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Amoxicillin separation from pharmaceutical solution by pH sensitive nanofiltration membranes

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ABSTRACT

In this study, pH-sensitive polysulfone (PSf)/polyacrylic acid (PAA) nanofiltration membranes were synthesized for separation of amoxicillin from pharmaceutical wastewater. Moreover, amoxicillin separation was enhanced by pH of filtration environment. In order to do so, a flat sheet ultrafiltration (UF) membrane with different pore sizes was prepared by the phase inversion process. A further layer of polyacrylic acid which is sensitive to filtration media pH was grafted onto this fabricated PSf UF membrane surface by UV-initiated graft. Efficiency of amoxicillin separation improved as a result of pH-sensitive nature of amoxicillin as well as surface activity and pH-sensitivity of developed nanofiltration membranes. The results confirmed that increase in molecular weight of polyethylene glycol (PEG) as the pore forming agent in the phase inversion stage, increased the pore size, the amount of acrylic acid deposition on the membrane walls and pH-sensitivity. Also, an increase in grafting intensity decreased the pore sizes and increased their surface charges as well as amoxicillin separation. AFM analysis showed that surface roughness decreases which reflect the reduction in deposition of acrylic acid onto membrane surface valleys. Since the membrane pores are electrically charged, which was confirmed by zeta potential measurement, when the pH of solution increases, the amoxicillin separation by these pH-sensitive membranes increases. Finally, the amoxicillin separation of synthesized nanofiltration membranes at pH = 10 successfully reached relatively high amount of 91%, while acceptable flux of 108.3 l h^{-1} m^2 was maintained. The SEM images also confirmed increase in membrane pore sizes due to increase of PEG molecular weight. The FTIR analysis revealed that the amount of amoxicillin fouled on the membrane surface declined at higher pH due to high repulsion of amoxicillin by membrane.

1. Introduction

Amoxicillin (AMX) is one of the most valuable and highly consumed antibiotics. Thus amoxicillin removal from pharmaceutical wastes offers many economical and environmental benefits. During recent years, recovery of antibiotics and valuable pharmaceutical compounds from wastes has been performed by various methods [1,2] such as oxidation [3–5], ultrasonic irradiation [6], adsorption [7,8], oxidation and reduction [9], membrane filtration [10,11], and combined treatments [12,13]. Studies indicate that membrane separation method is suitable for pharmaceutical applications due to its high efficiency and fulfilling separation without chemical compounds. Since the pore sizes of microfiltration and ultrafiltration membranes are greater than antibiotics, only nanofiltration and reverse osmosis membranes can be used for antibiotic removal [1,10,11,14]. Some studies reveal that filtration processes are highly efficient for removal of antibiotics from wastes. For instance, Zhang et al. [15] reported separation efficiency equivalent to 98.5–99.7%.

Different techniques are used for preparation of ultrafiltration membranes among which the phase inversion process is one of the most widely used methods. In this process, various types of organic [16,17], and inorganic [18–20] additives are used as pore-formers. Ultrafiltration membranes are then converted to nanofiltration membranes via different methods such as interfacial polymerization [21–23], and photopolymerization [24–27].

In this study, polysulfone/polyacrylic acid nanofiltration membranes were prepared through a two-stage process. The membranes were utilized for removal of amoxicillin from pharmaceutical wastes. In the first stage, polysulfone ultrafiltration membranes were fabricated by phase inversion method with polyethylene glycol as a pore forming agent. Different molecular weights of polyethylene glycol resulted in ultrafiltration membranes with different pore sizes [16,17].

In the second stage, photopolymerization of acrylic acid was applied to walls and openings of ultrafiltration membrane in order to prepare a polysulfone/polyacrylic acid nanofiltration membrane

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and to provide the desired characteristics of nanofiltration membrane. The nanofiltration membrane was subsequently utilized as a pH-sensitive membrane for desired filtration due to its capability to allow high water flux to pass and change its surface charge. In fact, utilization of pH-sensitive membranes is a method to improve filtration efficiency [28–34]. In this study, amoxicillin was used as the target antibiotic and effects of pH change, pore sizes, and morphology of membrane surface on determination of dominant separation mechanism were investigated. The effects of primary ultrafiltration membrane synthesis conditions, photopolymerization reaction conditions as well as the effect of feed pH on mechanism and efficiency of amoxicillin separation have been also investigated.

2. Experimental

2.1. Materials

Polysulfone with molecular weight of 75,000 Da was purchased from Acros Organics. Polyethylene glycol with four different molecular weights (400, 1500, 3000 and 4000 Da) and acrylic acid were supplied by Merck Company. Amoxicillin powder was purchased from Daana Pharmaceutical Company (Tabriz, Iran).

