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REMOVAL OF TETRACYCLINE FROM INDUSTRIAL WASTEWATER USING REVERSE OSMOSIS TECHNOLOGY

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ABSTRACT

The present work study the removal of Tetracycline from industrial wastewater by utilizing a pilot plant contains microfiltration system accompanied by the reverse osmosis membrane (RO**).** The impact of various conditions, including pressure (6-10 bar), pH (5-9) and initial concentration (10-100) mg/l at room temperature was investigated on the treatment efficiency and water permeability. The analysis indicates that the removal efficiency was risen to (99 percent) with increasing the pressure and Tetracycline concentration throughout the first 90 min. It was noticed that the flux is directly proportional to the pressure when it increased from 6 to 10 bars, on the other hand it was inversely proportional to the Tetracycline concentration. The Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS) were removed using an RO membrane with high efficiency reaching almost 99 percent.
Keywords: Tetracycline, Reverse Osmosis, Pilot Plant**,** membrane technology.

Introduction

The “World Health Organization (WHO)” says more than 1 billion people are unable to get clean water. Health monitoring authorities say that every day about 4,000 children die from waterborne diseases caused by water contamination around the world (Tang *et al*., 2002). Hence, because of environmental threats, the world is facing serious drinking water crisis. Due to human activities and the disposal of effluents from industrialization the available water supplies are contaminated. If proper treatment methodologies are not developed or adopted, more serious health problems will arise in the near future as a result of water contamination with waterborne pathogens due to increased pollutant discharge “(toxic chemicals, pharmaceuticals, heavy metals, fertilizers, sludge, endocrine disrupters, etc.)” into the water sources (Gaikwad *et al*., 2010). Pharmaceutical industry effluents are characterized by a high content of organic matter, deep color, toxicity, and high content of salt. Among all pharmaceutical substances with an environmental impact, antibiotics play an important role in both veterinary and human medicine, owing to their high usage levels. The production of antibiotic-resistant bacteria are the worst issue that can arise from the presence of antibiotics at low environmental concentrations (Elmolla *et al*., 2009; Gabelich *et al*., 2002). Antibiotics are persistent and bioaccumulative toxins and biologically active compounds that have been produced to impact organisms; thus, they have the potential to adversely affect either aquatic or telluric habitats, even at low concentrations in the range of (µg–ng) per liter. Furthermore, antibiotics can also induce antibacterial resistance in microorganisms and be responsible for multiple allergic reactions (Bound *et al*., 2002; Díaz-Cruz *et al*., 2008; Homem *et al*., 2010). Antibiotic residues are present in a variety of environmental matrices, such as hospital and wastewater treatment plants (WWTPs), surface and groundwater, soils and sediments (Batt *et al*., 2008; Benito-Peña *et al*., 2006; Homem *et al*., 2010). Some antibiotics such as erythromycin, ampicillin, tetracycline, ulphamethoxazole, and penicilloyl groups are released primarily into the atmosphere through excretion (about 30–90%), entering the WWTP where they are not fully eliminated, and contaminating natural waterways (Ding *et al*., 2005; Hernando *et al*., 2006).

Membrane technology has been reported as a potential alternative to the treatments currently being used for treating pharmaceutical-containing effluents. It has been found that membrane performance is strongly based on the physical properties of the membrane along with pollutant chemistry (Ginebreda *et al*., 2010). Microfiltration and ultrafiltration are typically low-pressure membranes that are primarily used to eliminate particulate matter consisting of comparatively larger particles that can be seen with the naked eye, while RO membrane fall into the category of high-pressure membranes and can be used to extract organic and inorganic micropollutants or divalent or multivalent ions (Watkinson *et al*., 2009; Yeomin *et al*., 2020).

The aim of this study is focused on the removal of Tetracycline from industrial wastewater by utilizing a pilotplant of integrated membrane filtration system for the removal of suspended solids accompanied by an RO membrane. The impact of RO on the extraction efficiency of tetracycline and permeate flux under various working conditions has been examined.

Material and Methods

Materials

Tetracycline antibiotic ($C_{22}H_{24}N_2O_8$) with molar mass (444.435 g/Mol) was obtained from Samarra Pharmaceutical

Industry (Iraq). **Fig. 1** shows the chemical formula of antibiotic.

