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SEPARATION OF WATER SYSTEMS CONTAINING SURFACTANTS

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ABSTRACT

The possibility of highly efficient treatment of wastewater containing surfactants (surfactants) to a critical concentration of micelle formation by ultrafiltration (UV) by preliminary binding of surfactants into poly-complexes is shown. The effects of the parameters of the separation process and the conditions for the formation of a poly-complex on the UV efficiency indicators have been studied.

Keywords: Ultrafiltration, Surfactants, Micelle Formation, Poly-Complex, Polyelectrolyte, Wastewater Treatment.
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INTRODUCTION

Baromembrane processes – reverse osmosis and ultrafiltration – as promising methods of wastewater treatment have also found application in the processes of neutralization of water systems containing surfactants (surfactants). The use of ultrafiltration or reverse osmosis for these purposes depends on the composition of the separated solution, and, in particular, on the initial concentration of surfactants. At concentrations exceeding the critical concentration of myelination (CMC), where surfactant molecules are associated and exist in a micellar form, ultrafiltration is used. When separating solutions containing surfactants up to CMC, where the surfactant is dissolved molecular dispersed and is in an electrolytically dissociated state, the use of ultrafiltration does not provide deep extraction of surfactants and therefore reverse osmosis is used.[1,2] Objective to study -the release of surfactants from water systems containing up to a critical concentration of mycelium formation by their rapid enlargement in size and subsequent ultrafiltration; to study the effect of the composition of the separated mixture and the parameters of ultrafiltration, the degree of surfactant extraction and the productivity of the process.

EXPERIMENTAL

However, neither ultrafiltration nor reverse osmosis provide separation of dilute surfactant-containing water systems at high productivity and with deep extraction of surfactants. This problem can be solved by preliminary enlargement of surfactant molecules electrolytically dissociated in dilute solutions and their subsequent ultrafiltration.[3,4] It is known[6] that counterions containing long aliphatic substituents, for example, surfactant ions, exhibit, depending on the charge sign of the hydrophilic part, a strong affinity for polycations or polyanions.[5] In addition, when polyelectrolyte is added to an aqueous system containing surfactants, its active centers – functional groups – serve as nuclei of micelle formation, and the CM for this type of micelle formation is lower than the CM for ordinary free surfactant molecules; in the presence of polyelectrolyte, the value of CMdecreases, and the formed micelles stabilize the polymer.[7] Consequently, the addition of a complexing polyelectrolyte provides enlargement in the size of diphilic surfactant molecules both due to micelle formation and due to the formation of a surfactant-polymer poly-complex. The high stability of the poly-complex formed by the electrostatic and hydrophobic interaction of surfactant-polyelectrolyte, as in the case of ultrafiltration of a highly stable polyelectrolyte-metal complex, causes high extraction efficiency.

The flow-type installation scheme with the circulation of the initial solution is shown in Fig.-1, The initial separable solution from tank 1 is fed by a plunger pump through a hydraulic accumulator 3 into separation cell 5, and the concentrate is returned to tank 1 via the circulation line 7, the operating pressure

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in the separation cell is controlled by a pressure gauge 4 and maintained by a constant fine adjustment valve 6. Laboratory studies of the main regularities of this process were carried out on conditionally pure wastewater from the production of synthetic detergents (SD) of the Shymkent software "Phosphorus" containing sodium alkylbenzenesulfonates ($C_{14}H_{29}C_6H_4SO_3Na$). Cationic polyelectrolytes – polydimethyldialliammonium chloride (PDDAC) and polyethylenimine (PEI) - were used as complexing agents.

