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Micellar Enhanced Ultrafiltration for phosphorus removal in domestic wastewater

Rafael Camarillo*, Isaac Asencio, Jesusa Rincón

Departamento de Ingeniería Química, Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha,
Av. Carlos III, s/n, Toledo 45071, Spain
Tel. +34 925 268800; Fax +34 925 268840; email: Rafael.Camarillo@uclm.es

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ABSTRACT

In this paper, a method of Micellar Enhanced Ultrafiltration (MEUF) with Hexadecyltrimethylammonium bromide (CTAB) is proposed to remove phosphate ions from treated domestic wastewaters from the reclamation station of University Campus of Toledo (Spain). This technique is able to reach phosphate rejection coefficients higher than 99% (a phosphate concentration in permeate of 1 mg/L if feed concentration is 95 mg/L). Additional experiments with Hexadecylpyridinium chloride (CPC) and Octadecylamine acetate (ODA) were performed to compare the behaviors of different surfactants. In the first stage, characterization (in terms of Chemical Oxygen Demand, Biological Oxygen Demand, Total Suspended Solids, Volatile Suspended Solids, phosphorus and nitrogen contents, pH, conductivity and turbidity) of real samples from reclamation station has taken place. After that, ultrafiltration experiments with semi-synthetic solutions in total recirculation mode were performed in order to optimize membrane hydrodynamic conditions and to analyze the influence of surfactant nature and concentration on permeate fluxes and phosphate ion rejection coefficients. Best results in terms of both phosphate rejection coefficient and permeate flux are 95% and 186.4 L/h m^2 (LHM) at 1 mM phosphate concentration, 0.1 mM CTAB concentration, 25°C, tangential velocity 3 m/s and transmembrane pressure 4 bar. One of the novelties of this research lies in the surprisingly high performance of unusually low surfactant concentrations (even 10% CMC). Finally, two more additional variables (temperature and pH value) were analyzed to study the further surfactant regeneration. Unfortunately, none of these methods seem to be suitable since they do not abate phosphate rejection coefficients to low enough levels.

Keywords: Phosphate; Eutrophication; Micellar Enhanced Ultrafiltration

1. Introduction

In order to avoid uncontrolled growth of algae in surface waters (eutrophication), concentration of compounds containing phosphorus and nitrogen in domestic and industrial wastewaters coming from reclamation stations must be minimized (Directive 91/271/CEE in European Union). At present, biological removal of nutrients is a very well-known method to remove phosphate ions in these reclamation stations [1].

However, this process is sensitive to changes in composition of feed water and seasonal changes in temperature. Furthermore, this treated water can still contain important concentrations of nitrogen and phosphorus.

Micellar Enhanced Ultrafiltration (MEUF) has been recently proposed as a membrane process to treat

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*Corresponding author

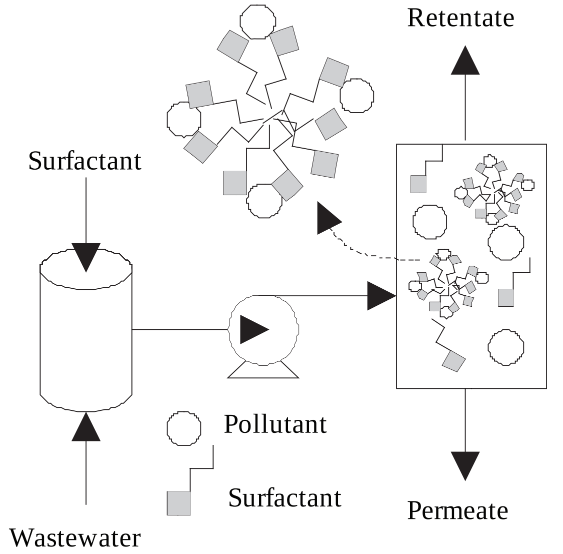

Fig. 1. Diagram of a Micellar Enhanced Ultrafiltration process.

wastewaters containing inorganic and/or organic pollutants in trace concentrations [2-5]. This technique combines high rejection coefficients of Reverse Osmosis (RO) with large permeate fluxes of treated water of Ultrafiltration (UF). It is based on a previous complex formation between surfactant micelles (aggregates of 50–100 molecules) and pollutants. In this way, complex cannot go though ultrafiltration membrane and, consequently, pollutants (micelle–pollutant complexes) concentrate within rejected stream. Meanwhile, permeate stream is almost pure water, only containing traces of surfactant monomers and pollutants that have not been complexed [3]. Fig. 1 shows a schematic diagram of MEUF process for the elimination of a pollutant ion.

