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Ametryn removal with nanofiltration membranes

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ABSTRACT

The wide use of herbicides is indispensable in the agriculture sector to control crop losses, at the same time it causes some environmental problem, i.e. pollution of water sources. A study on the application of nanofiltration membrane in the removal of one kind of herbicide, ametryn, in aqueous solution was carried out in order to evaluate the performances of membrane separation. Ametryn was spiked to the different water matrices feed to a cross-flow nanofiltration pilot-plant. The rejection of ametryn was improved with the presents of both inorganic and organic mater in synthetic water compared with spiked in reference distilled water. The rejection of ametryn was higher in tap water than in distilled water, whereas, the water flux was lower. This may be due to that the NOM in tap water enhanced the size exclusion and charge repulsion of NOM-ametryn complex; meanwhile, both the NOM and NOM-ametryn complex fouled the membranes in tap water.

Keywords: Water treatment; Nanofiltration; Herbicide; Ametryn

1. Introduction

Ametryn, one kind of the triazine herbicides, is a selective systemic pre- and post- emergence herbicide for killing grassy and broad-leaved weeds in banana, orange, coffee, keke, maize, sugarcane etc crops. Although its wide use allowed an enhancement of agricultural production by a significant improvement of the culture yields, the pollution of surface waters and groundwater by ametryn has become an issue in recent years [1]. Even at low concentrations, ametryn may produce disturbances in biocenosis, thus making the water unfit for direct municipal supply.

Traditional water treatment processes, such as absorption and oxidation, are not very fit for removing or degrading ametryn, due to their limited rejection, high cost and byproducts (THMs, organobromine and bromate during oxidation process). Nanofiltration separation for ametryn has no formation of byproducts, and this process is quite appropriate for automatic control. Meanwhile, NF is flexible for the change of water matrix. Furthermore, it could obtain a good rejection for micropollutants. Apart from pesticides [3], also heavy metals [4], natural and synthetic hormones [5] can be mentioned. Additionally, removal of micropollutants by nanofiltration can be combined with softening and removal of natural organic matter (NOM) [6,7]. An example of this is the water facility of Mery-sur-Oise, France where application of nanofiltration technology is reported to be a total success [8]. In view of these concerns, many studies on separation of herbicides using nanofiltration membranes have been done in recent years.

Despite the numerous investigations on specific forms of herbicides, atrazine, were conducted to study the performance of nanofiltration separation for microcontaminants removal [2,3,9–16], little attention was

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drawn to the herbicide of ametryn, another widely used herbicides in the world. This paper reports the results of a pilot-plant experiment on ametryn removal by nanofiltration membranes. pH, inorganic salts, natural organic matter (NOM) were investigated to study the influence on ametryn rejection by nanofiltration filtration.

2. Materials and methods

2.1. Reagents

All salts were prepared fresh using reagent grade chemicals dissolved in deionized water (tap water added in section 3.4). Table 1 shows the quality of experimental water. The sodium chloride and calcium chloride were prepared from the salts NaCl and $CaCl_2$. Ametryn and humic acid were purchased from Sigma–Aldrich.

2.2. Nanofiltration membrane and nanofiltration unit

The pilot consisted of a feed tank, a pump and a spiral module containing a 0.5 m^2 membrane. The membrane material used has an active polyamide layer and was obtained from Toray (Japan), whose properties are shown in Table 2. The experimental setup is shown in Fig. 1. The feed solution is pumped to the membrane by the raw water pump. The filtration in the module occurs in cross-flow. The retentate flow which is not passed through the membrane is recycled to the feed. The permeate flow can be removed or recycled to the feed tank. Sampling is possible from feed pipe, the permeate flow and retentate flow.

Table 1
Quality of experimental water

Experimental water	Deionized water	Tap water
pH	6.57–7.21	6.98–7.45
DOC, mg/L	0.295–0.311	4.60–6.92
NTU	0	0.15–0.45
Conductivity, µs/cm	<10	600–710
UV_{254}, cm^{-1}	<0.001	0.10–0.12

Table 2
Membrane properties

Top-layer material	Active polyamide
Salt rejection, %	55
Zeta potential, mV	–23
MWCO	230
Typical flux / Pressure	$7.5\times10^{-6}/4.5\times10^{5}$

