Evaluation of Membrane Resistance and Operational Variables for the Micellar-Enhanced Ultrafiltration of Ibuprofen Containing Aqueous Waste

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Abstract
Micellar enhanced ultrafiltration (MEUF) of Ibuprofen (IBU) from aqueous stream was carried out by using a 6KDa hollow fiber polysulfone membrane. The surfactant under study was sodium dodecyl sulfate (SDS) and effect of parameters such as initial IBU concentration, varied SDS concentration and operating pressure on the additional resistance and rejections of SDS and IBU were observed. The rejection of SDS and IBU decreased with the increase in operating pressure while the rejection of SDS increased with increasing SDS concentration. The surfactant recovery was attempted by using potassium iodide (KI) as the precipitant. The rejection of IBU and SDS were 90% and 65% respectively with 0.098MPa transmembrane pressure and 100 ppm IBU. More than 80% surfactant was recovered from the retentate stream.

Keywords: micellar enhanced ultrafiltration (MEUF), Ibuprofen (IBU), Sodium dodecyl sulfate (SDS), additional resistance, surfactant recovery.

Nomenclature
\( A \) area \((m^2)\)  
\( m \) mass \((kg)\)  
\( V \) volume \((m^3)\)  
\( \rho \) density \((kg/m^3)\)  
\( \pi \) osmotic pressure  

Subscripts
1 initial conditions  
2 final conditions

1. Introduction
The global demand for quality water, whether for purposes of drinking, sanitation, irrigation and industrial use, has been on a continuous rise and there has been overwhelming concern in recent years about water treatment and reuse requiring the strictest standards [1]. Pharmaceutically active compounds are of emerging concern because of their intrinsic biological activity, which can lead to fatal consequences [2]. It is estimated that approximately half of the pharmaceutical wastewaters produced worldwide are discarded without specific treatment [3]. The presence of pharmaceutical and personal care products (PPCP’s) in the environment has effects like development of antibiotic

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resistant microbes in the aquatic environment; retardation of nitrite oxidation and methagenosis and the potential increased toxicity of chemical combinations and metabolites [4].

The behavior of many trace contaminants of concern during treatment and in receiving environments is the subject of much study and several recent reviews [5, 6]. Conventional wastewater treatment plants were not designed to target trace contaminants, but instead are focused on removal of bulk constituents, such as solids and oxygen- demanding organic materials. Advanced treatment techniques such as membrane bioreactors, activated carbon and advanced oxidation are effective for removal of some PPCP’s, but efficacy varies and, in some cases, more toxic by-products may be formed [5, 7, 8].

Membrane technology has become the most popular technology amongst the drinking water purification and wastewater treatment technologies. Nanofiltration and reverse osmosis can be applied easily for these purposes but they are relatively high pressure operating techniques and thus with high energy requirements and membrane fouling on a mass scale. Microfiltration and ultrafiltration are strongly recommended technologies when there is space limitation and varied feed wastewater quality [9]. Also, it can be easily applied as they operate at comparatively at low pressure and the basic principle is size exclusion. But, the limitation is of small molecules which could escape from the membrane pores, thus by increasing the size by binding the low molecular weight compound with organic molecules like surfactants; this is the basis of micellar enhanced ultrafiltration. It has been very well have reported that the use of cationic surfactant for selective separation of antibiotics from wastewater with no effect of the other dissolved organic matter on the retention efficiency [10, 11].

Ibuprofen (IBU), categorized as an NSAID (non-steroidal anti-inflammatory drug) is the most commercially available drug for musculature and inflammatory disorders. IBU is a recalcitrant pharmaceutical which remains untreated in the common wastewater treatment plants and has negative impact on the aquatic systems [12, 13]. IBU has been reported to have a negative impact on the microbial communities and aquatic life [14, 15]. Based on the estimations by Bhattamishra et al. [16], it can be concluded that anionic surfactant sodium dodecylsulfate (SDS) provides a better solubilization behavior for ibuprofen in comparison to cationic surfactant cetyltrimethylammonium bromide (CTAB). Considering the low toxicity of anionic surfactant and its biodegradability as reported by Usharani et al. [17], makes its application in wastewater treatment obvious and environmentally benign.

In the present study, the MEUF of IBU using a polysulfone hollow fiber membrane with anionic surfactant SDS. Hollow fiber membranes are widely used in the industry for various purification processes, including wastewater treatment. The results reported herein provide a proof-of-concept for the feasibility of removing drugs by MEUF, while also providing greater insight into the physiochemical factors influencing the removal of contaminants from wastewater streams during MEUF. There have been no reports on such study in the literature, thus the present study is an attempt for practical application of MEUF for wastewater treatment.

