Ecological Engineering and Environment Protection, No 1, 2016, p. 65-72

INFLUENCE OF ELECTRICAL CHARGE OF REVERSE OSMOSIS MEMBRANES ON THE EXTENT OF FOULING THROUGH THE TREATMENT OF WASTEWATER FROM CERAMIC INDUSTRY

Sami A. Al Rawi, Valentin Nenov, Ahmed Aiden

Abstract: This paper presents the results obtained from industrial wastewater treatment plant in Ras Al Khaimah City (United Arab Emirates) using modified methods of reverse osmosis (RO) membrane with neutral surface charge instead of conventional membrane.

Various fouling effects influencing the surface characteristics of polyamide membranes were investigated by using primary treated water from ceramics manufacturing process and monitoring the fouling layer on the surfaces of the membranes. The obtained data were analyzed in choosing suitable membranes surpass hydrophobicity and minimum fouling deposition. Using of conventional polyamide with standard RO has faced many problems which let the system failed in treatment of industrial wastewater with high turbidity and high concentration of total suspended solids (TSS). Low fouling membranes have been used instead of conventional RO membranes in this study. The obtained results indicate less fouling of membranes surface and flux stability. The RO membrane modification solved the problem of treatment of wastewater from ceramic industry in Ras Al Khaimah (RAK) City, UAE.

Keywords: fouling, membrane, membrane modification, reverse osmosis, wastewater treatment

INTRODUCTION

Reverse osmosis membranes technology has an important role in enhancing of industrial wastewater using and purifying water by separating the dissolved solids, color, organic and inorganic pollutants where there is an urgent need for reusing of industrial wastewater at the Arab Gulf region and it is considered as an alternative preferred water sources. The demineralization industrial water played an important role in the present and it will play a more important role in the future.

Since the development of the first practical cellulose acetate membranes in the early 1960's and the subsequent development of thin-film composite membranes, the uses of reverse osmosis (RO) have expanded to include not only the traditional desalination process but also a wide variety of wastewater treatment applications. Several are advantages of the RO process which make it particularly attractive for dilute aqueous wastewater treatment [1]. Reverse osmosis membranes technology have been successfully used since 1970 and its applications become important in the various practical solutions. The global application extended to drinking water, also used in municipality sewerage water, recycling, power plants, and chemicals, desalinate water for medicine usage and industrial wastewater.

The RAK plant was commissioned in 2012, but the initial operator for RO was not free of troubles. The problems in plant were initially facing fouling of the membranes and very fast flux drop happened. When the traditional membranes changed to neutral charged type, it is controlled most of the Troubles. This research presents a review of the main troubles solution that happened through plant operation in RAK ceramic factory and presents a high success operation of the plant with focusing on the influence of the electrical charged of reverse osmosis membranes and finds effective solutions for the system.

The reverse osmosis plant treated industrial wastewater resulting from ceramics manufacturing and the wastewater is produced from preparation of many types of tiles, porcelain, sanitary, casting units, and various process activities such as glazing, decorating, polishing, and wet grinding. Wastewater is characterized with high turbidity and coloring, due to the very fine suspended particles of glaze and clay minerals. The pollutants include fine particles of clays, organic matter and insoluble silicates, and dissolved heavy metals such as lead and zinc, etc.

Wastewater treatment is just one component in the water cycle. However, it is an important component as it ensures that the environmental impact of human usage of water is significantly reduced. Treatment operation consists of chemical and physical processes, and aims to control all types of fouling in result of turbidity, TSS, BOD_5, COD, color, and heavy metal precipitates. Application membrane technology for treated industrial wastewater is very wide as a pretreatment prior to the RO process through multi-step treatment. It is based on screen unit, equalization tank, polymers chemical dosing units, static mixer, flocculation unit, settlement unit, multimedia sand filter, micro-ultrafiltration (MUF) unit and the last one is RO plant as shown in Figure 1.

