Marian GRĄDKOWSKI, Andrzej WINIARSKI, Karolina ŚWIGOŃ, Monika MAKOWSKA
Institute for Sustainable Technologies – National Research Institute, Radom, Poland

LABORATORY DEVICE FOR INVESTIGATION OF MICROFILTRATION PROCESSES OF AQUEOUS TECHNOLOGICAL FLUIDS

Key words

Separation, microfiltration, membrane techniques, regeneration, aqueous technological fluids.

Summary

The article presents the laboratory device for the investigation of microfiltration processes of aqueous technological fluids. The developed device was used to regenerate contaminated technological fluids applied in cleaning processes of preparing metal elements for the deposition of functional coatings. The results of conducted tests indicated that, at the time of the above mentioned regeneration procedure, a significant amount of contaminants was removed. The amount of contaminants in the fluid regenerated with the use of the developed device did not exceed the level of the initial (freshly prepared) technological fluid. The regenerated fluid only required the alkaline content to be supplemented in order for its initial physico-chemical properties to be restored. The method for the purification of technological fluids that was realised with the application of the developed device can be used in periodical oil and other contaminant removal from aqueous wash baths that are used in various technological processes. This will extend their operational time and will

significantly reduce the consumption of water and chemicals used to prepare the technological fluids.

Introduction

The environment pollution has reached the level that requires radical precautions to be taken. The elimination of existing waste creates new problems related to the necessity to utilise highly concentrated contaminants and pollutants. In such a situation, preventing the creation of new waste and the minimisation of its amount seems to be the most rational approach. This is particularly so in the case of the "environmental technologies" in which the production process is organised in a way to prevent any waste to leave the industrial plant. This complies with the worldwide idea of Cleaner Production that consists in the reduction of waste in the very area of their creation.

There are many processes that are already practically deployed in industry and which use various technological fluids. It is, for instance, the chemical treatment of the surface of metals, preceding the application of protective and functional coatings. At the time of their usage, these fluids are subject to contamination (i.e. with oil, fats, corrosion inhibitors, and mechanical contaminants) or ageing, which causes their crucial properties to weaken. However, this process is not always irreversible. In many cases, the contaminated fluid can undergo the regeneration process or some portion of its components can be recovered.

In recent years, a quick development of water-based technological fluids has been observed. The need of the Polish industry for this kind of specimen is estimated to reach several dozen thousand tons per annum. Such fluids are particularly used in the SME sector, mainly by the powder paint shops, galvanising plants and plants in which PVD/CVD technologies are used. The replacement of solvents with organic water baths does not fully eliminate ecological hazards. The used baths, according to the binding governmental act on waste (dated 27th April 2001, 2001.62.628 with further amendments), are included in hazardous waste and require precautionary actions to be taken.

The processes of separation realised with the use of various membrane techniques can be helpful in removing oil and other pollutants from aqueous technological fluids. In the processes of membrane filtration, the separation process is conducted physically (essentially with no chemical or biological changes), which allows the separated components to be recovered and reused [1, 2]. It can be applied to purify the fluids and to separate and condense substances suspended or diffused in the liquid. The systematic regeneration of the degreasing bath, for instance, allows, when microfiltration is applied, the reduction of liquid waste created in the process of degreasing the surface of metal components by nearly 40 times [3]. This results in a radical reduction in the use of water and chemicals, which circulate in the technological cycle for longer. However, this requires a consumption of certain amount of energy, which involves the increase of emissions coming from the energy generation process.

The effectiveness of the separation processes depends on the kind of the membrane used. The difference of chemical potentials on both sides of the membrane is the driving force of the transport of the substances through it. This difference can be caused by the pressure, concentration, temperature, or electrical potential differences [4]. Usually, many of those phenomena happen simultaneously, and the separation is possible because of the difference in the speed at which various substances are transported. The resultant effect of the phenomena is the TransMembrane Pressure (TMP), which significantly determines the effectiveness of membrane processes.

The filtration in the membrane system can take the form of dead end or the cross-flow [3, 5]. In the cross-flow processes, contrary to the dead end processes, the separated mixture moves parallel to the surface of the membrane (Fig. 1). Despite that, in order to avoid their fouling caused by the accumulation of the organic and non-organic substances, suspended particles and bacteria, the membranes need to be periodically cleaned. This is realised through back flush or chemical flush [6, 7].