2. Experimental

2.1. Chemicals

The Anionic surfactant, Sodium dodecyl sulfate, SDS (Thomas Baker) was used for all the MEUF experiments. The non-steroidal anti-inflammatory drug (from Sigma Aldrich, ST. Louis, USA) purchased was Ibuprofen Sodium Salt (Fluka, Sigma Aldrich, ST. Louis, USA); whose structure
is listed below along with its physiochemical characteristics in Figure 1. Methanol, Acetonitrile, and o-phosphoric acid (HiMedia) were of HPLC grade. All solutions were prepared in Deionized (DI) water (Merck Milipore) and all the other chemicals were used without further purification.

![Chemical structure of Ibuprofen sodium salt](image)

**Figure 1.** Chemical structure of Ibuprofen sodium salt [2-(4-(2-methylpropyl) phenyl) propionic acid], M.W. 228.26 g/mol; pK\(_a\) = 4.5; Log \(K_{ow}\) = 3.97.

### 2.2. Membrane

A pilot scale plant obtained from Pall India Pvt. Ltd. (Mumbai, India) was used for MEUF experiments. Membrane used was a tubular hollow fiber membrane with molecular weight cut-off (MWCO) of 6kDa (Microza Module) and cross flow area of 0.2 m\(^2\), with working pH range from 1 - 14. Before the commencement of the ultrafiltration experiment, the membrane was cleaned using 0.1N NaOH and then with deionized water. The pure DI water flux was obtained under standard test conditions with no transmembrane pressure (TMP) and membrane permeability was calculated. Pure DI water was calculated before and after the experiment to check for the fouling of the membrane module.

### 2.3. Experimental Set-up

The schematic of the ultrafiltration unit is shown in Figure 2. It consists of a feed tank (1) of capacity 5 L followed by Quattroflow 1000 Series pump (Shipped with Pilot scale plant obtained from: Pall India Pvt. Ltd., Mumbai, India) (2) which is merely a four- piston diaphragm pump and membrane assembly (3) which is divided into two sections. The first section consisted of tubular asymmetric hollow fiber polysulfone membrane with a membrane layer both on the inside, and on the outside of the fiber. The transmembrane pressure is developed by operating the feed \((V_1)\), retentate \((V_2)\) and permeates \((V_3)\) side valves, respectively. The operational variables were kept constant along the experiment, and measured by pressure \((P_i, P_o)\).

### 2.4. Procedure

In all the batch experiments, predetermined amounts of IBU and SDS were added into the DI water. Both the solutions were premixed adequately for micellization and then used for the ultrafiltration experiments. In each experiment, the initial feed volume was 2 L and after 1.5 L of permeate was collected. Permeate and the retentate were sampled and determined for the IBU and SDS concentration respectively, the permeate flux was determined by measuring the volume of
permeate collected per unit time. After each experiment the membrane was thoroughly washed to regain its permeability.

Figure 2. Schematic of the experimental setup: (1) Feed Tank, (2) pump, (3) membrane assembly, \( P_i \), Inlet Pressure; \( P_o \), Outlet Pressure; \( V_1 \), Feed Valve; \( V_2 \), Retentate Valve; \( V_3 \), Permeate Valve.

The retentate generated from each experiment, enriched with the surfactant was treated with potassium iodide (KI) to precipitate out SDS as potassium dodecyl sulfate (KDS). The kraft temperature of KDS is higher than that of SDS, thus the temperature of the KI and surfactant mixture is reduced and surfactant is recovered.

The permeate flux was calculated from the equation (Eq. 1) below.

\[
J = \frac{\Delta V}{\Delta t A} = \frac{J_f}{A}
\]

where, \( J \) denotes the permeate flux (m\(^3\)/m\(^2\)s), \( \Delta V \) is the change in volume of the permeate sample (m\(^3\)), \( \Delta t \) is the time difference (s), \( J_f \) is the permeate flux shown on the rotameter (m\(^3\)/s) and \( A \) denotes the effective membrane surface area (m\(^2\)).

When DI water is used in the ultrafiltration unit, the DI water flux \( J_w \) is given by the expression

\[
J_w = \frac{P}{\mu_m R_m} ; \quad R_m = \frac{P}{J_w \mu_w}
\]

where, \( J_w \) is the DI water flux (m\(^3\)/m\(^2\)s), \( P \) is the transmembrane operational pressure (P\(_a\)), \( \mu_w \) is the viscosity of DI water (10\(^{-3}\) P\(_a\).s at 25\(^o\)C), \( R_m \) is the hydraulic resistance of membrane itself (m\(^{-1}\)). \( R_m \) of the hollow fiber membrane at different pressures can be calculated by Eq. 2.