On the one hand, when pollutant has cationic nature (as heavy metal ions), anionic surfactants are used, like sodium dodecyl sulfate (SDS). On the other hand, in order to remove anionic pollutants (as phosphate or nitrate ions), cationic surfactants are used, like Hexadecylpyridinium chloride (CPC), Hexadecyltrimethylammonium bromide (CTAB), Octadecylamine acetate (ODA) and Benzalkonium chloride (BC). When concentration of these surfactants is higher than the so-called Critical Micellar Concentration (CMC), they tend to form micelles with positive surface electrical charge and, as a result, pollutant anions can interact electrostatically with them. Table 1 displays some features of these different cationic surfactants. The pH value is a key parameter in the process, since it affects equilibriums of different ionic species in solution and, therefore, their electrical charge [4].

Table 1
Features of different cationic surfactants

Acronym	CMC (mM)	M_w (g/mol)
CPC	0.90	358.01
CTAB	0.92	364.46
ODA	0.90	329.05
BC	5.0	339.30

The first aim of this paper is to study technical viability of a MEUF process to remove phosphorus from treated wastewaters generated in the reclamation station of Technological Campus of Ancient Weapon Factory, located on the banks of River Tajo in Toledo (Spain). This reclamation station treats up to 375 m^3/d of domestic wastewaters from toilets and showers of this Campus belonging to the University of Castilla-La Mancha. The water line of this installation consists of barscreens, a coagulation-flocculation unit, a dissolved air flotation unit, a secondary treatment with active sludge, a sand filter and a chlorine contact tank when treated water is used for irrigation or UV treatment when treated water is returned to River Tajo. The second aim of this research is to evaluate the ability of different variables (pH value, temperature) for the regeneration of surfactant once it has interacted with pollutant ions.

2. Materials and methods

In this work, the behaviors of three cationic surfactants, CTAB [CAS number 57-09-0], CPC [CAS number 123-03-5] and ODA [CAS number 2190-04-7], all of them of analytical grade and purchased from Sigma–Aldrich Co. (USA), have been studied. Potassium hydrogen phosphate, used as a source of phosphorus in semi-synthetic wastewaters, was also purchased from Sigma–Aldrich Co. (USA).

A laboratory-scale installation has been used for MEUF experiments. This installation consists of a two liters jacketed glass reservoir, a Liquiflo 37 F gear pump, a Selecta Frigiterm-10 circulation ultrathermostat, a Techfluid flowmeter (60–630 L/h), a Novasep Micro Carbosep 40 module with a Carbosep M5 membrane (MWCO 10,000 Da, 0.008 m^2), two Bourdon manometers and a needle valve. A diagram of this installation is pictured in Fig. 2.

This study has comprised different steps. Firstly, the characterization of real samples from reclamation station of Campus of Toledo, determining different typical parameters of raw and treated waters (COD, BOD, TSS, VSS, phosphorus and nitrogen contents,

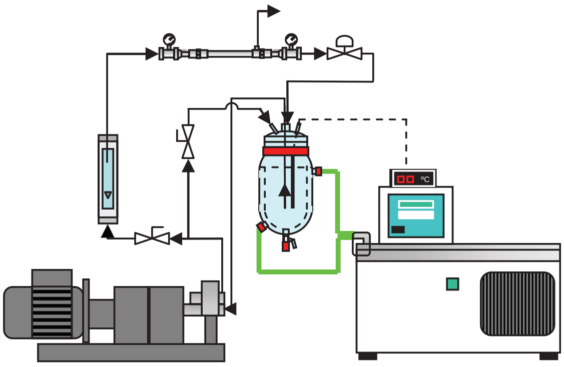

Fig. 2. Diagram of installation of ultrafiltration.

pH, conductivity and turbidity). After that, UF experiments with semi-synthetic solutions (real effluent samples with additional content in phosphorus) have been performed, optimizing hydrodynamic conditions of membrane in total recirculation mode (both retentate and permeate are returned to feed reservoir). In this step, influences of surfactant nature and concentration on permeate fluxes (J_v) and phosphate ions rejection coefficients (RP) are analyzed.