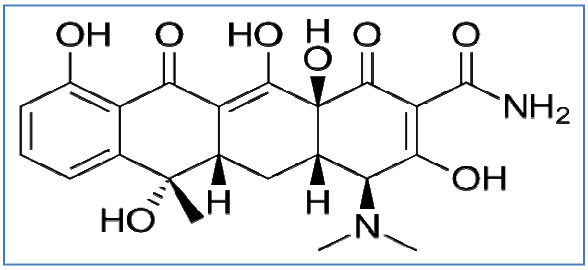

Fig.1: Chemical formula of Tetracycline

Sodium chlorides (99 percent purity, Mwt 58.44, and CDH-India), Hydrochloric acid with (40 percent purity, Mwt 36, from England BDH-E), and Sodium hydroxide (99.9 percent purity Mwt 39, and Merk- Germany) were used to change the pH and to gather the salts needed for the analysis.

Table 1: Specifications of micro filters (Green Life Co., Ltd.)

Type of membrane	**Microfilter**
Model	Yenvqee
Material	Poly-proline micro fibers
Module	Hollow fiber
Size(I.D,length)(inch)	(4x20) inch
Max operating temp ($C^{o)}$	38
Max applied (bar)	17.22
Pore size	(5,1) micron

Table 2 : Characteristics of RO Membranes (Vontron membrane technology co.,ltd).

Type of membrane	RO
Model	ESPA1-4040
Material	Composite polyamide
Module	Spiral wound
Size (I.D, length) (inch)	(4x40)inch
Effective area (m^2)	7.9
Max operating temp ($C^{o)}$	45
Max pressure (bar)	41.4
Manufacture	Hydranautics
pH range of water	2-10
Surface charge (mv)	-5

Three types of membranes were used in the pilotplant, two micron membranes with pore sizes of (5) and (1) micron respectively, and RO membrane. The micron membranes installed upstream of the RO housing. The characteristics of two micron filters and reverse osmosis referred to in Tables (1 and 2)

Experimental work

The tests were accomplished with a pilot plant as seen in Fig. 2 of Permeate Recycling. The model consists of two hollow fiber Microfilters with parallel use of RO cells, feed tanks, two types of pumps (low pressure of tap water positioned just after water tank and highly pressurized pump positioned just before cell membrane), valves, flow meter varies (2 to 150) l/min , and pressure gages. The dimensions of a device are (80 × 60 × 190) cm.

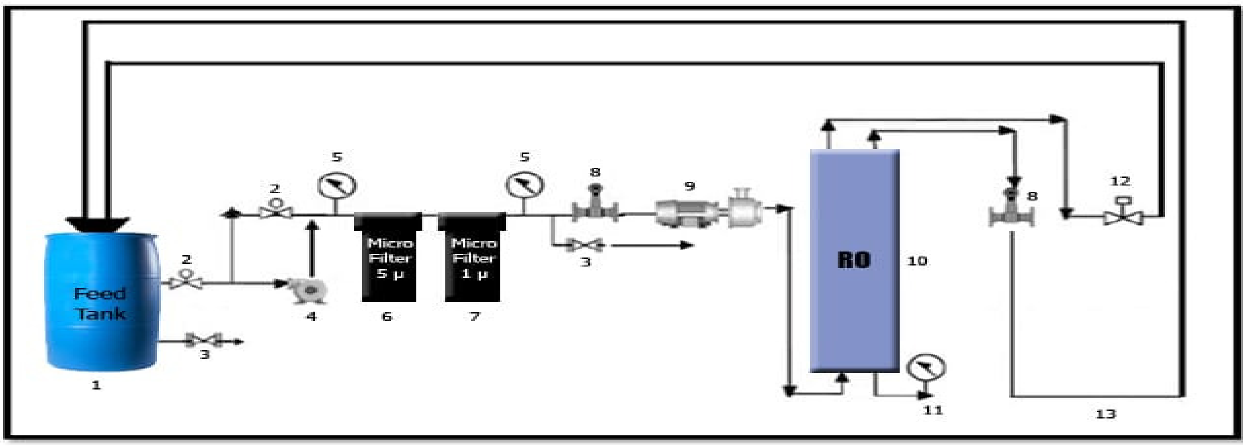

Fig. 2: Schematic diagram of the pilot plant
1-Feedtank, 2-By pass valve, 3-Outer valve, 4-Low pressure pump, 5 and 11-Pressure gauges, 6 and 7-Micromembranes, 8-Flow meters, 9 and 11-High pressure pumps, 10-RO membrane, 12-Outlet of the valve, 13- Permeater valve.