2.2. Preparation of polysulfone ultrafiltration membranes

Polysulfone (PSf) ultrafiltration membranes were prepared by phase inversion process using *N*-methyl-2-pyrrolidone (NMP) as the solvent. Using this solvent usually results in a macro void-free membrane [35]. Various additives such as polyethylene glycol [16,17], polyvinylpyrrolidone [36] and some organic materials such as lithium chloride [18–20], are used as pore former agents. In this study, polyethylene glycol (PEG) of different molecular weights were used as pore former.

Polysulfone was gradually added to *N*-methyl-2-pyrrolidone solvent in order to prepare a casting solution, during which solvent was refluxed and solution was heated continuously. During homogenization, casting solution temperature was kept below NMP boiling point (75 °C). PEG was then added to the resulting homogeneous solution and solution was stirred for 24 h. Prepared homogenous casting solution containing PSf: 17 wt.%; PEG: 8 wt.% and NMP: 75 wt.% was cast onto a clean glass plate with 350 μm casting knife and exposed to forced-convection evaporation conditions for 30 s. Then it was immediately immersed in a water coagulation bath at 25 °C to form membrane. A 24 cm^2 sheet of fabricated PS UF membrane was cut in size of cross-flow filtration module, and then tested. Various types of UF membranes were fabricated by using four molecular weights of PEG additive i.e. 400, 1500, 3000, and 4000. Synthesis process is elaborated in our previous work [27].

2.3. Preparation of polysulfone/polyacrylic acid NF membranes

Photoactive surface of UF membrane was prepared in photopolymerization reactor in presence of UV irradiation. Characteristics of acrylic acid monomers and photoactive nature of PS in presence of UV irradiation [37] lead to formation of a polyacrylic acid layer on top of PS membrane i.e. synthesis of NF membrane [27]. The photo reactor used for grafting AA on to the PSf UF membrane was a chamber in which the membrane was placed at the wall to be dipped in AA monomer solution, while the UV lamp (Philips, UVC, Model TUV8W-G8TS, Netherlands) was located at the center. The membranes were irradiated for 0–180 min. Then, they were removed from the reactor and washed with distilled water. The reaction mechanism is reported by Yamagishi et al. [38]. In this process, polymerization of acrylic acid atop the PS membrane surface causes a decrease in membrane pore sizes and leads to negative surface charge of membrane [39–41].

2.4. Filtration experiments

pH of amoxicillin solution was adjusted by addition of 1 M NaOH solution to feed tank. Considering feed tank volume and adjusted pH (6.8, 8.3 or 10), specific volume of 1 M NaOH solution was added to the feed tank. Prepared amoxicillin feed at concentration of 100 ppm was tested by NF membranes in a cross-flow filtration mode at 3 bar. Flux of filtration membranes was calculated by the following equation:

$$Flux\left(\frac{l}{h \cdot m2}\right) = \frac{l}{A \cdot t} \tag{1}$$

where l is the filtered volume of the feed, A the membrane area and t is the permeation time.

After filtration was done, concentrations of permeate and feed were measured by WTW Spec flex 6600 spectrophotometer (Germany) at 229 nm wavelength [42]. The amoxicillin concentration was estimated by using the standard curve. Finally, the separation percentage of amoxicillin was calculated according to the following equation:

$$R\% = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p and C_f are the permeate and feed concentrations, respectively.

2.5. SEM analysis

Cross-section of UF membranes prepared by different pore former materials were analyzed by SEM. To do so, samples were broken in the liquid nitrogen and then coated with a thin layer of gold for preparing a conductive film. The samples were then imaged in a HITACHI S4160 SEM (made in Japan) at 10^{-9} bar and voltage of 20 kV.

2.6. Atomic force microscopy (AFM) analysis

Atomic force microscopy analysis was done by Veeco device (Auto Probe-cp-research, USA). The analysis was performed in contact mode with the scanning speed of 2 Hz and a resolution of 256 × 256 pixels. In order to perform scanning, a silicon cantilever was used with a height of 10–15 μm and a diameter of 10 nm. The roughness parameter is a surface property of the membrane and has different definitions. For instance, Peak to Valley Distance is the distance between the highest point and the deepest surface points. Mean roughness is the surface mean value to the reference plane. Finally, root mean square (RMS) roughness is calculated through the calculation of data standard deviation. The Mean roughness (R_m) and RMS roughness are described as follows, respectively:

$$R_m = \frac{1}{N}\sum_{i=0}^{N}|Z_i - Z_{avg}| \tag{3}$$

$$R_{RMS} = \sqrt{\frac{\sum_{i=0}^{N}(Z_i - Z_{avg})^2}{N}} \tag{4}$$

where Z_{avg} is the average value of Z in a given zone, Z_i the current value, and N is the number of points in the zone of interest.