And finally, we have developed UF experiments with semi-synthetic solutions in which all experimental conditions are those optimized in previous step, except pH value and temperature, which have been analyzed as possible measures to regenerate surfactant micelles to be used in a second retention process of pollutant ions.

Total phosphorus concentration in different process streams has been measured by means of a digestion method with potassium persulfate and further spectrophotometric determination of orthophosphate. For this, commercial kits and spectrophotometer Hach-Lange DR 5000 have been used (Hach-Lange GmbH, Germany). Regarding surfactant concentration, it has been indirectly measured with a Total Organic Carbon analyzer Shimadzu TOC-VCSN (Shimadzu Co., Japan).

3. Results and discussion

3.1. Wastewater characterization

First of all, characterization of influent and effluent streams handled in reclamation station takes place. This characterization is developed according to standard methods usually applied by the analytical laboratory of reclamation station. As example, mean measures of different typical parameters for both streams within a period of 1 year are shown in Table 2. Maximum values are also shown in brackets.

Table 2
Characterization of wastewaters (maximum values in brackets)

Parameter	Influent	Effluent
COD (mg/L)	94.10 (297.02)	31.50 (193.70)
BOD_5 (mg/L)	113.02 (360.23)	1.15 (14.00)
TSS (mg/L)	99.92 (762.15)	17.00 (56.03)
VSS (mg/L)	39.52 (210.33)	11.87 (42.30)
TN (mg/L)	71.70 (650.37)	15.90 (57.70)
TP (mg PO_4^{3-}/L)	18.64 (65.45)	0.79 (2.20)
pH	7.43 (8.38)	7.35 (7.97)
Λ (μS/cm)	4,396 (34,800)	1,962 (8,300)
Turbidity (NTU)	63.35 (261.37)	16.82 (199.00)

From this Table, we can conclude that the present treatment scheme is able to fit treated water to disposal standards appeared in both European and Spanish laws (1 mg PO_4^{3-}/L in the case of phosphate). However, we must emphasize that reclamation station of Campus of Toledo is overdimensioned and, as a result, the treatment of this simple domestic wastewater is easy.

Reclamation stations handling larger wastewater volumes and/or industrial wastewaters usually face difficulties to abate nutrients concentrations in effluent stream [6]. Furthermore, environmental regulations are more and more stringent. For these reasons, an additional process of refining effluent stream from reclamation stations is necessary. In following MEUF experiments, phosphate concentration in effluent solution has been increased until a value of 1 mM (95 mg PO_4^{3-}/L) because this is a typical concentration used in bibliography with synthetic solutions [2,3]. In this way we could simulate the effluent from our reclamation station if biological removal process would not work properly.

3.2. Influences of surfactant nature and concentration

Next, ultrafiltration experiments in total recirculation mode are performed to analyze the influence of surfactant concentration on permeate fluxes (J_v) and phosphate rejection coefficients (RP). In this operation mode, both permeate and retentate streams are returned to feed reservoir to keep the constancy in experimental conditions. Since this paper has a length limited by editors, main discussion will only deal with CTAB (the surfactant with best features) and only a brief comparative with the other two surfactants will be described. In all experiments, phosphate concentration in feed was 1 mM (about 95 mg/L) and our target will be to reduce this concentration under 1 mg/L. Regarding surfactant concentration and taking into