Experimental Procedure

The experimental procedure can be described by the followings:

a. Tetracycline solution was prepared in five concentrations of 10, 20, 50, 80 and 100 mg/l by mixing the Tetracycline powder with tap water in the feed tank, to test the impact of concentration on the removal of Tetracycline.

b. Specific pressures; for each Tetracycline concentration, 6, 8 and 10 bars were applied to test the effect of pressure on the removal of Tetracycline.

c. Preparation of tetracycline-salt mixture solutions containing tetracycline with the addition of pure sodium chloride to tap water. The concentrations of TDS were: 600, 2000, 3000 mg/l, with the (constant concentration of tetracycline, pH and pressure applied) to test the impact of time on TDS removal.

d. Specific pressures; 6, 8 and 10 bars with a constant concentration of (TDS and Tetracycline) were applied to test the effect of pressure on the removal of Tetracycline and permeate flux.

e. Preparing different concentrations of the Tetracycline 10, 20, 50, 80 and 100 mg/l. With constant pressure, to study the relation between tetracycline concentration and permeate flux.

f. Studying the effect of different pH (5 , 7, and 9) on the removal efficiencies. The initial feed pH variance was controlled by adding dilute (0.1 M) of NaOH and HCl to the feed tank.

Sample Analysis

All samples were analyzed in laboratory of Al-Khwarizmi College of Engineering-University of Baghdad. Shimadzu spectrophotometer UV-1800 UV-VIS (japan) was used to measure the absorbance of light by tetracycline at 362 nm wavelength to determine Tetracycline concentration. The removal efficiency (R) is calculated by equation (1), (Al-Abachi *et al*., 2005).

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad ...(1)$$

Where R is retention factor (%), C_p is concentration in the permeate (mg/L), $C_f$is feed concentration (mg/L).

Flux is calculated by using equation (2) (Christy *et al*., 2002).

$$J = \frac{Q_p}{A_S} \qquad ...(2)$$

Where:

J: permeate flux (l/m.h.bar).

Q_p: permeate flow rate (l/hr).

As: membrane surface (active) area" (m^2).

Results and Discussion

Effect of Tetracycline Concentration on the Removal Efficiency

The removal efficiency of Tetracycline at various concentrations using RO membrane at constant pressure 10 bar and pH=9 is shown in Fig. 3. The elimination of Tetracycline exceeds 99.8%. It should be noted that the efficiency of removal improved by increasing the Tetracycline concentration. Such findings clearly showed that at the lower-concentration, the membrane fouling was mainly due to the blockage of the pore. Through increasing the concentration of the feed, cake formation was found to be more influential on the membrane surface (Harris *et al*., 2002).

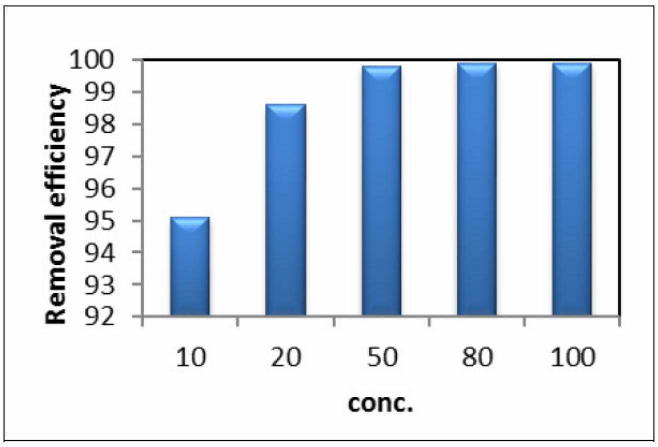

Fig. 3: Removal Percentage of Tetracycline at different concentration using RO membrane at (P=10 bar, pH=9)

Effect of Pressure on Tetracycline Removal Efficiency.