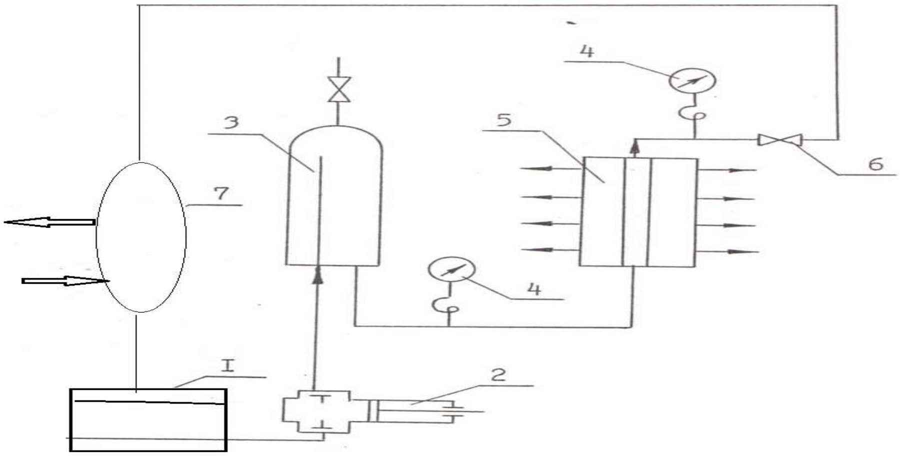

Fig.-1: The Scheme of the Installation with the Circulation of the Initial Solution .1 - Container for the Initial Solution; 2 - Plunger Pump; 3- Accumulator;4- Pressure Gauge; 5- Filter Element;6- Control Valve; 7- Heat Exchanger

RESULTS AND DISCUSSION

The process of enlarging surfactants by binding them into a poly-complex and removing it from water systems by subsequent ultrafiltration, as a combined method consisting of two stages, depends on many factors that can influence one or another stage. The process of complexation-ultrafiltration (CUF) is a combined, consisting of two stages, the method depends on many factors that can influence one or another stage. The value of the ratio of the content of the component to be removed and the complexing agent in the solution has a determining effect on both the complexing reaction and the ultrafiltration process. The effect of this ratio on the degree of surfactant extraction during ultrafiltration of the surfactant-polyelectrolyte poly-complex significantly differs from the known patterns of ultrafiltration of a binary polymer-metal complex.[8,9,10] This is due to the peculiarity of the binding of diphilic surfactant molecules with polyelectrolyte and the formation of the surfactant-polyelectrolyte poly-complex. By comparing the isotherms of electrostatic and total binding of sodium dodecyl sulfate with PEI, it was found that polybasic macromolecules with alkyl sulfates bind not only due to Coulomb interaction but also through hydrophobic interactions between nonpolar parts of surfactants and polyelectrolytes, which makes a significant contribution to the stabilization of the poly-complex.[11] The predominance of a certain type of interaction between surfactants and polyelectrolytes is largely determined by the ratio of the content of surfactants and polymer complexing agent in the solution, n =[surfactant]/[polyelectrolyte]. At low values of n, i.e., with an excess, the surfactant complexing agent binds to polyelectrolyte mainly electrostatically. Electrostatic binding of alkyl sulfates to poly-basins, for example, PEI macromolecules, leads to hydrophobization of polyelectrolyte chains and binding of the olefin part of surfactants. The electrostatic and hydrophobic interaction of hydrophilic and hydrophobic surfactant parts in the polybasic tangle significantly stabilizes the poly-complex. In addition, as mentioned above, an increase in the proportion of polyelectrolytes in the solution leads to an increase in the number of surfactant molecules associated with micelles.[11] These reasons explain (Fig.-2) the high degree of surfactant extraction during the ultrafiltration of the poly-complex at low values of n, i.e. with an excess of the ligand fraction in the solution. An increase in n, i.e. an increase in the relative concentration of alkyl sulfates in the solution leads to an increase in the electrostatic binding of surfactants with a polybase, which reaches a limit value at n = 0.8 and does not change with a further increase in n. At the same time, the hydrophobicity of the polybase increases, i.e. Surfactant mainly binds to polyelectrolyte due to hydrophobic interactions, the contribution of which in the formation of an associate increases with an increase in the concentration of surfactants in the solution.