In resistance-in-series model, the permeate flux in the ultrafiltration system can be expressed by the equation (Eq. 3)

\[
J = \frac{P - \Pi}{\mu_p R_t} = \frac{P - \Pi}{\mu_p (R_m + R_f)}
\]

where, \( J \) is the permeate flux (m\(^3\)/m\(^2\)s), \( \Pi \) is the osmotic pressure across the membrane (P\(_a\)), \( \mu_p \) is the viscosity of permeate, \( R_t \) is the total resistance (m\(^{-1}\)) and \( R_f \) is the additional resistance due to deposition of the solute and concentration polarization.
In this study, the osmotic pressure was insignificant in comparison to the operating pressure and the viscosity of permeate & retentate are similar to DI water. Thus, the equation for additional resistance ($R_f$) can be given as follows.

$$R_f = \frac{P}{J\mu_w} - R_m$$  \hspace{1cm} (4)

### 2.5. Analysis

The concentration of IBU was measured using high performance liquid chromatography HPLC (Knauer pump k-200; Detector k-120), equipped with a C18-RP (WATERS Technologies) at a wavelength of 220nm. The solvent composition for IBU determination was 75:25 acidified water (pH 3.0) and acetonitrile respectively. The SDS concentration was measured using an indirect-UV capillary electrophoresis (Agilent Technologies Pvt. Ltd.).

### 3. Results and Discussion

#### 3.1. Effect of Operating Pressure

**3.1.1. Effect of operating pressure on the permeate flux and additional resistance**

The effects of operating pressure on the flux of permeate at a constant IBU concentration of 100 ppm and constant SDS concentration of 9mM. From Figure 3, it is evident that as the operating pressure increased there is an increase in the permeate flux. As the Operating pressure increases, there is a convective transport of fluid across the membrane surface. This is also evident from the Equation 3, where the increase in pressure leads more transport of solution across the membrane and overcomes the osmotic pressure and the resistance. Also, there is an increase in the additional resistance $R_f$ with the increasing pressure which is illustrated from Figure 3. Beyond 0.15 MPa operating pressure there is a slight increase in the additional resistance, this can be attributed to the fact that the resistance increased due to adsorption of the drug on the membrane surface and concentration polarization, which is not significant beyond 0.15 MPa [18].

![Figure 3. Effect of operating pressure on the permeate flux and additional resistance.](image)

**3.1.2. Effect of operating pressure on the observed IBU and SDS rejection**

The effect of operating pressure on the rejection of IBU and SDS was studied and has been
presented in Figure 4. From the experimental data it is evident that the rejection of both IBU and SDS decreased with the increase in operating pressure. This can be attributed to the fact that at higher operating pressures the micellization is compact and therefore decreases the micelle solubilization capability. Thus, less amount of IBU is solubilized in the micelles at a higher operating pressure [19]. In addition, the increase in effective driving force caused the augmentation in the convective transport of solutes filtered through the ultrafiltration membrane to the permeate solutions [20].

![Figure 4. Effect of operating pressure on IBU and SDS rejection.](image)

3.2. Effect of Feed SDS concentration

3.2.1. Effect of feed SDS concentration on the permeate flux and additional resistance

At a fixed IBU concentration of 100 ppm and 0.098MPa the initial SDS concentration was varied from 4mM and 82mM. It is evident from Figure 5, that the permeate flux decreases sharply with a gradual increase in the feed SDS concentration. As per the calculation from Equations 1 – 4, the hydraulic resistance of membrane (RM) at 0.098MPa the additional membrane resistance (Rf) increased from 6.72 x 10^{-7} m^{-1} to 26.59 x 10^{-7} m^{-1} with an increase in feed SDS concentration. The primary reason for the increase in additional resistance can be attributed to the fact that at the membrane surface, due to the free surfactant monomers and IBU molecules, cake formation takes place. Thus, membrane fouling and concentration polarization at the membrane surface leads to decrease in permeate flux. At SDS concentration above CMC value, the deposited layer offered more resistance as micelles aggregate to offer more resistance which can be seen in Figure 5. As the SDS concentration increased from 9mM to 82mM the resistance increases.

3.2.2. Effect of feed SDS concentration on the observed IBU and SDS rejection

From Figure 6, it is clear that as the feed SDS concentration increased from 4mM to 82mM, the SDS rejection increased from 48.34% to 75.12% due to the increase in the aggregation number of the SDS micelles. Figure 6, also shows that even at low SDS concentration well below the CMC with the surfactant micelle concentration to be negligible, the IBU rejection was more than 80%. Similar results were reported by Huang et al. [18], and the reason was such high rejection values is due to the concentration polarization effect, leading to a SDS layer deposition on the membrane.
surface where the concentration might have exceeded the CMC values of SDS. Thus, micellization occurs on the membrane surface leading to IBU rejection. Another important observation is that as the SDS concentration increases the CMC values, the micelle formation leads to IBU solubilization in the surfactant micelles core and higher rejections are expected. But the figure shows that as the SDS concentration increased above CMC value, the rejection decreased from 91.41% to 84.96%. Also, the SDS rejection increased with increasing SDS concentration above CMC value and maximum rejection was achieved at a CMC value which is 10 times more than the original value. This phenomenon is due to the leakage of SDS micelles from the ultrafiltration membrane because of change in the micellar shape from spherical to cylindrical or plate like micelles. These types of micelles can easily pass through the pore of the ultrafiltration membranes [21].