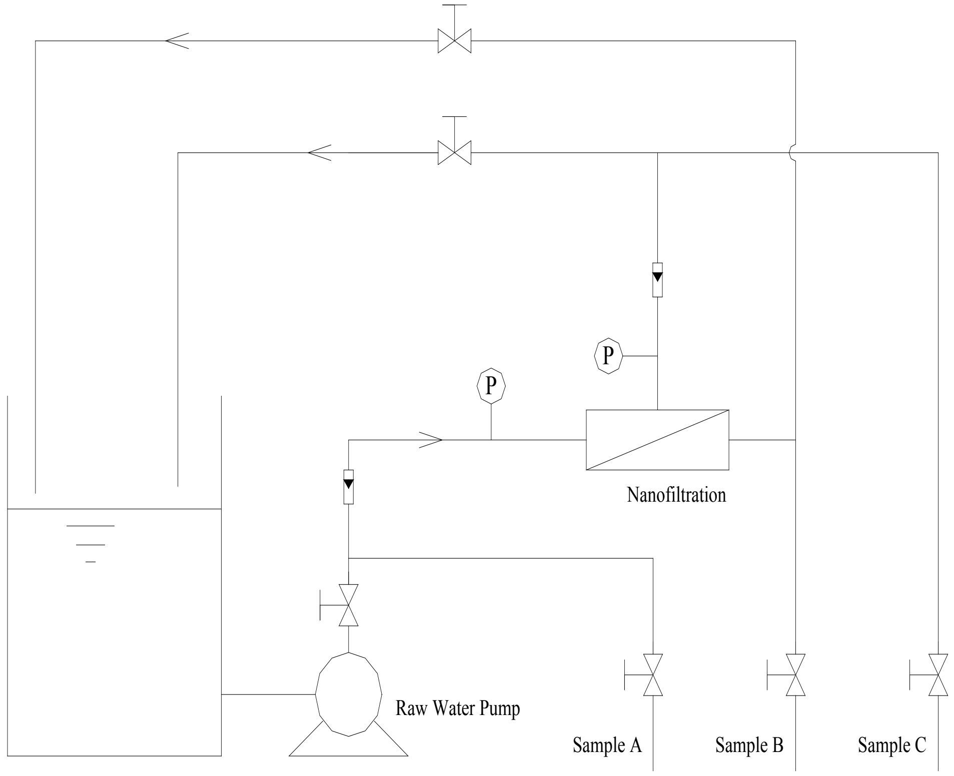

Fig. 1. Schematic experimental unit for NF.

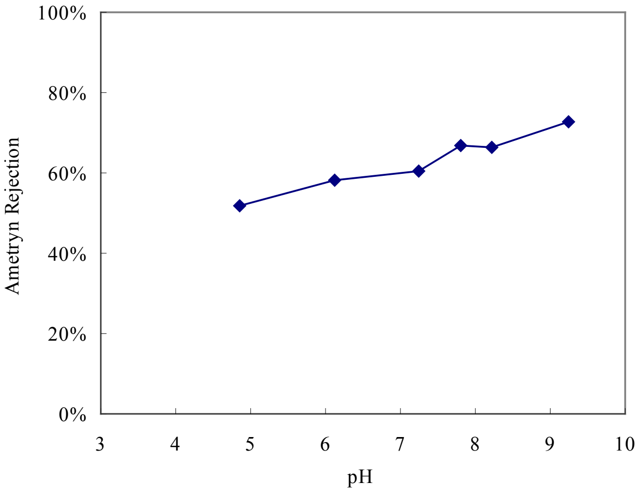

Fig. 2. Effect of pH on rejection of ametryn.

2.3. *Analytical techniques*

Ametryn analysis was carried out by using high performance liquid chromatography (HPLC) with 240 nm wavelength spectrophotometric detection (LC-2010AHT HPLC). The system equipped with shim-pack VP-ODS column (150 mm × 4.6 mm), was performanced with mobile phase of acetonitrile. Dissolved organic carbon (DOC) analysis was carried out on TOC-VCPN equipment for total organic carbon (TOC) determination. DOC corresponds to TOC the after preliminary filtration of the water to be analyzed through 0.45 μm mesh size membranes.

