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Original scientific paper

OZONATION OF NANOFILTRATION PERMEATE OF WHEY BEFORE PROCESSING BY REVERSE OSMOSIS

Yurii G. Zmievskii[1]*, *Volodymyr V. Zaharov*[1], *Olexandra S. Rudenko*[2], *Iryna M. Biletskaya*[1], *Valeriy G. Myronchuk*[1]

[1] National University of Food Technology of the Ministry of Education and Science of Ukraine, Vladimirskaya str. 68, 01601, Kiev, Ukraine;
[2] V.I. Vernadskii Institute of General & Inorganic Chemistry of the NAS of Ukraine, Palladin Pr. 32/34, 03142, Kiev, Ukraine

During nanofiltration processing of whey a significant amount of permeate is generated. In some cases this permeate is treated by reverse osmosis to get purified water for technological needs. Dry substances are not used, because they contain practically the same amount of organic and inorganic components. Mineral substances can be used for the mineralization of drinking water purified by reverse osmosis. However, the presence of organic compounds complicates the process of separation, as well as reduces the specific productivity of reverse osmosis membranes at the concentration stage. Therefore, the search for methods of destruction and removal of organic components is grounded.

In the presented work, experimental studies of ozonation and sorption of organic compounds by activated carbon were carried. It has been shown that ozonation improves the degree of sorption purification by six times. Sequential treatment with ozone and subsequent filtration through the layer of activated carbon improves the specific productivity of reverse osmosis membranes by 30% at the stage of treatment of the nanofiltration permeate, while their selectivity remains unchanged.

KEY WORDS: ozonation, reverse osmosis, adsorption, permeate, nanofiltration

INTRODUCTION

Whey is a valuable by-product produced by the manufacture of solid, dairy cheeses, and casein (1). The modern technology of its processing consists of the following sequence of technological operations. First, the residues of milky fat and casein fraction are separated in a centrifugal separator. Then, after pasteurization and cooling to 8-12 °C, the whey is concentrated by nanofiltration to a content of dry substances of 18-22%. The final condensation takes place in vacuum evaporator plants, after which whey goes to the crystallizer, where lactose crystals are formed.

* Corresponding author: Yurii G. Zmievskii, National University of Food Technology of the Ministry of Education and Science of Ukraine, Vladimirskaya str. 68, 01601, Kiev, Ukraine, e-mail: yrazm@meta.ua

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The treated whey is dried in a spray dryer, cooled and packaged. Such product has wide applications in the food industry, since up to 40% of minerals are removed at the nanofiltration stage (2), which influences positively organoleptic markers.

However, an unresolved problem is effective use of nanofiltration permeate, which is produced in amount of about 650 dm^3 per 1000 dm^3 of processed whey. This is due to the low content of dry matter (0.4-1.2%) and approximately equal amounts of organic and inorganic components (1.1-2 g/dm^3 of lactose and ≈1.8 g/dm^3 of total content of inorganic ions, such as Na^+, K^+, Cl^-) (1, 3, 4). However, the permeate composition is unique for each individual production and depends on the conditions of separation, composition of milky whey, quality of membranes, and duration of the nanofiltration process. At most industrial plants, nanofiltration permeate of milky whey is drained into the sewage system.

Among separation techniques which allow concentration of low-molecular organic substances and inorganic ions, reverse osmosis is the most commonly used due to simple equipment, ease of scaling and soft separation conditions (5, 6). This method is applied to water desalination (7, 8), particularly in the food and beverage industry (9, 10). Some industrial plants apply reverse osmosis to concentrate whey (11). Then, the obtained purified water is used further, for instance, for washing of the equipment, while the concentrate is discharged to the sewage system.

In previous works (12, 13) we investigated the processes of treatment of model solutions of nanofiltration permeate by reverse osmosis and membrane distillation in a combination with electrolysis. The purpose was to obtain concentrates of mineral salts that could be used to mineralize drinking water purified by reverse osmosis. However, the experiments with real solutions showed that the majority of organic compounds are transported through the ion exchange membranes simultaneously with inorganic ions. This decreases the quality of the obtained concentrates. Reverse osmosis was also applied to concentrating the permeate, which is formed during nanofiltration. It was also proved that the organic components in nanofiltration permeate reduce the specific productivity of the reverse osmosis membranes.

