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ADVANCED TREATMENT OF PHARMACEUTICAL WASTEWATER BY NANOFILTRATION AND OZONATION

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ABSTRACT: *In this research, we aimed at treating the pharmaceutical wastewater, applying two systems that combined: ozonation- nanofiltration. We investigated the effect of ozonation before the nanofiltration. Pharmaceutical wastewater were treated with ozone, and the effects of the ozonation time and the flow rate on the flux, the membrane fouling and the COD retention were measured. The fouling of the NF DL membrane was studied. We compared the observed permeate flux during filtration with conventional nanofiltration (no preozonation), and with hybrid ozonation–nanofiltration process. In the filtration tests with ozonation, the permeate fluxes and the removal of the organic compounds was higher than that seen without ozone pretreatment. These results demonstrate the effectiveness of the hybrid system compared to the conventional polishing configuration.*
KEYWORDS: *Pharmaceutical wastewater, nanofiltration, ozonation*

INTRODUCTION

Wastewater of pharmaceutical industry is characterized by high organic matter contents, toxicity, deep color, and high salt contents. The removal of these contents from the pharmaceutical wastewater has been a big task of the most industrial park wastewater treatment plants in Hungary. The treatment of pharmaceutical wastewater requires some complementary techniques that could efficiently remove pollutants and enable the wastewater to be discharged into receiving water or be reused for industrial purposes (Xinyu et al., 2010). Membrane processes such as nanofiltration (NF) with high efficiencies in removing organic and inorganic pollutants can overcome the shortcomings of the traditional methods. The membrane separation processes offer various advantages, e.g. a compact system, easy control of operation and maintenance, and low needs for chemicals. The main limitation of the membrane processes is the flux decline caused by membrane fouling, which may result from plugging of organic and inorganic materials in the membrane pores (thermal water). Membrane fouling is a main obstacle to the application of membrane techniques in pharmaceutical wastewater treatment (Byung et al., 2007). Ozonation is considered to be one of the most promising processes with which to control the levels of organic pollutants in wastewater. Several studies have also been published on ozone pretreatment prior to membrane filtration. These studies have shown a decrease in membrane fouling when the filtered effluent was first degraded by ozone. (Mika et al., 2008 and László et al., 2009). Ozone has been reported to improve filtration efficiency. This effect has been called, among other things, microflocculation or ozone microflocculation (Langlais et al., 1991). By combining the oxidation characteristics of ozone and membrane technology, a better quality of water is expected to be produced more easily and at lower cost (Norman et al., 2008).

Ozone is a very powerful oxidant for water and wastewater treatments, and once dissolved in the water, reacts with a high number of organic compounds in two different ways: by direct oxidation, as molecular ozone, or by indirect reaction, through the formation of secondary oxidants such as free radicals, especially hydroxyl radicals (Byung et al., 2007). By means of ozonation, it is expected to achieve great color and COD eliminations and an increase of the biodegradable organic carbon for later physical or biological stages (Benítez et al., 2008).

In this work, experimental study on NF for advanced treatment of a real complex pharmaceutical wastewater was carried out. The primary aim of this research was to assess the potential use of an integrated ozone and NF process for improving the NF performance in a preozone-NF hybrid scheme. The role of ozonation was specifically examined, focusing on the followings: (1) the reduction of fouling due to the integration of ozonation prior to the NF membrane process and (2) the oxidation efficiency both before and after the NF process.

MATERIALS AND METHODS

The wastewater was collected from a pharmaceutical processing plant in Hungary whose is characterized by high organic matter contents, toxicity, deep color, and high salt contents (Table 1.).

We evaluated the feed water quality and monitored the process quality. The plant discharge the treated waste water to a dead channel, the limit for COD of treated water is 150 mg/L.