The relation between Tetracycline removal efficiency and pressure at a concentration of 100 mg/l and pH = 9 is shown in Fig.4. The removal increases with increasing the pressure; this means that the dynamic force improves with increasing operating pressure and decreases the resistance through the membrane and regulates the thickness of the boundary layer, leading to compaction of the membranes. In Fig. 4 The efficiency of removal hits 99.8% at 10 bars. This result agrees with (Koyuncu *et al*., 2008; Shahlaa *et al*., 2018) findings.

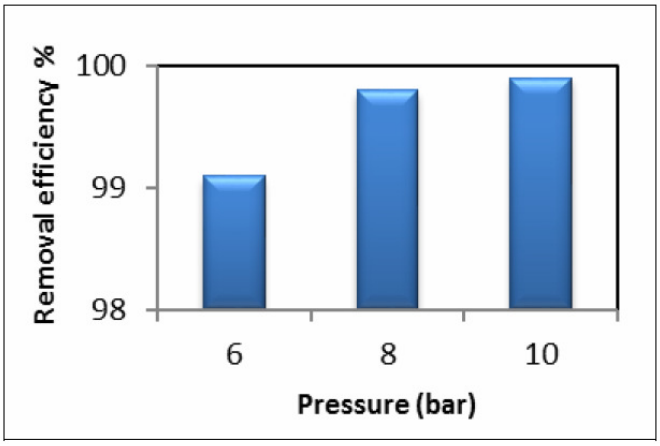

Fig. 4: Percentage removal of tetracycline at different pressure using RO membrane at (conc.=100 ppm, pH=9)

Effect of pH on the Removal Efficiency

The relationship between the pH and Tetracycline removal efficiency is shown in Fig. 5. Due to the fact that the rise in pH would result in a rise in the precipitation of dissolved salts, which would foul the membrane surface and thereby increase the resistance to the passage of Tetracycline through the membrane. On the other hand, decreasing the pH of the solution by adding HCl acid would increase salt solubility and consequently decrease the rate of salt scaling on the membrane surface, which contributes to a reduction in the osmotic pressure of the solution and consequently to the removal of Tetracycline (Ismail *et al*., 2008).

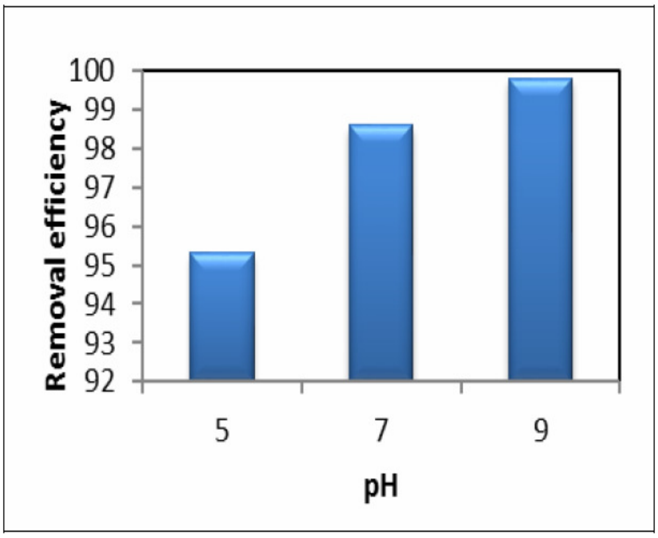

Fig. 5: Percentage removal of Tetracycline at different PH using RO membrane at (pressure=10 bars, conc. = 100 ppm)

COD Removal

The COD removal reaches up to 99 % after (90) minutes. This can attributed to the efficient removal of Tetracycline by RO membrane as shown in Fig. 6.