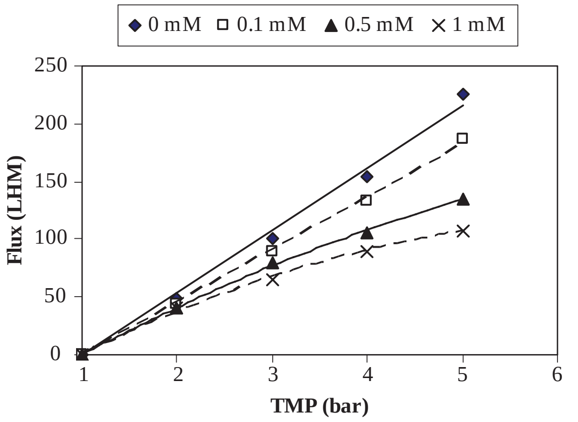

Fig. 3. J_v-TMP profiles in MEUF experiments at different CTAB concentrations (phosphate concentration = 1 mM, v = 3 m/s, T = 25°C).

account some previous studies [7,8], we decided to use a surfactant concentration as low as possible (0.1–1 mM), for both reagent savings and as a tool of fighting against fouling. In Figs. 3 and 4, permeate flux-transmembrane pressure (J_v-TMP) and phosphate rejection coefficient-transmembrane pressure (RP-TMP) profiles, respectively, for total recirculation experiments with CTAB are depicted.

According to Fig. 3, a concentration polarization phenomenon is observed when increasing concentrations of CTAB are added to feed solution, but only at concentrations near 0.5 mM CTAB. In this way, when surfactant concentration is higher, permeate flux profiles are not linear and they tend to asymptotic values for high transmembrane pressures. Furthermore, the surfactant added in the feed can cause membrane fouling due to the formation of a gel layer or pore clogging, which also results in the reduction of permeate flux [2]. This interaction between surfactant molecules and zirconia membrane can be explained taking into account that zirconia atoms are strong Lewis acid sites [9]. Therefore, interaction between active layer of the membrane and amine groups of CPC or CTAB (Lewis bases) can lead to a fouling phenomenon that justifies the drop observed in the permeate flux [10]. Nevertheless, the decline in flux in cross-flow ultrafiltration is less than in dead-end ultrafiltration (used in several studies in bibliography) because of turbulence improvement upon membrane surface [4].

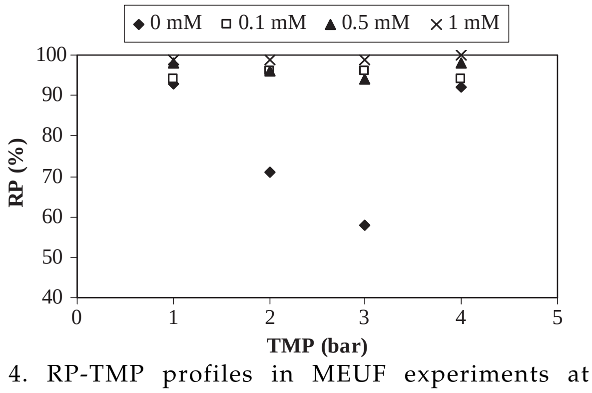

Fig. 4. RP-TMP profiles in MEUF experiments at different CTAB concentrations (phosphate concentration = 1 mM, v = 3 m/s, T = 25°C).

As shown in Fig. 4, the rejection of phosphate ions is higher than 90% when a CTAB concentration higher than 0.1 mM is used. This value contrasts to that obtained for the same concentration of phosphate in the absence of surfactant. Anyway minimum phosphate ions rejection coefficients of about 55% are obtained at intermediate transmembrane pressures. This can be explained if we consider that at neutral pH values zirconia active layer is negatively charged and it is able to reject electrostatically phosphate ions [11]. The high rejection of phosphate with increasing concentrations of surfactant is due to the binding power between micelles and pollutant ions is proportional to their valences [2,3]. Furthermore, the phosphate with valence 2 or 3 plays a role as a bridge between micelles so that the size of micelles is larger. For this reason, we have considered negligible the influence of nitrate in all experiments since nitrate concentration in samples was always lower than 10 mg/L in all semi-synthetic solutions (almost 10 times lower than phosphate concentration). Moreover, nitrate ions possess only one third of electric charge than phosphate ions. Nevertheless, there are deeper studies about the synergistic effects of both nitrate and phosphate ions on the removal of a third pollutant [4,12].