At the time of the separation of elements on the membrane, the flux of the fluid undergoing the regeneration procedure (feed) is divided into the concentrated flux of contaminants (retentate) and the flux of the filtrate (permeate). Both the permeate and the retentate can be the final product of that process [1]. The regenerated fluid can be re-circulated through the membrane module until the components of the retentate reach suitable condensation.

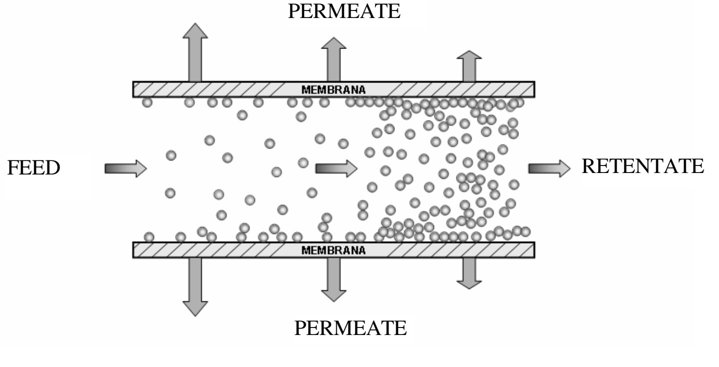


Fig. 1. Diagram of the fluid cross-flow in membrane separation processes

The separation can progress according to the sieve mechanism (microfiltration, ultrafiltration), that consists in the permeation of the particles smaller than the membrane pores through the membrane or it can run according to the diffusion mechanism (nanofiltration, reverse osmosis, pervaporation) [8]. The separation mechanism depends on the size of separated particles and the membrane applied; however, the boundary between individual techniques is blurred.

Microfiltration is a low-pressure process, in which membranes with a diameter between 0.01 to 10 μm are used. This enables the separation of suspensions or colloids from aqueous solutions. The membranes for microfiltration are made of organic polymers and non-organic materials such as ceramics, metal, or glass with the use of various micro-pore structure production techniques. In the microfiltration process, TMP is relatively low and it is 0.1–0.5 MPa. Darcy's law describes the dependency between the flux of permeate J_v and TMP in the microfiltration process [1]:

$$J_v = L \cdot \Delta P$$

where:

- L – flux of permeate calculated to the pressure unit (the permeability of the membrane),
- ΔP – transmembrane pressure.

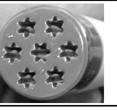
The aim of the work was to develop the laboratory device for the microfiltration of contaminated technological fluids used in the process of preparing metal surfaces for the deposition of functional coatings and to verify its functionality.

1. Experimental conditions

The research focused on the solution of the commercial concentrate (5% v/v) used for the preparation of the technological fluid in municipal water (initial fluid). This concentrate is applied at the Surface Engineering Department at the Institute for Sustainable Technologies – National Research Institute (ITeE – PIB) in Radom in the cleaning process of the metal elements before the application of functional coatings. The commercial concentrate is the aqueous, alkaline mixture of anionic and amphoteric surfactants, sodium trioxosilicate and complexing agents, whose quantitative composition has not been revealed by the producer. Both the initial fluid and the fluid contaminated, at the time of operation, with grease washed off the surface of metal elements and mineral particles, were subject to tests.

The analysis of the problem indicated that, in the case of the tested fluid, the most successful is its regeneration with the membrane microfiltration of the cross-flow type, in which chemically resistant ceramic tube membranes made of zirconium, aluminium and/or titanium oxides are used (Tab. 1). These membranes have a composite structure of multiple layers (active thin-film layer, deciding on the separation abilities of the membrane, on a porous support layer). They are characterised by high mechanical and chemical resistance (they can be cleaned with the use of strong acids or bases), which allows for their chemical regeneration and long-term operation.