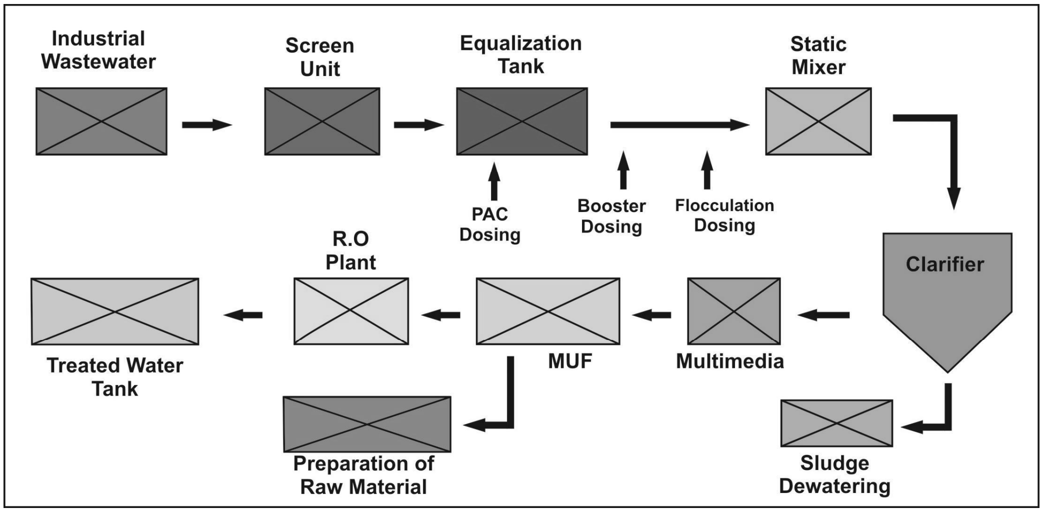

Fig. 1. Technological schema of wastewater treatment process in RAK, U.A.E

The objective of the research is to deal with the effects of fouling of the membrane coming from industrial wastewater of a ceramic factory (with daily discharge of 2000 m³/day). Wastewater contains high concentration of colloidal particles, suspended and dissolved inorganic. The turbidity reaches up to 22000 NTU and TSS to 19600 mg/l [2]. After treating water by unconventional process and using new coagulation materials with new technique micro ultrafiltration, turbidity has reduced to around 1 NTU and TSS less than 5 mg/l. The treated water from MUF is divided into two streams, the first one is directed to ceramics factory to be used for raw materials preparation, and the second one goes to reverse osmosis in aiming to reduce additionally total dissolved solids (TDS) to the acceptable level. Such water quality is required for other processes of ceramics manufacturing.

MATERIALS AND METHODS

Wastewater. The used water source in this study was industrial wastewater (2000 m³/day) coming from ceramics manufacturing process divided into two streams. Capacity of each one is 1000 m³/day and the softening membranes were used in treatment plant in Ras Al Khaimah City, U.A.E. The turbidity and other pollutants in this raw water are abnormal as shown in Table 1.

Practical experiments for this type of raw water was done on June 2012 for testing purposes, where the RO plant is chosen in capacity of 45 m³/hr, fed with treated water by coagulation, flocculation, sedimentation and MUF process and got very low turbidity, less than 1 NTU which equal 99,99 % removal. The purpose of the RO plant is to remove water salinity and other remaining pollutants in order to be able in reuse it in ceramics manufacturing process.

Case Study of RAK Ceramics. Ceramic industry is one of the important industries in RAK, UAE. This sector of industry offers thousands of jobs for multi-nationality labors and officers and makes big contribution to the economics of the state of UAE. In general, there are different types of produced products:

1. White ware: China, earthenware, pottery, porcelain, stoneware and vitreous ware;
2. Structural clay products: Building brick, face brick, sewer pipe and drain tile;
3. Refractories: Firebricks; silica, chromite, magnesite, magnesite-chromite brick, silicon carbide and zirconia refractories, aluminium silicate and alumina products;
4. Specialty ceramic products.