According to our results, experiments with CTAB concentration of about 0.5 mM do not improve permeate flux nor phosphate rejection coefficients obtained with CTAB concentration of about 0.1 mM (phosphate rejection coefficients of 95%). For this reason, in further experiments with CTAB, a concentration of 0.1 mM will be used. It must be emphasized that this concentration is 9 times lower than the CMC for CTAB (Table 1). The satisfactory rejection coefficients for phosphate are due to accumulation of surfactant near membrane, which makes possible the formation of micelles even when bulk surfactant concentration is lower than CMC [7].

On the other hand, surfactant rejection is also an important factor for the effluent to be discharged in the environment. CTAB concentrations were indirectly measured by a Total Organic Carbon method. In this way, constant surfactant concentrations of 0.05 mM are measured in permeate stream within all the concentration range essayed in feed stream (0.1–1 mM). The surfactant rejection increased with its concentration

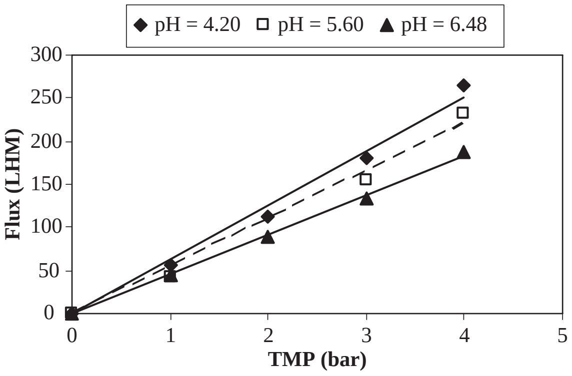

Fig. 5. J_V-TMP profiles in MEUF experiments at different pH values (phosphate concentration = 1 mM, CTAB concentration 0.1 mM, $v = 3$ m/s, $T = 25$°C).

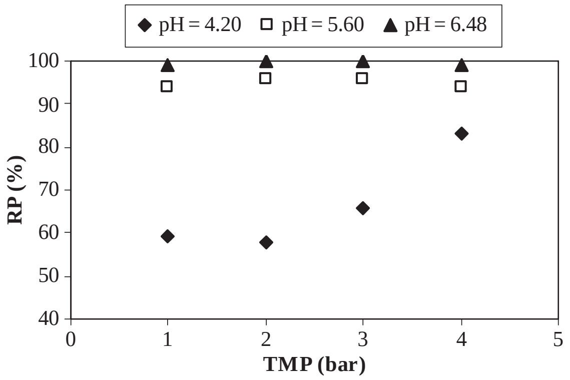

Fig. 6. RP-TMP profiles in MEUF experiments at different pH values (phosphate concentration = 1 mM, CTAB concentration 0.1 mM, $v = 3$ m/s, $T = 25$°C).

in the feed. These results are coherent with those appearing in bibliography [2,4]. This means that the size of the CTAB micelles is large enough not to pass through the membrane pores. On the contrary, the monomers of surfactant pass through membrane, being the monomeric concentration of surfactant almost the same without regard to the concentration of surfactant essayed.

Regarding experiments with CPC and ODA, we can conclude that none of them can compete with CTAB in similar operation conditions. In this way, CPC or ODA concentrations should be increased over 1 mM to obtain phosphate rejection coefficients of about 95%, with a resulting loss of permeate flux of about 30% in both cases. These worse performances of CPC and ODA in comparison with CTAB were already reported in bibliography [4].

3.3. Influence of pH value and temperature

Once technical viability of proposed MEUF method to abate phosphorus concentration in wastewaters with low concentrations of surfactant has been proved, in the second part regeneration of surfactant is studied. This regeneration step is of prime importance if we want to improve economy of process. According to bibliography, there are at least two important ways to regenerate surfactant once micelles have interacted with ions: changing pH value [4] and temperature of solution [13,14]. We describe results only for CTAB, since experimental tendencies of results for CPC and ODA are similar.

In Figs. 5 and 6, experimental values of permeate flux and phosphate rejection coefficients for MEUF experiments at pH 4.20, 5.60 and 6.48 are depicted. The rest of experimental conditions are CTAB concentration 0.1 mM, phosphate concentration 1 mM, tangential velocity v = 3 m/s and temperature 25°C. From Fig. 5 we can conclude that permeate flux decreases as pH value increases. This result can be explained because at lower pH values, zirconia membrane active layer is more positively charged and repels positively charged CTAB micelles. This leads to a flux enhancement because of a lower fouling of membrane [9].