Table 1. Characteristics of a ceramic tube membrane used for the construction of the microfiltration module

Feature	Value
Structure	
Producer	Fairey Industrial Ceramics Inc.
Type	Seven Stars
Material	Al_2O_3, TiO_2, ZrO_2
Number of canals	7
Length, [mm]	600
Diameter, [mm]	20
Hydraulic section, [mm^2]	43
Filtration area, [m^2]	0.06
Nominal diameter of pores, [µm]	0.2
Maximum working temperature, [°C]	140
Maximum operational pressure, [MPa]	0.8
Bursting pressure, [MPa]	1.4
Work environment reaction, [pH]	0.5÷14

The attempt to regenerate the contaminated technological fluid required the construction of the filtration module, including the membrane with characteristics presented in Tab. 1. This module is an operational element of the laboratory device *MMD-8*, developed at ITeE – PIB in Radom.

2. Device for the regeneration of aqueous technological fluids

Investigation of the effectiveness of the aqueous technological fluid regeneration was conducted in the laboratory with the use of the *MMD-8* device (Fig. 2) built particularly for those tests. The device is composed of a membrane, suction-feeding, regeneration (back-flush), and control modules. Moreover, it is equipped with three containers for regenerated fluids, permeate, and clean fluid for cleaning membranes with the application of the back-flush procedure.

The circulation of the technological fluid is presented in Fig. 2b. The regenerated fluid is drawn from the container with the use of the sucking tube and through the open valve (14) and is fed to the feeding pump (5). Before the device is started, because of the capacity of the membrane module, the circulating pump (2) and the membrane module (3) are flooded with regenerated fluid (or other similar fluid) fed through the distribution valve (21). When the device is started, the pumps (2) and (5) are switched on as well. Simultaneously, control and control-measurement systems are switched on. The circulating pump (2) directs the cleaned fluid to the membrane module (3). In order to maintain the assumed fluid flow velocity along the surface of the membrane, retentate leaving the membrane module (3) is recirculated through the outlet tube (6) to the sucking side of the pump, which creates the circulation cycle. The outlet tube is equipped with flow regulating valve (7) and electronic flowmeter (8), which allow one to set suitable fluid flow velocity and pressure before the inlet to the membrane module (3). The outlet tube (6) is split and the branch is equipped with a flow regulating valve (7), allowing the retentate to be drained out of the circulation cycle. This can be performed permanently or periodically. The fluid flowing through the membrane module partly permeates through the membrane and fills the casing of the module (3) from where it then flows through the solenoid valve (9) to the upper outflow and through the electronic flowmeter (10) to the branch with the solenoid valve (11). Depending on the position of the solenoid valve, the permeate fills the washing fluid container (1). Once the container is filled up to the assumed level, the valve (11) is closed and the flux of fluid is directed to the regenerated fluid (permeate) container.

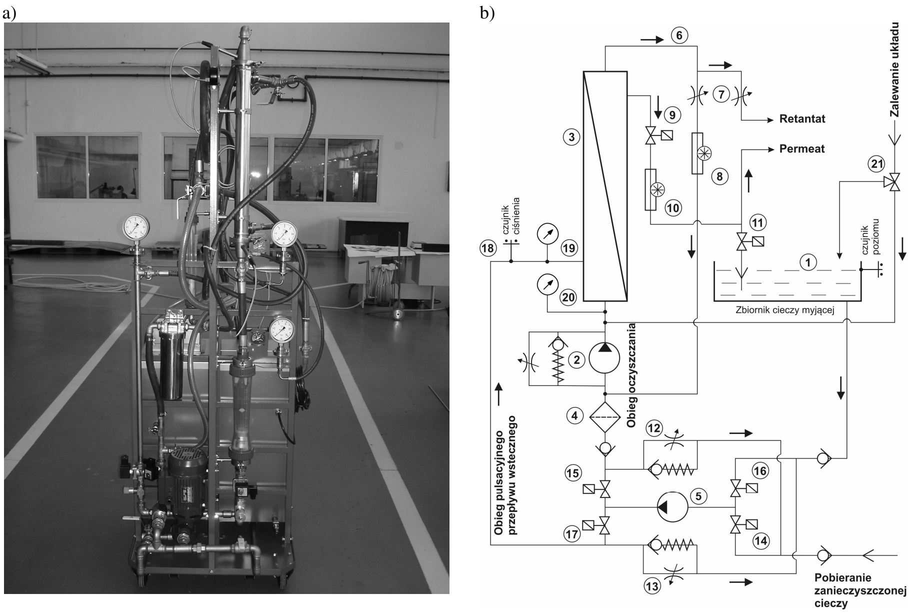


Fig. 2. *MMD-8* device for the regeneration of aqueous technological fluids: a) general view, b) hydraulic diagram

