is due to the fact that the presence of NaCl reduces the adsorption intensity of this compound. In turn, in the case of sulfadiazine, the limiting factor is pH. As stated on the basis of the results in the stationary system, the adsorption of this component is most intense at pH = 6.5. Above this pH value, the adsorption intensity of sulfadiazine decreases. In turn, for wastewater III (pH = 8, conductivity = 180 µS/cm as NaCl, surface tension 65 mN/m) it can be stated that the mass of tetracycline removed slightly increased, while the mass of sulfadiazine removed decreased. In the case of tetracycline, this is due to the fact that for pH = 8 the adsorption intensity of this substance is greater than for solutions with pH = 6.5 and 7. Additionally, the adsorption intensity increased so much as a result of the higher pH value of the solution that the negative effect of the presence of ions is partially leveled. On the other hand, in the case of sulfadiazine, a significant decrease in the mass removed from wastewater III is a consequence of further increasing the pH value of the solution. For wastewater IV (pH = 5.5, conductivity = 220 µS/cm as NaCl and $FeCl_2$, surface tension 65 mN/m) it can be stated that the mass of tetracycline removed significantly increased, while the mass of sulfadiazine removed decreased. In the case of tetracycline, this is due to the formation of Fe^{2+} complexes with antibiotic particles, the intensity of which significantly increases in the flow system. In addition, the formed complexes are retained by the membrane as a result of filtration. In turn, in the case of sulfadiazine, a significant decrease results from the aforementioned squeeze-out effect resulting from the presence of iron ions. It should also be noted that the

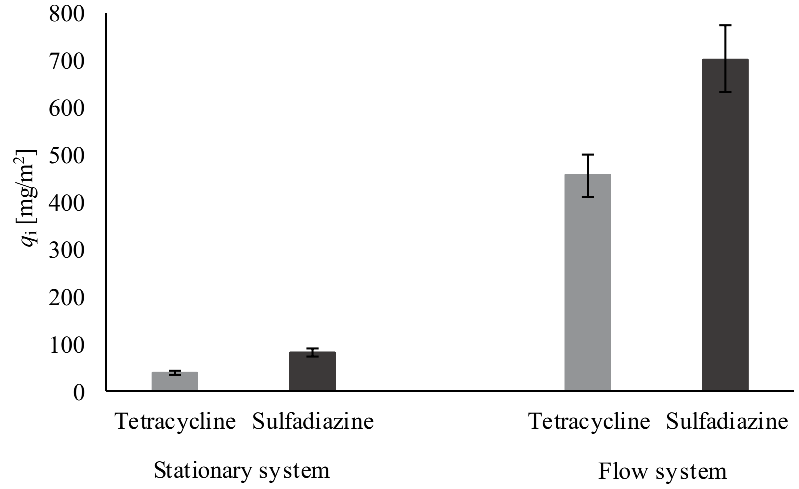

Fig. 9. Mass of removed antibiotic in the stationary system and in the flow system.

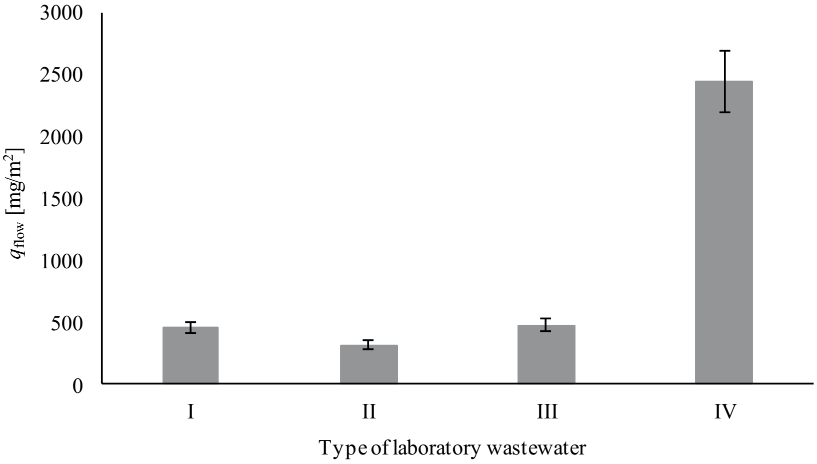

Fig. 10. Mass of adsorbed tetracycline in flow system.

obtained q_{flow} values are lowered by the lower surface tension of wastewater II, III and IV. It should therefore be concluded that the obtained values of the removed mass of antibiotics are the resultant of several effects related to the presence of compounds affecting pH value, conductivity and surface tension. However, in each case, it is

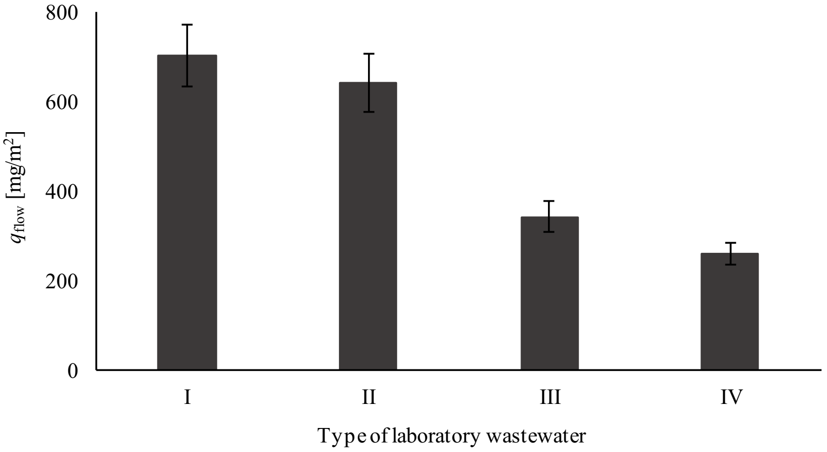

Fig. 11. Mass of adsorbed sulfadiazine in flow system.