The situation can be improved by modifying membranes with nanoparticles of inorganic ion-exchangers (14-17) or removal of organics from the permeate solution before the membrane process. The organic compounds can be removed from aqueous solutions, for instance, by means of destruction (18) and adsorption (19). One of the promising approaches to destruction and removal of organic compounds is the process of ozonation of solution, followed by filtration through the bed of activated carbon (20). Therefore, the purpose of this work was to apply this approach to the pre-treatment of nanofiltration permeate that is formed during whey processing before concentrating by reverse osmosis.

EXPERIMENTAL

Milky whey, produced by Pyriatyn Cheese Plant (Group of Enterprises "Milk Alliance", Ukraine), contained 6.2 % of dry matter, 0/9 % proteins, 4.6 % lactose, and 0.5 % of inorganic components. This liquid was used for preparation of nanofiltration permeate under laboratory conditions. The equipment for filtration was described in detail earlier,

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except for the cell (21). However, in this case, the roll flow-type module produced by Keensen Technology Co. Ltd. (China) was used, the module was supplied with a nanofiltration membrane of effective area of 0.56 m^2. The filtration process was carried out for 3 h, and 4 liters of permeate was obtained at 0.5 MPa.

Preliminarily, the whey was treated using a microfiltration apparatus supplied with a cartridge separating element (BCCF, Aquafilter, USA).

A dead-end laboratory setup with an effective membrane area of $1.3 \cdot 10^{-3}$ m^2 was used for concentrating nanofiltration permeate under laboratory conditions. A reverse osmosis membrane RM Nanotech (Russia) was used after previous filtering distilled water through it at the working pressure until a steady flux was established.

The chemical oxygen demand (COD) for nanofiltration permeate was determined according to Kubel's method (22), and its value was 11,400 mg/dm^3.

The nanofiltration permeate of milky whey obtained under industrial conditions (by Pyriatyn Cheese Plant, Ukraine) was also used in our investigations, the COD was estimated was to be 400 mg/dm^3. In this case, the membranes produced by GE Osmonics Company (USA) were used.

At the same plant, the nanofiltration permeate was treated by reverse osmosis using the membrane produced by GE Osmonics Company (USA). A pressure drop was kept at 3 MPa. Removal of the organics from the concentrate obtained during the process of reverse osmosis, was also studied. The COD value was 5000 mg/dm^3.

A laboratory apparatus was used for ozonation of the nanofiltration permeate (Figure 1). The system included a generator of ozone (Ecozone 6-AW, Digidrol, Ukraine) as well as an oxygen concentrator (JAY-8, China). The efficiency of the process of ozone generation was 6 g/h.

The operation principle of the apparatus is as follows. After the vacuum pump is switched on, air passes through a dehumidifier filled with silica. The rate of air pumping is controlled with a rotameter. The air is enriched with oxygen in a concentrator, then the gas is passed through the ozonizer, where ozone is generated due to the electrical discharge. The resulting gas mixture enters the reactor, where it passes through the processed solution. Since foam can be produced in the nanofiltration permeate, a foam catcher is installed after the reactor. Further, the ozone-gas mixture gradually falls into two Drexel bottles and filled with a KI solution. The remaining mixture of gases is released into the atmosphere through a vacuum pump. After ozonation, the solution was passed through the column filled with activated carbon (Desotec Organosorb, Belgium). The height of the adsorbent bed was 16 cm, the diameter of the column was 6 cm, the superficial solution velocity was 1.5-2.5 m/h. For comparison, only adsorption was used for removal of organics from the permeate solution obtained under laboratory conditions.