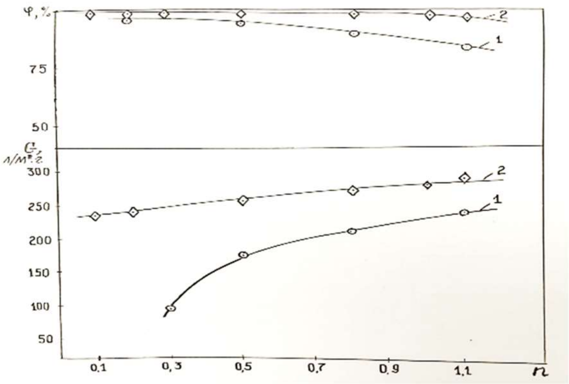

Fig.-2: The Dependence of the Main Characteristics of the Wastewater Separation Process of the Production of CM Shymkent Software "Phosphorus" on the Molar Ratio (n) of Surfactants: PEI (1, o) and Surfactants: PDDAC (2,). UAM – 300 Membrane. P=4.5 atm. pH=9.6. S ex. Surfactant = 200 mg/l

Such a feature of the formation of a surfactant-polyelectrolyte poly-complex, in contrast to the known patterns of ultrafiltration of a binary polymermetallic complex, causes high extraction efficiency even with a ligand fraction below the stoichiometric ratio. This is confirmed by the obtained data presented in Fig.-2. With an excess of the ligand, due to an increase in the concentration of solutes in the solution, the phenomenon of concentration polarization increases, which negatively affects the main characteristics of separation[12-13]. The level of concentration polarization is determined by the hydrodynamic factors of the separation process, in particular, the flow rate of the separated solution relative to the membrane. In contrast to the known patterns obtained during ultrafiltration of both polymermetallic complexes[8,9] and individual surfactants[12], during ultrafiltration of the surfactant-polyelectrolyte poly-complex, there is a noticeable decrease in the purification efficiency with an increase in the flow rate (Fig.-3). This, in our opinion, is due to the fact that the surfactant in solution with a small excess of PDDAC is in two forms: micellar and in the form of a poly-complex, while the size of the latter is significantly larger. An increase in the flow rate leads to a decrease in the thickness of the gel layer on the membrane, which itself has an additional filtering effect mainly for micellar surfactants. This assumption is supported by a sharper decrease in the separation efficiency with an increase in the proportion of micellar surfactant in the solution (curve 2, Fig.-3). The different nature of the influence of the flow rate on the degree of extraction and the productivity of the process increases the requirements for finding optimal hydrodynamic conditions when designing membrane devices and installations.

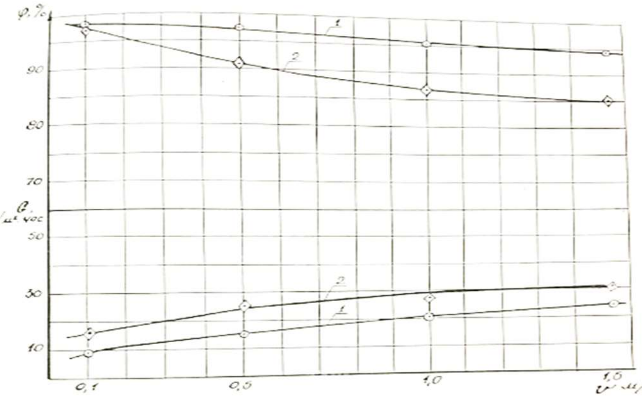

Fig.-3: Dependence of the Main Characteristics of the Wastewater Treatment Process of CM production on the Flow Rate Of The Separated Raster at Values n = Surfactant:P CB = 0.5 (1, o) and n = Surfactant: PDDAC = 0.8 (2,). UAM – 200 Membrane. P= 1.5 atm. Sish. Surfactant = 200 mg/l

The interaction between polyelectrolyte and surfactant, which has reached its maximum at a certain value of n, can increase at certain pH values. This indicates that the nature of the interaction of polyelectrolyte with surfactants and the formation of a poly-complex stabilized by electrostatic and hydrophobic interactions is determined both by the diphilicity of the interacting components and the nature of the functional groups and their ionization in solution, which largely depend on the pH value. An increase in the degree of ionization of macromolecules of the polymer complexing agent leads to the deployment of a polyelectrolyte chain.