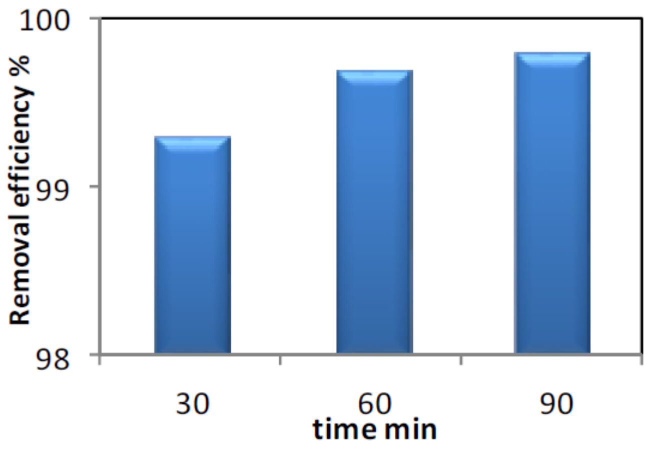

Fig. 6: COD removal after (30,60,90) minutes, TDS=3000, concentration=100mg/l, pH = **9** and pressure=10 bars for tetracycline

TDS Removal

The TDS removal with time is presented in Fig. 7. The TDS initial concentration was 3000 mg/l, Tetracycline concentration was set at 100 mg /l, a pressure of 10 bars, and pH=9. All experiments were performed for 90 min to maintain stable state conditions. The RO membranes are efficient in removing the salt from the wastewater. The efficiency of removal for mixing tetracycline-salt solution reaches up to 99.8 %.

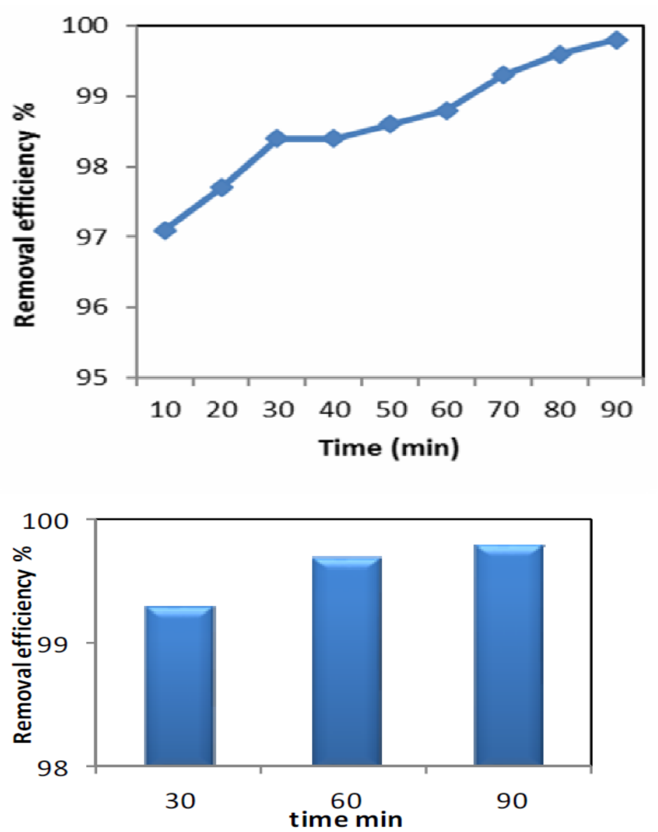

Fig. 7: TDS percent removal percentage with time for the wastewater contaminated with tetracycline using RO membrane

The Effect of Tetracycline Concentration on Permeate Flux

The time variation of permeate flux at different tetracycline concentrations and operating pressure are shown in Figs. 8,9, and 10. The effect of tetracycline concentrations on the permeate flux with time at operating pressure equals to 6 bars is shown in Fig. 8. Tetracycline concentration of 20, 50, and 100 mg/l were used. The flux ranges between 25.8 to 9.3 (l/m^2. h) At a concentration of 20 mg/l. While at 50 mg/l, flux ranges between 22.6 to 11.2 (l/m^2.h). Finally, for 100 mg/l the flux was between 16.9 - 11 (l/m^2.h). All these testes achieved at the same TDS concentration (3000 mg /l) and pH = 9.