Table 1. Characteristics of the raw water

	Conductivity (μS)	COD (mg/l)	Turbidity (NTU)
Raw water	2250	1387	23

First time we used ozone pre-treatment prior to membrane filtration. The ozone gas was generated from oxygen (Linde, 3.0) by the Ozomatic Modular 4 ozone generator (Wedeco Ltd., Germany). The actual generated ozone-gas output was controlled by the inlet air flow rate as regulated by a rotameter to within 1-3 $dm^3\ min^{-1}$. The ozone-containing gas was bubbled continuously through a 6.0 dm^3 batch reactor during the treatment. The treatment time was 10, 20 min. The ozone concentration of the bubbling gas was determined with a UV spectrophotometer (WPA Lightwave S2000) directly at 254 nm, before and after the passage through the reactor (Table 2.).

Table 2. The absorbed ozone concentration

Time / Flow rate	10 min	20 min
1 $dm^3\ min^{-1}$	16.58 mg	23.45 mg
3 $dm^3\ min^{-1}$	4.86 mg	6.17 mg

After the ozonation the solution was supplied to the membrane system. A laboratory-scale apparatus was applied in the experiments. A tubular membrane with a filtering surface area of 0,024 m^2 was placed in the NF module. Polyamide film membrane with 75% $CaCl_2$ retention, were used for nanofiltration. All measurement was carried out at 8 l/min cross-flow velocity, 30 bar transmembrane pressure and 25°C temperatures.

Table 3. Characteristics of the membrane

Membrane	Material	Max. pH
AFC30	Polyamid film	1.5-9.5
Max. pressure	Max. temperature	Retention
60	60	75% $CaCl_2$

As the filtration process continues, fouling will eventually occur. This causes the permeate flux to decay with time. The decaying permeates flux is described by the power law:

$$J = J_0 t^{-k} \quad (1)$$

where t is time, J_0 is the initial flux and k is the fouling rate constant. Both J_0 and k can be calculated from the measured data by using the curve-fitting technique (Kertész et al., 2008).

Determination of the COD was based on the standard method involving potassium-dichromate oxidation; for the analysis, standard test tubes (Lovibond) were used. The digestions were carried out in a COD digester (Lovibond, ET 108); the COD values were measured with a COD photometer (Lovibond PC-CheckIt). The absorbance of solutions at 255 nm relating to the presence of humic substances was measured with a UV spectrophotometer (WPA Lightwave S2000).

RESULTS

We investigated the effect of ozone pretreatments before the NF. The flux is shown in the function of the time of the NF in Figure 1. It was found, that the ozone pretreatments were effective, the ozone treatment improved the flux values. The ozone dose at the applied ozone concentration range had not affected significantly on the flux. The results show that, the lower absorbed ozone amount caused higher improving in the flux. The highest flux values obtained with the 4.85 mg/l absorbed ozone dose.

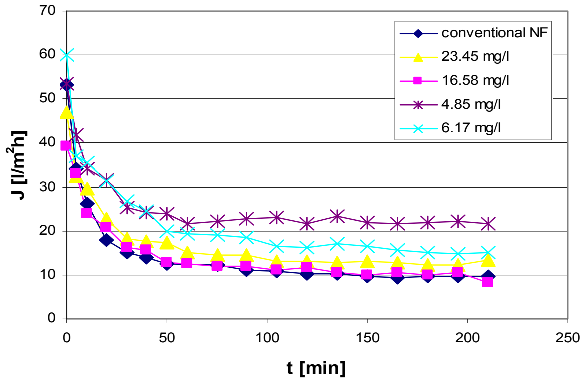

Figure 1. Effect of ozone dosage on permeate flux

The average permeate fluxes (J) shows the filterability of the solution. (Figure 2) These results are in accordance with the fouling index (k) results: ozone treatment results increased permeate flux and decreased fouling index. The k can be calculated from the measured flux data by using a curve-fitting technique. It was found, that (in accordance with the permeate fluxes) ozone treatment decrease the fouling index. The ozone dose has no significant effect on the k, but the lower ozone doses results no significant decreasing in fouling of membranes. These results confirm the suppose that the ozone treatment have microflocculation effect on the particles of the waste water, the larger flocculated particles can not move into the membrane pores, resulting decreased fouling index. It may be remarkable result for the practice of the membrane techniques, because the decreased fouling of membrane pores may results increased membrane life-time.