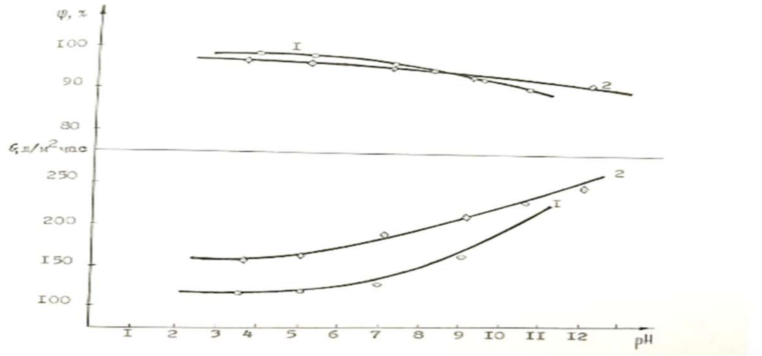

Fig.-4: Dependence of the Main Characteristics of the Separation Process of Surfactant-PE (1, on UZAM-300) and Surfactant-PCB (2, on UZAM-400) on the pH of the Mixture. P= 1.5 atm. Sish. Surfactant = 200 mg /l. n = Surfactant/ Polyelectrolyte = 0.5

At the same time, the availability of functional groups of the complexing agent for surfactant ions increases, as a result of which the electrostatic binding of the detergent with polyelectrolyte increases. These factors explain the increase in the degree of surfactant extraction at the pH values of poly basin ionization (Fig.-4.). In addition, a decrease in pH increases the sorption of surfactants and polyelectrolytes on the surface and in the pores of membranes, reducing the effective pore size, which leads to an increase in the retention capacity of the membrane.[12] The decrease in the degree of surfactant extraction in alkaline media is explained by the weakening of the electrostatic interaction due to a decrease in the degree of ionization of the functional groups of polyelectrolyte[14]. At the same time, in contrast to the process of extraction of metal ions by the KOUF method, the degree of surfactant extraction is high in a wide pH range, which is explained by the above-mentioned features of the enlargement of alkyl sulfates in size. The peculiarity of the formation of the surfactant-polyelectrolyte poly complex is also reflected in the regularities of the influence of working pressure on the main characteristics of the ultrafiltration process. It is known that during ultrafiltration of a binary polymermetallic complex, due to the deformability of the macromolecules of the complexing polyelectrolyte, the holding capacity of the membrane decreases with increasing operating pressure.[14] As mentioned above, the surfactant-polybase poly complex has a spherical shape and is highly stable due to the electrostatic and hydrophobic bonds of polyelectrolyte with detergent[17]. The hydrophobic interaction of polyelectrolytes with surfactants leads to crosslinking of individual segments of macromolecules, resulting in reduced flexibility of the polymer. Such compaction of the resulting poly complex is resistant to the deforming action of the permeate flow, which increases with increasing working pressure. Based on the above, it can be assumed that with an increase in the working pressure during the ultrafiltration of the poly complex surfactant–polymer (polyelectrolyte) the degree of detergent extraction does not decrease as in the case of ultrafiltration of a binary polymer-metal complex. In addition, an increase in the operating pressure entails an increase in the permeate flow and an increase in the accumulation of surfactant-polymer associates on the membrane surface.[15] This leads to the formation of a gel layer on the surface of the membrane, which is an additional filtering partition, acting as the active layer of the membrane increasing its retention capacity. With an increase in working pressure, compression and self-sealing of the gel layer is possible, as a result of which its retention capacity improves and, in general, the extraction efficiency of the process increases. As mentioned above, the concentration of surfactants in the separated solution significantly affects its structure and properties which determine the choice of a particular membrane separation method. The addition of complex polyelectrolytes to a solution containing surfactants up to CM changes its composition due to the enlargement in the size of surfactant molecules by both complexation and micelle formation. When separating such systems, the patterns of ultrafiltration are similar to the patterns of ultrafiltration of solutions containing surfactants above CM, which is confirmed by the data obtained (Fig.-5.). The increase in the retention capacity of the membrane with an increase in the initial concentration of surfactants in solution is also explained by an increase in the stabilization of the poly complex due to hydrophobic interactions, which increase with an increase in the concentration of both surfactants and macromolecules. An important problem in the process of ultrafiltration complexation is the solution to the issue of concentrate processing. The processing of a concentrate containing a polymer and a recoverable component, as noted earlier, is aimed at the regeneration of the complexing agent and the disposal of the recoverable component that makes up the value.