The loss of fluid in the circulation cycle in the membrane module, that is caused by the outflow of permeate, is filled up with the contaminated fluid through the constantly working feeding pump (5). This pump works both at the time of cleaning and at the regeneration of the membrane. The parameters of the feeding pump (5) are maintained with the suitably set flap check valves (12) and (13) mounted in the pressure branch of the pump.

Directly after the *MMD-8* device is switched on, the cleaning process of the technological fluid starts and, due to the opening of the solenoid valves (14) and (15), the pump (5) feeds the fluid into circulation. As a result, the regenerated fluid is fed through the initial filter (4) to the intake side of the circulating pump (2), which then feeds the fluid onto the membrane module with particular efficiency. The output of the feeding pump is chosen in a way to allow the cleaned fluid to flow through the membrane canal with the velocity not lower than 3.5 m/s. The flow speed is controlled with the use of the electronic flowmeter (8) and additionally regulated with the control valves (7) installed in the outflow tube (6). The cleaning of the fluid is the result of its permeation through the membrane and the condensation of contaminants in the fluid drained through the outflow tube (6) in the form of the retentate.

The efficiency of the cleaning process is controlled with the use of the flowmeter (10). When it drops down below the minimum assumed value, the back-flush procedure starts. The solenoid valves (14), (15), and (9) are closed at the time of this procedure, and simultaneously the solenoid valves (16) and (17) open. At that time the feeding pump (5) pushes the fluid from the washing fluid container (1) through the pressure tube, where the regulated pressure pick-up (18) and manometer (19) are mounted, to the lower stub pipe of the membrane module. When the pressure in the membrane module (3) reaches its maximum value assumed (twice as high as the working pressure in the cleaning regime), the valves (16) and (17) close and valves (14), (15), and (9) open. The system returns to the cleaning process and this cycle automatically repeats until the device is switched off. In order to increase the efficiency of the control over the regeneration process, the manometer (20) is placed in the feeding system of the membrane module. The device is also equipped with turbidimetric sensor installed in regenerated technological fluid (after cleaning) container.

3. Research results

The experiments with the use of the laboratory device for investigation of separation processes with the application of membrane techniques were carried out on the basis of previous technical assumptions. The membrane module has been preceded by filter medium with the filtration accuracy of 5 μm. The exploited fluid used for cleaning the surface of metal elements has been regenerated in two independent cleaning cycles (the average of both cycles has been given as the result of the measurement). The experiment was conducted in a way in which the volume of the retentate made the 10% of the initial volume (60 dm^3) of the fluid subject to cleaning. The initial fluid, the regenerated fluid (feed) together with the permeate and the retentate were subject to physico-chemical analysis. At the time of cleaning, basic parameters, whose values determine the technological usefulness of this kind of fluids (turbidity, electrical conductivity, pH) were determined. The value of the turbidity shows the scale of contamination of fluids with solids and oils dispersed at the colloidal level. The electrical conductivity and pH indirectly indicate of the contents of soluble chemical substances used to prepare the fluid. After cleaning, the contents of oil (hydrocarbons), which extracted from the permeate and the retentate by petroleum benzene, was also determined. The results were then compared to the contents of oil in the initial fluid and the contaminated fluid (feed). The determined physico-chemical properties of individual fluxes of regenerated technological fluid are presented in Tab. 2.

Table 2. Physico-chemical properties of technological fluid regenerated with the use of *MMD-8* laboratory device

Tested fluid	Turbidity [NTU]	Electrical conductivity [S/m]	PH	Oil contents [ppm w/w]
Initial fluid	12±3	0.55±0.03	9.2±0.1	24±5
Feed	43±4	0.54±0.03	9.4±0.1	3220±150
Permeate	3±1	0.47±0.03	8.8±0.1	55±5
Retentate	390±27	0.46±0.03	8.7±0.1	$5.4 \cdot 10^4 \pm 3 \cdot 10^3$

As the data from Tab. 2 show, the tested technological fluid is contaminated at the time of its usage. Both the solid particles and oils washed off the surface of cleaned metal elements can be the contaminants. This is indicated by the level of turbidity and the oil contents in contaminated fluid, which, compared to the initial fluid, are much higher. The data concerning the electrical conductivity and pH indicate that the contents of dissolved chemical substances in the feed is similar to that in the initial fluid.