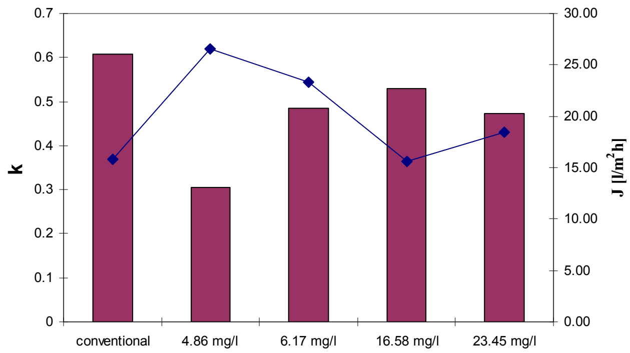

Figure 2. Effect of ozone dosage on the membrane fouling

The hybrid technology decreased the COD of the solution from 1300 mg/l below 50 mg/l in each sample. It was found, that the efficiency of COD removal improves with the ozonation. The higher ozone flow rate caused higher COD decrease, even if the ozone dosage was smaller. The higher COD retention at higher flow rate may be explained by microflocculation effect of ozone treatment. The ozone treatment cause the microflocculation of the particles, the greater particles can be filtered from waste water with better efficiency. The higher ozone concentration does not cause significantly smaller COD removal.

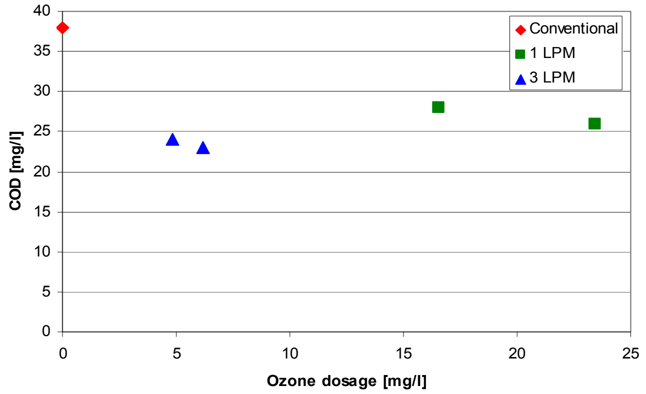

Figure 3. Effect of ozone dosage and flow rate on the COD in the permeate

Finally, it is also interesting to establish the partial contribution of the two stages individually considered to the global effectiveness of the combined process. These contributions are represented in Figure 4. Thus, the NF membrane process stage provided a major contribution in the three pollutant parameters, while the ozonation stage contributed in a less extent in the three remaining indices. The removal of COD during the ozonation stage provided higher contribution.

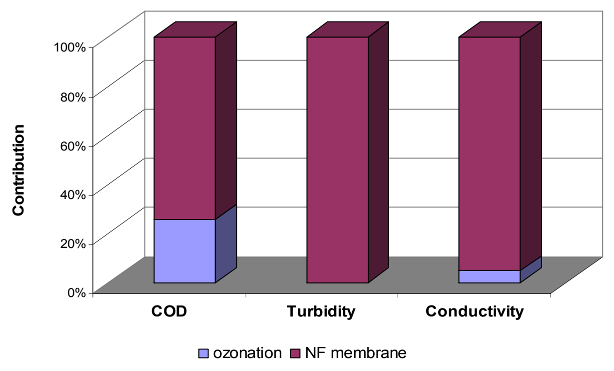

Figure 4. Contributions of the global removal int he ozonation and NF membrane combined process

Summary / Conclusions

The effectiveness of a combination of the membrane separation technique and ozone treatment was investigated for the removal of COD from pharmaceutical waste water. The results obtained by examining the effect of ozone treatment on filterability of the waste water show that the ozone pretreatment enhanced the flux and decreased the fouling during membrane filtration. This phenomenon can be explained by microflocculation effect of ozone treatment. This means also that the decreased fouling of membrane pores may enhance the life-time of the membrane.

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