![Figure 5](image5.png)

**Figure 5.** Effect of feed SDS concentration on the permeate flux and additional resistance.

![Figure 6](image6.png)

**Figure 6.** Effect of feed SDS concentration on the observed IBU and SDS rejection.
3.3. Effect of Initial IBU Concentration

3.3.1. Effect of initial IBU concentration on the permeate flux and additional resistance

To study the effect of initial IBU concentration, the SDS concentration was fixed at 8mM and an operating pressure of 0.098MPa. From the Figure 7, for a varying IBU concentration from 20ppm to 100ppm, the permeate flux decreased, but at a smaller magnitude. The decrease in the permeate flux and the increase in the additional resistance was because of the continuous adsorption of the IBU molecules and deposition of layer on the membrane.

![Figure 7. Effect of initial IBU concentration on the permeate flux and additional resistance.](image)

3.3.2. Effect of initial IBU concentration of the IBU rejection and SDS rejection

Figure 8, shows that the IBU rejection was higher at lower concentration of 20ppm but the rejection slightly decreased with the increase in IBU concentration, which can be attributed to the complete solubilization of IBU at lower concentration than at higher concentrations. The SDS rejection was unaffected with very small changes in the rejection with increasing IBU concentration. This can be attributed to the increase in the aggregation number of the micelles in the presence of the large concentration of IBU that could make the micellization process easy.

3.4. Current limitations of MEUF and the practical implications for wastewater treatment

MEUF of IBU containing aqueous stream displayed higher rejection values as compared to the ultrafiltration. The most important limitation of the MEUF process is the loss of the surfactant monomers and other micellar aggregates through the membrane surface [11]. Though SDS is a non-toxic surfactant, its mass concentration in the wastewater gives toxic effect to the aquatic organisms [22].

Thus, recovery of the SDS would be an economical way of dealing with its massive polluting behavior. Purkait et al. [23] have reported a two-stage chemical treatment method based on the reactivity of the surfactant with an alkali salt which leads to the precipitation of the surfactant and then precipitating the surfactant with the help of a metal halide. They also reported more than 90% recovery of CPC from a CPC-eosin mixture. Wu et al. [24] had reported a similar way of recovering surfactant, but the precipitation was reported on the basis of the kraft temperature.
Below the kraft temperature, the surfactant precipitates and thus can be separated from the aqueous stream. The kraft temperature of potassium salt of dodecyl sulfate (KDS) is much higher than the kraft temperature of SDS which is reported to be 35°C. Thus, below this temperature KDS precipitates and it can be separated.

Figure 8. Effect of initial IBU concentration on the permeate flux and additional resistance.

3.5. Recovery of SDS from the retentate stream
For the recovery of surfactant the method given by Wu et al. [24] was followed, in which potassium iodide in the 2:1 molar ratio was added to the retentate stream containing different concentration of SDS. From the Figure 9, it can be seen that as the concentration of SDS increased, the precipitation of potassium dodecyl sulfate (KDS) also increased which can be attributed to the fact that at 2:1 KI to molar ratio the surface tension in the KI-SDS solution breaks and the K⁺ influence increases leading to formation of KDS which can be separated by lowering the temperature of the solution to less than 25°C [24]. They also reported the effective application of KDS for MEUF and a better surfactant than SDS as the kraft temperature of the KDS (35°C) is higher than that of SDS (16°C).

Figure 9. Recovery of SDS from the retentate stream, with precipitation carried out at 20°C and KI to SDS molar ratio 2:1.
4. Conclusions

The permeate flux and the additional resistance along with rejection of SDS and IBU was studied and analyzed using micellar enhanced ultrafiltration. The presence of anionic surfactant SDS, facilitated the removal of non-steroidal anti-inflammatory drug, Ibuprofen, demonstrating that MEUF can be applied for the removal of PPCP’s from aqueous streams. The permeate flux and the additional resistance increased while the rejections of IBU and SDS both decreased with operating pressure. As the feed SDS increases, higher rejections of SDS was observed with a marginal decrease in the IBU rejections. To make the process economical, the surfactant from the retentate stream was recovered by using precipitation and separated based on the principle of kraft temperature. Thus, with proper selection of surfactant, MEUF can be successfully designed for the separation of pharmaceutical active compounds from wastewater.

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References


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