With increasing concentration of tetracycline, the permeate flux was reduced due to increasing osmotic pressure and concentration polarization on the membrane surface (AL-Bastaki *et al*., 2007; Berek *et al*., 2018; Kristia *et al*., 2009), Also, when the concentration of the feed solution reaches the concentration of the solute on the surface of the membrane or boundary layer, there will no longer be a concentration gradient in the boundary layer and therefore no back transport of the solute and that leads to zero flux. Membrane fouling occurs at the experimental period by adsorption of tetracycline onto the membrane surface (Shahlaa *et al*., 2018). Fig. 9 And Fig. 10 show the same results for operating pressure of 8 and 10 bars, respectively.

Fig. 11 illustrates the relationship between Tetracycline concentration and the flux at different operating pressure and the TDS is 3000 mg/l. It should be noted that, due to the accumulation of solute on the membrane surface, the fluxes decrease linearly with increasing concentrations at the same strain, resulting in rising the polarizing layer and decreasing fluxes. This result agrees with (AL-Bastaki *et al*., 2007).

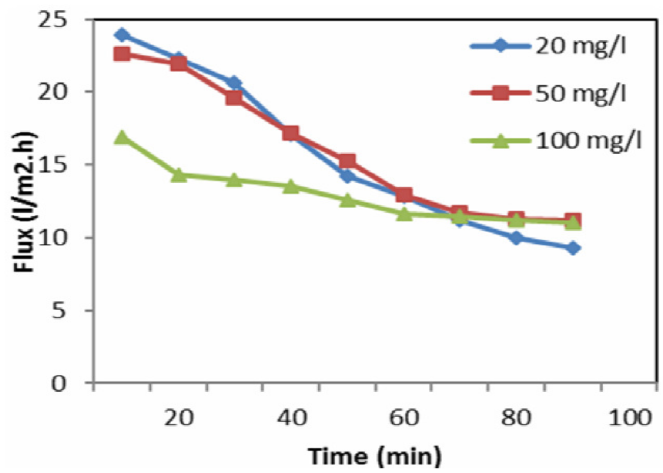

Fig. 8: Permeates flux with time for the tetracycline at the different concentration(P=6 bars)

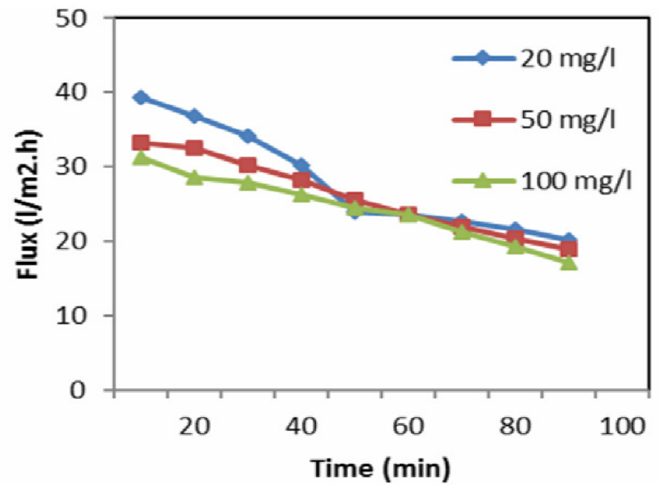

Fig. 9: Permeates flux with time for the tetracycline at the different concentration(P=8 bars)

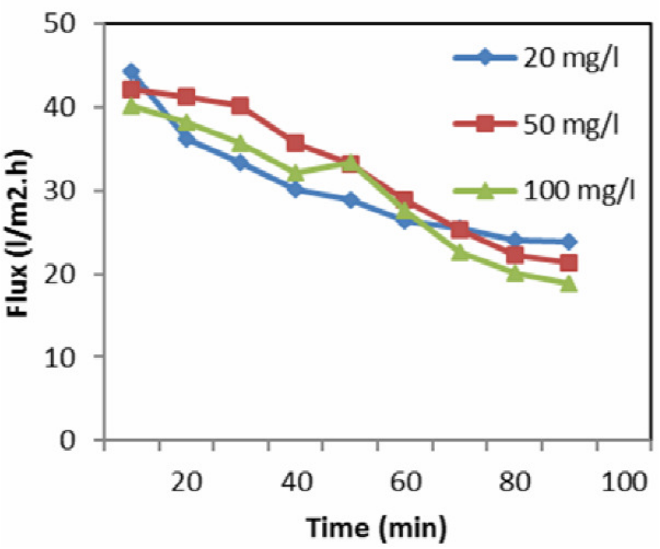

Fig. 10: Permeates flux with time for the tetracycline at the different concentration(P=10 bars)