Service and ancillary units provide water and energy requirements as well as maintenance, storage, packaging, testing and analysis needs.

Raw Materials, Products and Utilities. The principal raw materials are sand, feldspar, ball clay, china clay, kaolin, talc and other materials that are used during the manufacturing process, such as soda ash, sodium silicate, calcium carbonate, plasticizers and lubricants. Glaze materials are used to modify the surfaces of the products. Glaze is prepared from sand, feldspar ($6Na_2O.SiO_2.Al_2O_3$), soda ash, binder, dolomite, water. Chemicals are also used in the lab for quality control and analysis. Natural gas and mazut (fuel oil) may be used in the kiln as fuel. Through ceramics manufacturing process huge amount of raw water discharged which contain various types of metals by its nature are carrying charges have the influence on filtration and separation process will affect on membranes surface leading to membranes deterioration.

Table 1. Characteristics of wastewater of RAK ceramic factory according to lab test

PARAMETERS	UNITS	RESULTS
Total Suspended Solids (TSS)	mg/L	19700
Total Dissolved Solids (TDS) at 180 °C	mg/L	1400
pH at 25°C	-	7.8
Conductivity at 25°C	µS/cm	1300
Turbidity	NTU	22000
Total Hardness as ($CaCO_3$)	mg/L	147
Total Alkalinity to pH 4.4	mg/L	200
Total Nitrogen	mg/L	8.3
Biochemical Oxygen Demand (BOD_5) for 5 days at 20° C	mg/L	420
Chemical Oxygen Demand (COD)	mg/L	990
Total Organic Carbon (TOC)	mg/L	116
Boron (B)	mg/L	5.5
Silica as (SiO_2)	mg/L	24
Total Iron (Fe)	mg/L	26.2
Cadmium (Cd)	mg/L	LT 0.01
Strontium (Sr)	mg/L	0.56
Barium (Ba)	mg/L	0.70
Nickel (Ni)	mg/L	LT 0.22
Zinc (Zn)	mg/L	12.6
Lead (Pb)	mg/L	0.22

Membranes Filtration Selection. The success of membranes process depend on the selection of the membranes materials, and minimize effect of organic and inorganic fouling onto the membrane surface, chemical resistance, high permeate flux, and suitable cost. The traditional composite RO membrane polyamide type carrying negatively surface charged cannot be used in industrial water treatment field, due to flux reduction and fouling of the membrane. “Organic polymers are the most widely used commercial membrane materials. They are usually constructed by coating a thin active polymeric layer onto a microporous support to provide desirable mechanical strength while having higher water permeability and chemical resistance.” [3]. Chemically modified polyamide membrane (where the membrane surface is made a neutral charge) is resistant to various available compounds with negative or positive charge in water and to variable values of flux at acidic and alkaline pH.

RO Plant. The reverse osmosis (RO) process uses a semi-permeable membrane allowing the fluid that is being purified to pass through it, while rejecting the pollutants. RO is one of the techniques able to remove a wide range of dissolved solids from water [4]. Reverse osmosis filter have a pore size around 0.0001 micron found to desalinate water. The feed water enters the RO membranes under enough pressure to over osmotic pressure and pass through the semi-permeable membrane not allowing the salts and other pollutants to pass through membranes micro pores and discharged through the rejected stream (Fig. 2). The salts removal from the water reach to 99 % of the total dissolved salts. In addition to remove all particles, collides, organic and inorganic compounds, bacteria from the feed water, the RO build is considered as a last stage of the treatment plant. The purpose of RO is to reduce the TDS from 1400 mg/l to maximum 250 mg/l and rejected water is only 15 %.

RO Plant Design Parameter. The design parameters of Somicon Low Fouling Membrane (SLFM) for RO plant are shown in Table 2.