The treatment of the exploited fluid with the use of the developed laboratory membrane device caused a radical decrease in its contamination level. This considered the turbidity (from 43 NTU to 3 NTU) and the oil contents (from over 3000 ppm to slightly above 50 ppm) as well. At the time of the tests, slight alkalisation of the fluid was also noticed; however, at the time of filtration, its pH was significantly lowered (by ca. 0.5) both in the case of the permeate and the retentate. This can be the result of the removal of some alkaline components from the fluid. Further, more detailed research is needed to explain the differences in the physico-chemical properties of permeate an initial fluid.

The electrical conductivity of initial and contaminated fluids was similar, and it was slightly higher than the conductivity of permeate and retentate. The drop in electrical conductivity of the latter could result from the removal of ions from the solution, which were the component of the surfactants used to emulsify the oil washed off the surface of cleaned elements and then removed.

The regenerated fluid should be reused in the process of cleaning the surface of metal elements. However, the lower value of pH and electrical conductivity noticed after filtration indicate that it is necessary to complete the regenerated fluids with alkaline components that determine the functionality of the applied wash baths.

Conclusions

The laboratory device for investigating the processes of the regeneration of aqueous technological fluids has been developed with the use of ceramic tube membranes. The functionality of the device has been verified by experimental treatment of the contaminated technological fluid. On the basis of the results of physico-chemical analysis of the fluid before (feed) and after regeneration (permeate and retentate) that related to the characteristics of the initial fluid, it has been concluded that proposed method of regeneration enables the removal of solid particles and oils. It has been stated that the level of the contaminants in the regenerated fluid has practically not exceeded the level of contaminants present in the initial fluid. However, both the electrical conductivity and pH of regenerated fluid were lower in comparison to the contaminated fluid. This shows that, during the treatment, some ionic substances were removed from the technological fluid and the regenerated fluid requires the complement of alkaline components. More detailed research is needed to determine the type and amount of these substances.

The conducted preliminary tests confirmed the usefulness of the developed device to investigate the microfiltration processes of the aqueous technological fluids containing surfactants.

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Reviewer:
Wojciech PIĄTKIEWICZ

Laboratoryjne stanowisko do badania procesów mikrofiltracji wodnych cieczy technologicznych

Słowa kluczowe

Separacja, mikrofiltracja, techniki membranowe, regeneracja, wodne ciecze technologiczne.

Streszczenie

W artykule przedstawiono stanowisko laboratoryjne do badania procesów mikrofiltracji wodnych cieczy technologicznych. Za pomocą tego stanowiska przeprowadzono próby regeneracji zanieczyszczonej cieczy technologicznej, stosowanej do oczyszczania powierzchni elementów metalowych, na które następnie nanoszono powłoki funkcjonalne. Na podstawie przeprowadzonych badań stwierdzono, że podczas regeneracji zużytej cieczy usunięto z niej zasadniczą część zanieczyszczeń. Zawartość zanieczyszczeń w cieczy zregenerowanej za pomocą opracowanego stanowiska laboratoryjnego prak-

tycznie nie przekraczała poziomu zanieczyszczenia wyjściowej (świeżo sporządzonej) cieczy technologicznej. Zregenerowana ciecz wymagała jedynie uzupełnienia zawartości preparatów alkalicznych w celu przywrócenia jej pierwotnych charakterystyk fizykochemicznych. Zrealizowana za pomocą opracowanego stanowiska metoda oczyszczania cieczy technologicznych może znaleźć zastosowanie do periodycznego usuwania oleju i innych zanieczyszczeń z wodnych kąpieli myjących, stosowanych w różnych procesach technologicznych. Umożliwi to wydłużenie czasu ich eksploatacji, a w efekcie znaczącą redukcję zużycia wody i chemikaliów, używanych do sporządzania cieczy technologicznych.