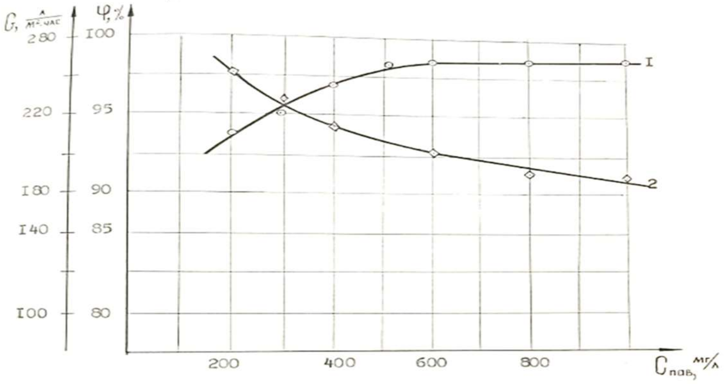

Fig.-5: Dependence of Extraction Efficiency (1) and Productivity (2) of the Ultrafiltration Process of the Surfactant – PDDAC System on the Initial Surfactant Concentration. UAM – 450 Membrane. P = 4.5atm, n = 0.5

In contrast to the known methods of processing a concentrate containing polyelectrolyte and a low molecular weight component – a metal ion, the separation into concentrate components of the poly complex ultrafiltration process is difficult due to the high content of surfactants in the solution. Therefore, from economic considerations, the concentrate is supposed to be used for various purposes. For example, a concentrate containing a poly complex can be used as part of a mixture for dust suppression in various sectors of the national economy. For example, a /15/ composition for dust control is known, including polydimethyldiallylammonium chloride (PDDAC) and salts of alkyl aromatic sulfonic acids of the formula: $C_{14}H_{29}C6H_4SO_3Na$; with the following ratio of components by weight %: sulfite-alcohol bard - 0.5-5.0; a mixture of PDDAC and alkyl sulfates - 0.5-1.5.

CONCLUSION

The use of the concentrate of the ultrafiltration process of the surfactant- PDDAC poly complex for these purposes will exclude the use of expensive alkyl sulfates and fresh water. At the same time, along with achieving environmental efficiency, economic efficiency will also be achieved. The concentrate containing the surfactant polyelectrolyte poly complex can be used as a complexing agent in the process of purification of metal-containing effluents by the method of complexation - ultrafiltration. In solution, the poly complex binds the metal ion and is removed to form a triple polymermetallic complex surfactant-polyelectrolyte-metal ion. In this case, the stability constant of the complex increases in comparison with the stability of the binary polymer-metal complex. As a result, the degree of extraction of metal ions increases. The solution concentrated on surfactants and PDDACs can also be used in the production of building materials, in particular, in the production of concrete and reinforced concrete, as stabilizing active additives, which significantly increases the strength of concrete. Based on the conducted research, it can be concluded that the proposed method opens up great prospects in the field of purification of surfactant-containing solutions.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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