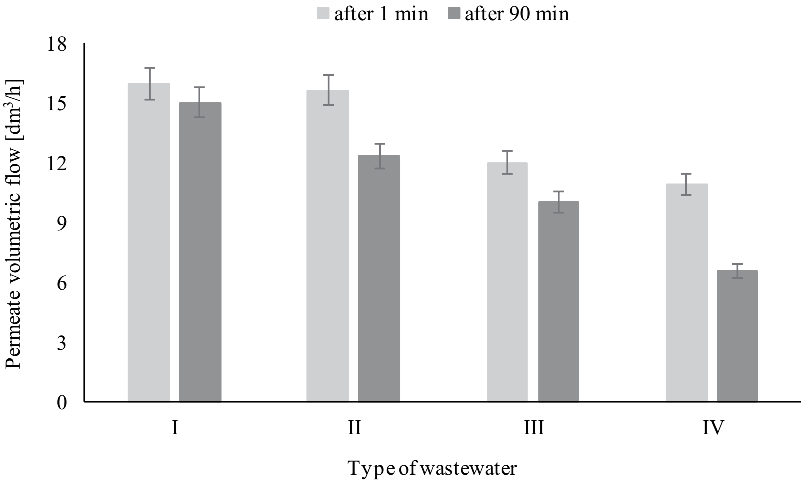

Fig. 12. Permeate volumetric flow of wastewater with tetracycline.

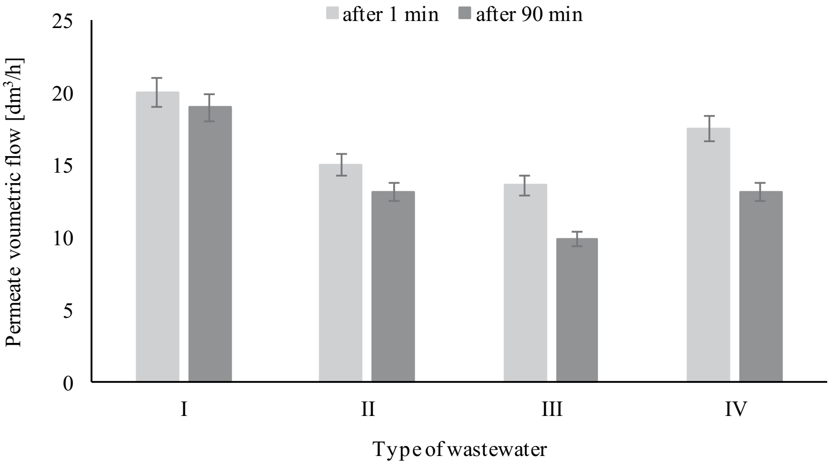

Fig. 13. Permeate volumetric flow wastewater with sulfadiazine.

possible to determine the limiting factor affecting the mass of antibiotic removed.

On the basis of the tests carried out in the flow system, the influence of the wastewater composition on the obtained permeate volumetric flow was also determined. The obtained results are shown in Figs. 12 and 13.

On the basis of the obtained results (Figs. 12 and 13) it can be concluded that for wastewater II, III and IV, lower permeate volumetric flows were obtained. This is due to the presence of additional components that affect the physico-chemical properties of the solutions and may also be related to the formation of various types of complexes that are formed during the process. The potential formation of complexes can be confirmed by the results of the permeate volumetric flow drop after 90 min of the process. These percentage changes are greater for wastewater II, III and IV than for wastewater I. It should also be noted that the largest decrease in the volumetric flow of permeate and the largest percentage decrease of this flow was obtained for wastewater IV containing tetracycline. This effect may be confirmed by the formation of Fe^{2+} complexes with tetracycline. These complexes accumulate on the surface of the membrane, which increases the flow resistance and consequently decreases the permeate volumetric flow.

4. Summary

On the basis of the conducted tests, it can be concluded that the composition of wastewater has a significant impact on the mass of the antibiotic removed in the filtration and adsorption process. In addition, the composition of the wastewater also affects the amount of permeate obtained.

The mass of substance removed depends on several effects related to the individual components of the wastewater. However, in many cases, it is possible to determine the factor limiting the efficiency of the removal process for a given wastewater composition. Most often, this parameter is pH value, which in the case of antibiotic removal using calcium carbonate should be about 6.5 for sulfadiazine and 10 for tetracycline. In turn, the effect of conductivity on the removal of antibiotics depends on the concentration and type of salt. The same concentration of the same salt may have the opposite effect on the intensity of removal of a given substance. It should therefore be noted that the efficiency of the removal process of a given antibiotic strictly depends on its chemical structure. In order to intensify the process, the influence of the physico-chemical parameters of the solution should be analyzed for a specific group of compounds.

Acknowledgments

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