The concentration of ozone in the gas phase was determined by iodometric method. The gas phase passed through a Drexel bottles (see Figure 1) filled with a solution of potassium iodide, reacting with ozone. Then, this solution was titrated with sodium thiosulphate, and the amount of ozone that reacted was calculated.

The nanofiltration permeate of whey, which was obtained under industrial conditions, was used for separation by means of reverse osmosis at 4 MPa, using a KS-C membrane produced by NanoTech (Russia). The apparatus for reverse osmosis was described earlier

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(21). For comparison, the liquid after ozonation and adsorption was also treated by reverse osmosis. The content of inorganic ions in the permeate and concentrate was determined similarly to (16).

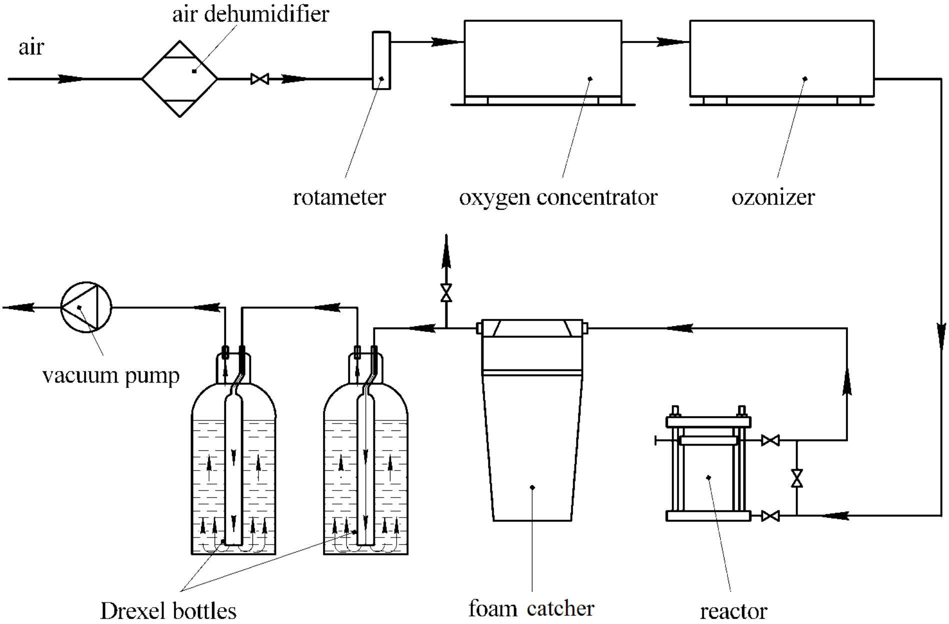

Figure 1. Scheme of the laboratory apparatus for ozonation.

RESULTS AND DISCUSSION

First of all, the industrial samples of nanofiltration permeate and concentrate after reverse osmosis were treated with ozone for 20 min. The rate of air flow through the system was 240 dm^3/h, the concentration of ozone in the gas phase was 25 mg/dm^3. The process was accompanied by significant foam formation. As a result, the turbid solution became transparent indicating degradation of macromolecules (Figure 2). The COD value decreased down to 2280 mg/dm^3 for reverse osmosis concentrate. In other words, the concentration of organics in this liquid was lower more than two times in comparison with the pristine solution, Thus, the ozonation technique allows us to decrease sufficiently the content of organic substances, but additional purification is needed. Regarding the nanofiltration permeate, a decrease of the COD value is not so sufficient (from 400 down to 360 mg/dm^3). However, the solution also becomes more transparent. Comparing with the unconcentrated nanofiltration permeate, the concentrate after reverse osmosis contains more degradable substances, and these substances evidently provide yellow color of the liquid.