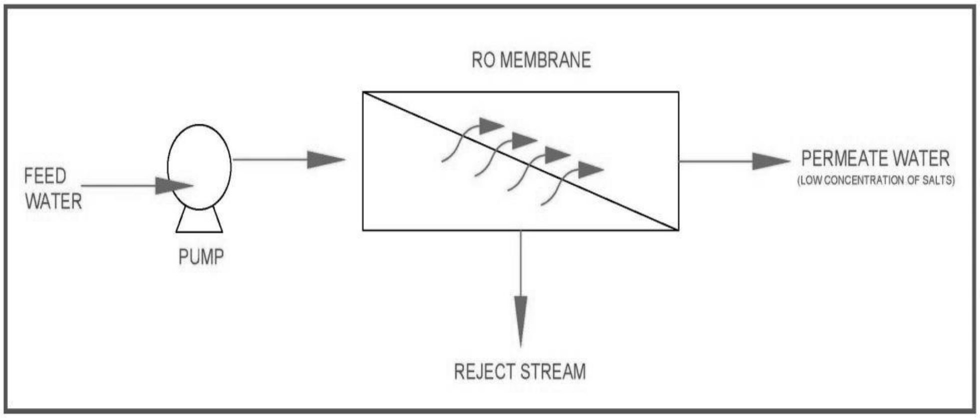

Fig. 2. Principal scheme of RO system

Table 2. RO plant parameters

Feed water source	Last stage of industrial wastewater treatment plant from RAK Ceramics Factory
Pre-treatment before RO	Micro ultrafiltration (MUF)
TDS in feed water	1400 mg/l
RO capacity	45 m^3/hr
Total number of the membranes	30 membranes
Recovery design	85 %
Membranes type	Neutral charged
Maximum feed flow for each membrane	19 m^3/hr
Each membrane area	37 m^2
Average water temperature	28 ºC
TDS in treated water	125 – 250 mg/l
pH range continuous operating	2 – 11
Operation pressure	12 – 16 bar
Maximum silt density index (SDI)	5

RESULTS AND DISCUSSION

Membrane Flux. Reverse osmosis membranes are used to reduce total dissolved solids through the operational process. As it is noted, the low fouling membrane type SLFM maintains stable flux during the operation, while the conventional membranes are experiencing sharp flow decrease. The fouling has a profound effect on the flux of membrane. To reduce fouling rates of the membrane it is taken in consideration modifying membrane chemistry, providing neutrally charges to minimize adsorption of organic and inorganic pollutants on the membrane surface. Fig. 3 shows membrane condition life does not exceed fifty days although trying with reclamation by chemical cleaning and continuous backwash.

Experience from commercial membrane wastewater treatment plants has demonstrated that there are key design parameters which must be followed to prevent membrane fouling [5]. Fouling of the membranes leads to decrease of permeate flux, and that is an evidence of its significant in increasing of the feed pressure to maintain the design permeate flow. Figure 3 shows the flux drop for the conventional membranes through operation time and the stability for the SLFM membranes. The premature failure of conventional membrane is made of polyamide become more negatively charges of (–5 to – 21 mV) at pH between 4 and 10 [6]. It can be observed that Ca^{2+}, Fe^{3+}, Mg^{2+} and Al^{3+} cannot prevent from attraction on the membrane that leads to depositing on the surface of the membranes causing clogging on the membrane micro pores.