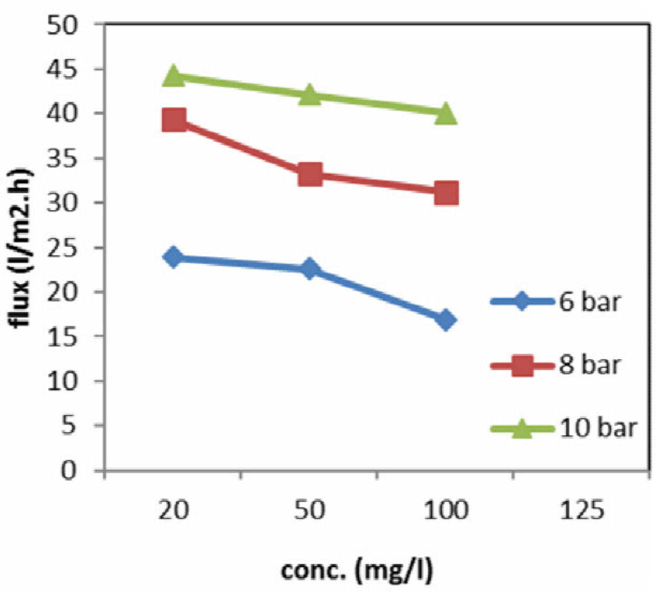

Fig. 11: The Relation between Concentration and Flux at different Pressure

Effect of the Pressure on the Flux

Referring to the Figs. 8 to 10, if the pressure increases from 6 to 10 bars, the flux increases due to the solution-diffusion model and the resistance of the membrane surface is overcome (BeCheerNg, 2013; Greene *et al.*, 1996). For each run the operation time was 90 min. The coefficient of mass transfer and the polarization concentration layer increase with increasing operating pressure (Chiu *et al.*, 1999; Mahmood, 2020). The relationship between Tetracycline pressure and flux is seen in Fig. 12, when the TDS is 3000 mg/l and the concentration of Tetracycline is 100 mg / l. The flux rises linearly by increasing the pressure under the same operating conditions. This is due to pressure gradient on driving force (Baier *et al.*, 1987).

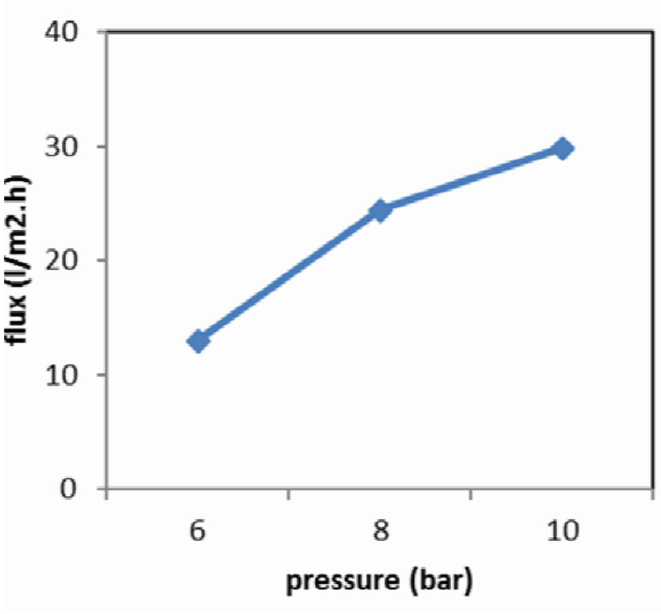

Fig. 12: The relation between pressure and flux at tetracycline concentration = 100 mg/l

Conclusion

A. RO membrane has proved to be an efficient wastewater method for extracting tetracycline, TDS and COD.

B. The Removal percentage increases in RO membrane with increasing concentration of Tetracycline, pH, and pressure.

A. Permeate flux from the RO membrane is proportional to applied pressure, but is inversely proportional to the concentration of Tetracycline.

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