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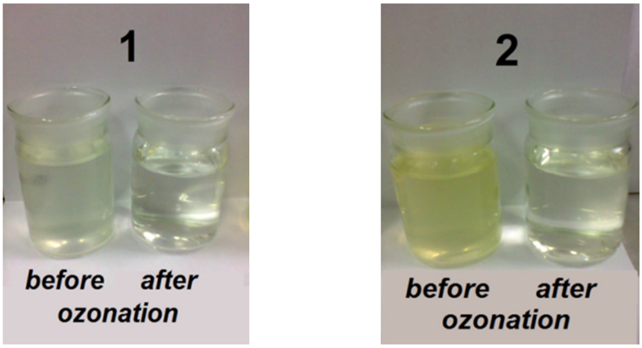

1 - NF permeate of whey; 2 - NF permeate of whey concentrated by reverse osmosis

Figure 2. Samples before and after ozonation

Further attention was focused on the combination of ozonation and sorption processes. The nanofiltration permeate of milky whey obtained under laboratory conditions was purified from organics. The large value of COD for the pristine permeate solution indicates lower selectivity of the nanofiltration membranes than that of the membrane used under industrial conditions. The results are given in Figure 3.

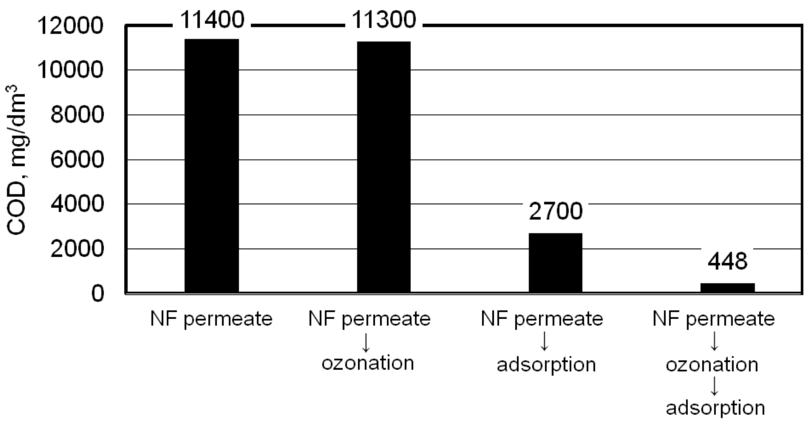

Figure 3. Experimental data of the ozonation and adsorption process involving nanofiltration permeate obtained under laboratory.

It can be seen that the ozonation caused no sufficient decrease of the content of organic substances in the nanofiltration permeate, probably because of the impeded destruction of large macromolecules. The adsorption produced more than a four-fold decrease in the COD value. At last, the minimal content of organic substances was reached after the ozonation followed by adsorption, which is in agreement with the literature (23, 24). As

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known, the ozonation of organic substances causes breaking C-C bonds, followed by the formation of oxygen-containing groups, particularly dissociated ones (–COOH) (25). On the other hand, materials based on activated carbon contain both hydrophilic and hydrophobic pores (26). Ion exchange groups are located in the hydrophilic pores. Moreover, ozone can oxidize the surface of activated carbon (additional hydrophilization). As a result, additional -OH groups appear on the surface. These groups are responsible for anion exchange. Thus, the reason of enhanced adsorption can be additional contribution of the ion exchange mechanism to adsorption.

When considering such treatment as preparation of the solution before its reverse osmosis concentration, two functions of activated carbon are important. The first one is the maximal removal of organic substances from the solution. The second function of activated carbon is the destruction of ozone traces, their content in the solution can reach several milligrams per liter under ambient temperature. When the nanofiltration permeate is used further for separation by means of reverse osmosis, ozone removal is necessary to prevent destruction of the membrane. However, ozone is unstable (its half-life is 20 min. (27)), and tends to transform to oxygen. Thus, the solution must be stored for some time or heated before processing by reverse osmosis.

Nevertheless, under industrial conditions, the increased processing time or additional technological process (heating) creates a significant number of organizational problems. Therefore, first of all, in order to deactivate the oxidizing agent, it is necessary to apply filtering of the solution through the bed of activated carbon.

Appropriate studies have been carried out to confirm the positive effect of the combination of ozonation and adsorption. In this case, the process of reverse osmosis was studied. As found, ozonation followed by adsorption reduced the COD value from 400 to 100 mg/dm^3. The results are shown in Figure 4.