3. Results and discussion

3.1. *Influence of pH on ametryn removal*

Until now, little attention has been drawn to influence of pH on membrane performance in herbicides removal by nanofiltration. However, this factor must not be neglected as the role of pH is important in determining the stability of membrane [17]. In this study, pH was adjusted by HCl or NaOH to investigate the effect on ametryn rejection efficiency. The effect of pH on the ametryn removal is presented in Fig. 2 with initial concentration of ametryn 100 μg/L. As can be seen from Fig. 2, the rejection efficiency was improved with the pH increased. The increase of ametryn rejection at high pH observed could be caused by the hydration swelling of the membrane skin layer [18]. This could result in shrinking of membrane pore size, which could be speculated by the phenomena that the flux was decreasing. And thus, reduced the permeation of solute through the pores of the membrane. Therefore, to get a high rejection of ametryn with membrane separation, high pH was suggested.

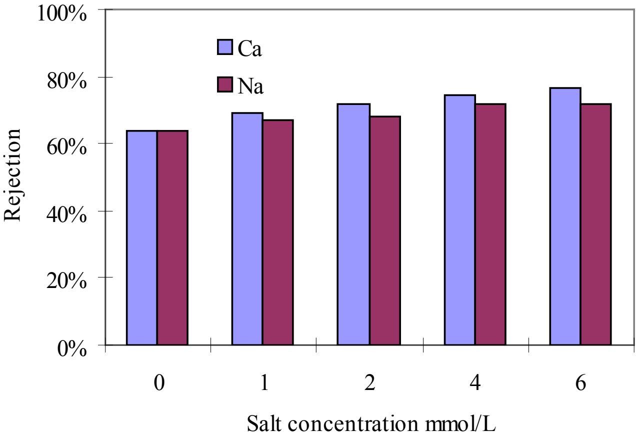

Fig. 3. Effect of inorganic salts on rejection of ametryn.

3.2. *Influence of inorganic salts on ametryn removal*

Membrane separation efficiency depends on the membrane material as well as on the chemical nature of the feed solutions. In the case of electrolyte solutions membrane performances are greatly affected by steric hindrance and electrostatic effects, Donnan partitioning and dielectric exclusion, and by the type of the electrolyte used. Therefore, it is important to study the effect of ion concentration on herbicide rejection. Fig. 3 shows the effect of inorganic salts on rejection of ametryn. Based on Fig. 3, it is obvious that the rejection was improved with the increase of inorganic concentration. This may be due to the reduction in the electrostatic forces of intramembranous repulsion which is reflected by a reduction effect in the actual sizes of the pores [19]. Consequently, better elimination of the herbicides is observed. As for the effect of the different inorganic matter on the herbicide removal percentage, it appears to be different for

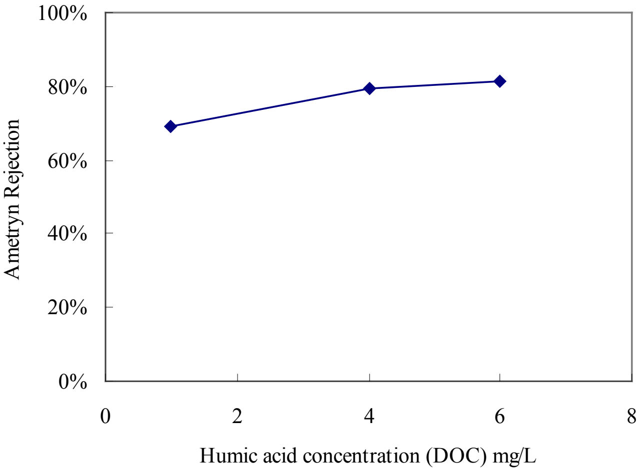

Fig. 4. Effect of humic acid on rejection of ametryn.

the two kinds of inorganic salts, NaCl and $CaCl_2$. The presence of Ca^{2+} offers higher elimination compared to Na^+. This phenomenon may be explained by the fact that divalent ions could block the membrane pores easier for their larger size. Indeed it has been evidenced that ion adsorption might play a significant role in nanofiltration [20], which may narrow the membrane pores and lead to higher rejections. Besides, there is another explanation that divalent ions are much more effective at shielding membrane charge. Both of the effects could decrease the transport of pesticides. As a result, better performance for ametryn separation with the presence of Ca^{2+} was witnessed.