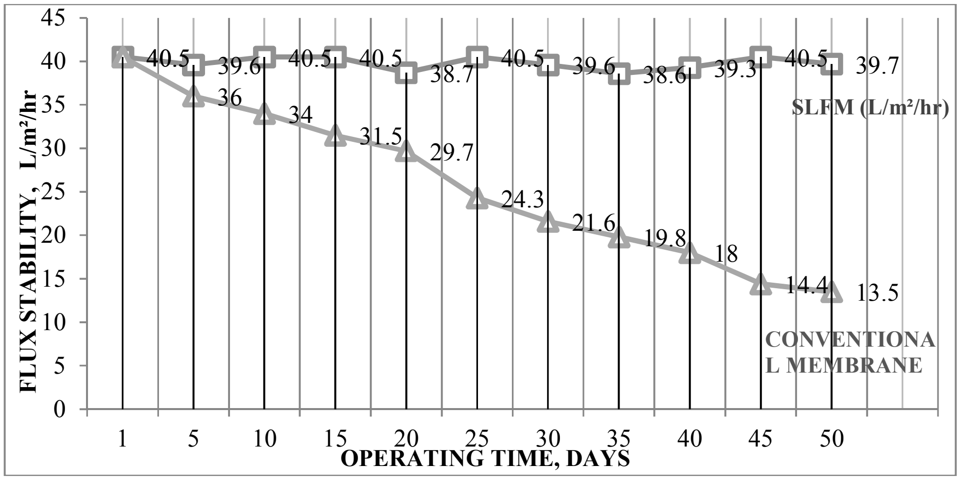

Fig. 3. Flux change through the filtration cycle

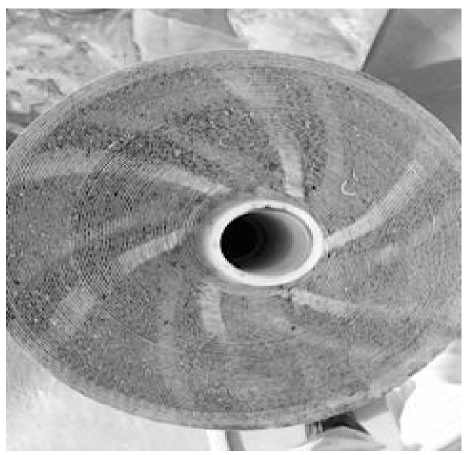

Fig. 4. Polyamide conventional membrane clogged with fouling

During the operation, the conventional membrane is completely covered with layers of deposition, as image in Figure 4 shows membrane surface clogged with fouling and TSS.

pH Effect. SLFM chemical modifying during casting process to get a membrane neutral charge and increase hydrophilicity minimize the adsorption of fouling of the membrane, where it can operate with any case whether the water acidic or alkaline, the surface charge over a pH range of 3 – 10, where it is noted that the effect of zeta potential is very low and maintain a relatively neutral surface charge of 2 mV at pH between 7 and 11. Fig. 5 shows the changes of the potential of conventional and SLFM membrane surface at both acidic and alkaline pH values [7].

SLFM neutral membranes characterized by its resistance ionic fouling types, either if it carries positive or negative charges, also with unaffected with pH alkaline and acidic, while conventional membranes polyamide type deteriorates quickly, especially at pH between 5 and 10, a range in which the change of zeta potential is considerable. In such conditions the usage of conventional membranes is considered inappropriate especially in case of treatment of industrial water carrying pollutants with positive charges causing deposition on membrane surface, as shown in Fig.5.

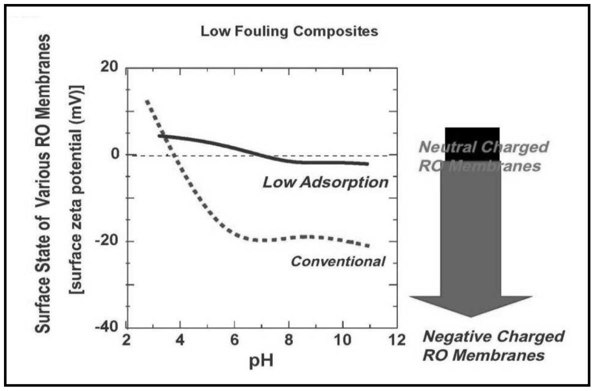

Fig. 5. Change of the potential of conventional and SLFM membrane surface at different pH

Membranes Modifying. Polyamide conventional membrane was a chemically modified to convert from negative charge to a neutral charge of membrane. Fig. 6 shows an RO module with enhancement to reduce RO fouling tendency. The low fouling membranes have a neutral surface charge and are more hydrophilic in nature, which minimizes the adsorption of charged, hydrophobic organic foulants to the membrane surface and is more efficiently removed by chemical cleaning [8]. Through the usual process it is used traditional membranes carrying negative charges.