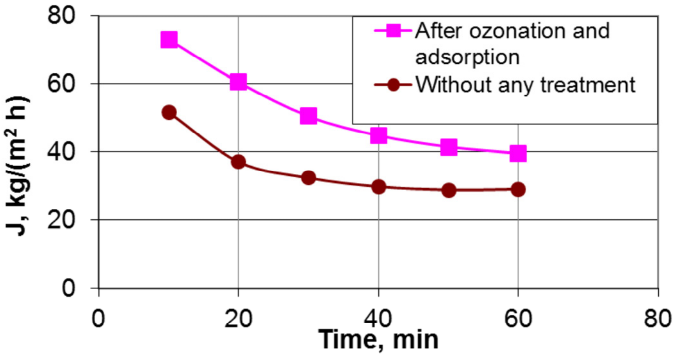

Figure 4. Permeate flux through the reverse osmosis membrane as a function of time.

It is seen that the productivity of the reverse osmosis membrane is higher by 33-40% if the solution was treated with ozone. The selectivity towards inorganic ions was about 95% in both cases. The improvement of rejection ability of the membrane is evidently

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caused by lower content of organics in the liquid after preliminarily ozonation and adsorption.

It should also be noted that ozonation disinfects the solution. Under industrial conditions, the tank of temporary storage of the permeate before reverse osmosis has to be washed with chemical reagents using hot water at least once every two days. If the ozonation process is properly organized, the frequency of washing should be significantly reduced, however, it should be checked in the production conditions and investigated separately.

CONCLUSIONS

Treatment of nanofiltration permeate of milky whey by ozone followed by filtration through the bed of activated carbon was investigated. The synergetic effect of the combination of these processes can be due to a change of the composition of organic substances and appearance of -OH anion exchange groups on the surface of activated carbon under the influence of ozone. This allowed increasing the permeate flux through the reverse osmosis membranes by 33-40% without deterioration of selectivity. It is assumed that the disinfectant effect of ozone will reduce the cost of chemical reagents and hot water used in dairy enterprises for the washing of temporary storage tanks for nanofiltration permeate before reverse osmosis.

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ОЗОНИЗАЦИЈА ПЕРМЕАТА НАНОФИЛТРАЦИЈЕ СУРУТКЕ ПРЕ ПРОЦЕСИРАЊА РЕВЕРСНОМ ОСМОЗОМ

Јуриј Г. Змијевски[1], Володимир В. Захаров[1], Олександра С. Руденко[2], Ирина М. Билецкаја[1], Валериј Г. Мирончук[1]

[1] Национални универзитет прехрамбене технологије Министарства образовања и науке Украјине, Владимирска ул. 68, 01601, Кијев, Украјина

[2] Институт опште и неорганске хемије "В. И. Вернадски" Националне академије наука Украјине, Паладин пр. 32/34, 03142, Кијев, Украјина

У току обраде сурутке нанофилтрацијом настаје знатна количина пермеата. У неким случајевима се пермеат подвргава реверсној осмози да би се добила пречишћена вода за технолошке потребе. Суве супстанце се не користе из разлога што практично садрже подједнаке количине органских и неорганских компоненти. Минералне супстанце се могу користити за минерализацију пијаће воде пречишћене реверсном осмозом. Међутим, присуство органских једињења усложњава процес раздвајања, а такође смањује специфичну продуктивност мембрана реверсне осмозе у фази концентровања. Према томе, основана су настојања да се пронађу методе разарања и уклањања органских компонената.

У овом раду су представљени резултати експерименталног испитивања озонизације и сорпције органских једињења помоћу активног угља. Показано је да озонизација побољшава степен пречишћавања сорпцијом шест пута. Озонизација после које следи филтрација кроз слој активног угља побољшава специфичну продуктивност мембрана у реверсној осмози 33-40% у фази обраде пермеата нанофилтрацијом, док њихова селективност остаје непромењена.

Кључне речи: озонизација, реверсна осмоза, адсорпција, пермеат, нанофилтрација

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