Regarding phosphate rejection coefficients (Fig. 6), they only reach 60% value at pH 4.20. This fact is in agreement with Iqbal et al. [4], since pollutant anion charge changes with pH value. In this case, phosphate anions are less dissociated when pH value decreases from natural pH value 6.48, interactions between micelles and phosphorus species are weaker and phosphate rejection coefficient decreases. The value obtained at pH 4.20 would not be suitable for a complete regeneration of CTAB. Lower pH values were not essayed as they would require massive acid reagent quantities at industrial scale.

Figs. 7 and 8 display permeate flux-transmembrane pressure and phosphate rejection coefficient-transmembrane pressure for MEUF experiments at different temperatures. The rest of experimental conditions are unchanged according to previous

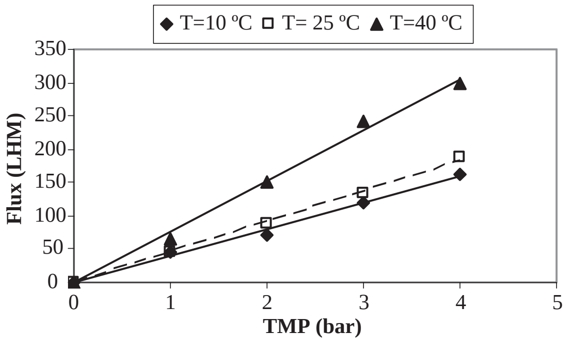

Fig. 7. J_V-TMP profiles in MEUF experiments at different temperatures (phosphate concentration = 1 mM, CTAB concentration 0.1 mM, $v = 3$ m/s).

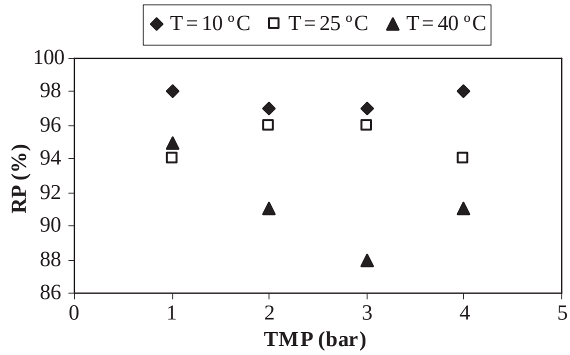

Fig. 8. RP-TMP profiles in MEUF experiments at different temperatures (phosphate concentration = 1 mM, CTAB concentration 0.1 mM, v = 3 m/s).

experiments. Results for permeate flux (Fig. 7) are coherent, since an increase in temperature provokes a decrease in solution viscosity and a subsequent increase in permeate flux. Nevertheless, in the case of phosphate rejection coefficient (Fig. 8), minimum values (higher than 87%) are obtained for higher temperature. This fact is due to two main causes: (1) at higher temperature electrostatic interaction between pollutant anion and surfactant becomes weaker and the micelles break up into monomers or shift to smaller ones [13]; (2) increasing temperature enhances fluxes and drainage rates of micelles across membrane [14].

4. Conclusions

We can conclude that a MEUF process with CTAB can be successfully applied to reduce phosphate concentrations in semi-synthetic solutions coming from a reclamation station of domestic wastewaters. The proposed method seems to be a promising technology to abate trace concentrations of nutrients and other pollutants in effluents from both domestic and industrial reclamation stations, if we take into account that legislations in the matter of disposal are more and more stringent. The best results (95% in phosphate rejection coefficient and 186.4 L/h m^2 in permeate flux) are obtained at 1 mM phosphate concentration, 0.1 mM CTAB concentration, 25°C, tangential velocity 3 m/s and transmembrane pressure 4 bar. At all experimental conditions essayed, CTAB showed a better performance than CPC and ODA. Nevertheless, neither changing pH value nor temperature seem to be a concluding way to regenerate surfactant in a second stage for none of the surfactants studied, since phosphate rejection coefficients are not reduced to suitable levels. According to bibliography [15], precipitation of surfactant could be a better way to achieve this aim.

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