We faced technical troubles lead to membranes performance failure, due to the depositing of fouling of the membrane and the inefficiency of chemical clean that lead to system failure which necessitated reversing to type of membranes carrying neutral charges.

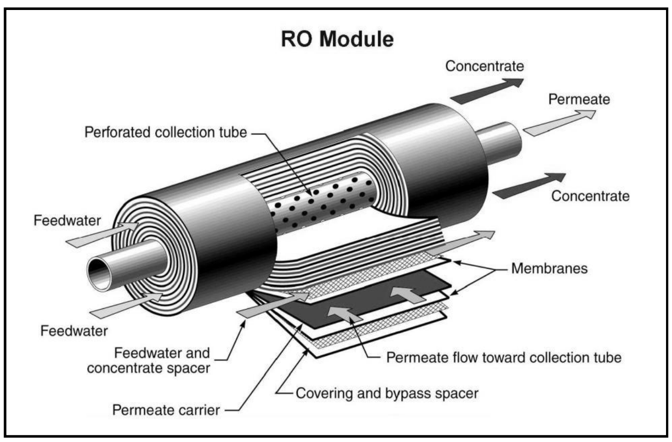

Fig. 6. RO module

SLFM membranes have operated without flux drop and maintenance stable salt rejection for 50 days and above. Design flux 45 m³/hr with a recovery of 85 %, the plant operator with consistent performance and chemical cleaning used only once through operation time while in case conventional membrane noted flux loss happened on the first week and through 50 days of operation CIP done 10 times without successful results.

The results obtained presented in the Table 3 show different production between conventional membranes and SLFM neutral membrane.

Operational Effect and Cost Relationship. Table 4 shows a comparison of operational effect and cost relationship for SLFM and conventional membrane.

Based on the treatment results it was shown that the high turbidity (22000 NTU) can be reduced to 0.47 NTU. However the TDS is remained unchanged (in the specific case further treatment to reach the level of salt content to 250 mg/l is needed). In applying polyamide membrane chemistry modifying, the benefits of new modifying membrane various positive effects have been observed, such as less wastewater rejection compare with conventional membrane, lower operation cost, lower power consumption, unchangeable flux in acidic and alkaline conditions, and finally longer technological life of membrane was ensured.

Table 3. Comparison between volumetric production of SLFM and conventional membranes

Operating Day	Conventional Membrane, m^3/hr	Neutral Membrane, m^3/hr
1	45	45
5	40	44
10	38	45
15	35	45
20	33	43
25	27	45
30	24	44
35	22	43
40	21	44
45	16	45
50	15	44

Table 4. Operational effect and cost relationship for both types of membranes

SLFM Membrane		Conventional Membrane
1	Low operation cost and low power consumption	High operation cost and high power consumption due to feed pressure increasing
2	No need chemical cleaning, maybe after 90 – 120 days	Frequent chemical cleaning required (one time every ten days)
3	Not required accurate monitoring	Due to operation problem, it is required a permanent monitoring
4	Membrane replacement every 40 months	Membrane replacement required every two months
5	Operation cost is 0.85 $\$/m^3$	Operation cost is 3.7 $\$/m^3$
6	Unaffected with pH, alkaline and acidic pH (3 –10)	Very affected with pH, especially in alkaline and best effect only at pH between 3 and 4
7	Maintained surface charge between –3 to + 5mV	Large different between surface charge from +12 to – 20 mV

CONCLUSIONS

Using conventional RO membranes is not always an appropriate way in treatment of industrial water. It is common the designed process to fail because the influence of electric charges of reverse osmosis membranes and the various fouling loading are not taken in consideration. A good example is the failure of the conventional membranes in Industrial Area of Ras Al Khaimah in dealing with pollutants of organic nature and inorganic ions as well, causing fast attraction between ions and the surface of the membranes, which leads to the deterioration of membrane surface and flux losses.