3.3. *Influence of NOM on ametryn removal*

The humic acid shows some influence on ametryn rejection efficiency by nanofiltration filtration, as shown in Fig. 4. The existence of humic substance has a positive effect on ametryn removal with rejection increase from 69% to 81% when the water NOM content varies from 1 to 6 mgl^{-1} of DOC. This observation was in line with the observation by Boussahel et al. whose work showed that the presence of organic matter (humic acid) improved the elimination of some pesticides [15]. The phenomenon may be attributed to the formation of complexes between humic acids and herbicide, which enhance the rejection by steric exclusion. Chiou indicated that hydrophobic humic substances of high molecular weight are not very soluble in water and display a stronger interaction with non-ionic complexes such as triazines [21]. This interaction between herbicides and humic substances can be attributed to a large number of functional groups characterizing the structure of humic materials. Humic acids are larger molecules and exhibit great hydrophobicity, therefore, the retention of herbicides should be greater when treated together with humic acids.

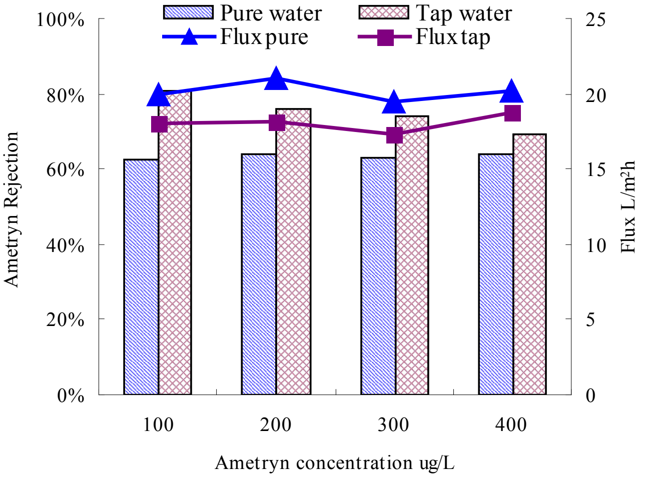

Fig. 5. Effect of ametryn concentration on membrane performance.

3.4. *Influence of ametryn concentration on rejection efficiency*

To study the influence of the ametryn concentration on membrane performance, a new series of experiments was set up with different amount of ametryn spiked to pure water and tap water, respectively. The concentration of the ametryn ranged from 100 µg/L to 400 µg/L, and the tap water was Shanghai city municipal supplied tap water with DOC 1.3 mg/L, total dissolved solids 334 mg/L. Fig. 5 shows the ametryn rejection and membrane flux with TMP 0.8 MPa. It can be seen from Fig. 5 that rejection removal efficiency is not significantly different with pure water of varied ametryn concentration. The results do not indicate that there is an effect of the pesticide concentration on elimination efficiency. This finding is in agreement with the works done by Zhang et al. [10] and Ahmad et al. [3]. But for tap water, in all cases the elimination efficiency is higher than in pure water spiked with ametryn, and the retention decreased with feed ametryn concentration increased. These phenomena can be explained by the fact that the presence of NOM and inorganic matter in tap water enhances the size exclusion, hydrophobicity of NOM-ametryn complex and makes electrostatic repulsion appear during transport through the membrane [10], and also the absorption of ametryn on the membrane surface or macromolecule in tap water by inorganic slats bridging. Consequently, the removal efficiency of ametryn is higher in tap water than in pure water. Meanwhile, the partial substance in tap water which subject to react with ametryn, is not great enough as compared with the experimented ametryn concentration (up to 400 µg/L), therefore, the rejection of ametryn declined with ametryn concentration increment, but higher than in pure water. With respect to membrane permeability, the membrane flux was kept almost constant about 20 L/m^2 with different feed ametryn concentrations for pure water, while it caused a slightly lower permeate flux with tap water. An explanation for this combined effect of invariable flux in pure water and declined flux in tap water is contaminant concentration. The experimented fouling potential in pure water spiked with ametryn is not more than 400 µg/L, just for ametryn; thereby, the flux is kept almost constant. But according to tap water, the NOM and inorganic matrix may cause membrane fouling, so the flux is lower than that in pure water. Also the reason that the osmotic pressure in tap water is higher should not be neglected. It plays a role in making the flux lower as well.

4. Conclusion

In this study, the feasibility of nanofiltration membranes for the rejection of ametryn was evaluated with the perspective of understanding the performance of nanofiltration membranes with a different water matrix. It was found that the rejection efficiency was improved with the pH increased. The presence of organic matter and inorganic salts improved the elimination of ametryn either by forming macromolecules with them or by reducing the pore size of the membrane. The effect of ametryn concentration can be excluded from consideration when it comes to flux performance. The results clearly indicate that NF has a good capacity to remove ametryn from water.

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