REFERENCES

1. Afonso M., V. Geraldes, M. Rosa, M.De Pinho, (Nanofiltration Removal of Chlorinated Organic Compounds from Alkaline Bleaching Effluents in a Pulp and Paper Plant), Water Res, Vol. 26, 1992, 1639-1643.

2. Al Rawi S. A., V. Nenov, A. Aidan, E. Al Essawi, (Optimization of Coagulation Process in High Turbidity Discharged from Ceramic Factories), IJMRAE, Vol. 6, 2014, 69-80.

3. American Water Works Association (AWWA) Membrane Technology Research Committee (1998), Porter (1990) and Pinnau and Freeman (2000).

4. Fu F., Q. Wang, (Removal of Heavy Metal Ions from Wastewater: A Review), J Environ Manage, Vol. 92, 2011, 407-418.

5. Bartels C. R., (Reverse Osmosis Membranes for Wastewater Reclamation), http://www.membranes.com/docs/papers/New%20Folder/Reverse%20Osmosis%20Membranes%20for%20Wastewater%20Reclamation%20Article.pdf. Retrieved on September 22, 2012.

6. Bates W.T., (1998) (Reducing the Fouling Rate of Surface and Waste Water R.O Systems), Hydranautics, Rockton, IL. USA – IWC-98-08.

7. Somicon Ltd., Membrane, Process and Pharmaceutical Technology, Somicon AG – Switzerland, http://www.somicon.com/.

8. Hydranautics LFC1 Membrane Application Update, August 1999.

ВЛИЯНИЕ НА ЕЛЕКТРИЧНИЯ ЗАРЯД НА МЕМБРАНИ ЗА ОБРАТНА ОСМОЗА ВЪРХУ ТЯХНАТА ПРОПУСКЛИВОСТ ПРИ ТРЕТИРАНЕ НА ОТПАДЪЧНИ ВОДИ ОТ КЕРАМИЧНАТА ПРОМИШЛЕНИСТ

Сами Ал Рави, Валентин Ненов, Ахмед Ейдан

Резюме. Статията представя резултати от използването на метода на обратната осмоза за допречистване на промишлени отпадъчни води от керамичния завод в град Ras Al Khaimah (O.A.E.). Иновацията в изследването е използването на модифицирани мембрани с неутрален заряд вместо широко приложимите конвенционални полиамидни мембрани. Последните са трудно приложими при третиране на отпадъчни води от керамичната промишленост чрез метода на обратната осмоза, тъй като тези води се характеризират с висока мътност и с висока концентрация на неразтворените вещества. Наличните данни показват, че конвенционалните полиамидни мембрани бързо се задръстват и значително се намалява тяхната пропускливост. Този ефект е причинен от негативния заряд на конвенционалните мембрани, привличащ положително натоварени частици с органичен и неорганичен характер, които създават отлагания върху мембраните. В настоящето изследване са използвани модифицирани мембрани и данните за тях са сравнени с тези за конвенционалните мембрани. Получените резултати показват, че модифицираната конвенционална мембрана с неутрален товар е с подобрена пропускливост и количеството на пермеата е стабилно през целия период на експлоатация. Модифицираната мембрана за обратна осмоза бе успешно приложена за решаването на проблемите при пречистването на отпадъчните води в завода в Ras Al Khaimah (O.A.E.).

Ключови думи: мембрани, отпадъчни води, обратна осмоза, пропускливост

Engineer Sami Al Rawi, PhD student
Burgas "Prof. Asen Zlatarov" University
Department of Ecology and Environmental Protection
address: 1, Y. Yakimov Str., 8010 Burgas
e-mail: alrawisami@yahoo.com

Professor Valentin Nenov, PhD
Burgas "Prof. Asen Zlatarov" University
Department of Water Treatment
address: 1, Y. Yakimov Str., 8010 Burgas
tel.: 00359 56 716480; e-mail: vnenov@btu.bg

Assistant Professor Ahmed Aidan
American University of Sharjah
Department of Chemical Engineering
e-mail: aidan@aus.edu