Arabian Journal of Chemistry (2021) 14, 103230

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Extraction of penicillin G from aqueous solution using a membrane contactor: Numerical investigation

Yan Cao [a], Afrasyab Khan [b], Shaheen Sarkar [c,*], Ahmad B. Albadarin [c]

[a] School of Mechatronic Engineering, Xi'an Technological University, Xi'an 710021, China
[b] Institute of Engineering and Technology, Department of Hydraulics and Hydraulic and Pneumatic Systems, South Ural State University (SUSU), Lenin Prospect 76, Chelyabinsk 454080, Russian Federation
[c] Department of Chemical Sciences, Bernal Institute, University of Limerick, V94 T9PX Limerick, Ireland

Received 10 March 2021; accepted 17 May 2021
Available online 23 May 2021

KEYWORDS

Membrane;
Modelling;
Pharmaceutical wastewater;
Penicillin G;
Simulation

Abstract In the current study, the treatment of pharmaceutical wastewater containing penicillin G treatment using a hollow fibre membrane contactor was investigated. A mathematical model based on the finite element method was developed. The extraction was performed using Shellsol TK as organic solvent containing 5% Aliquat 336. The effect of feed pH, flow rate and temperature were examined for the extraction of penicillin G from aqueous solution. The results showed that there is reasonable good agreement between experimental data and modelling values. It was found that increasing temperature from 10 °C to 30 °C increases the penicillin G extraction from 33% to 54%. Also, penicillin G extraction was decreased from 34.7% to 25.1% with increasing pH from 5.5 to 6.5 while it grew to 45.8% when the pH of feed solution was 7. Furthermore, the results showed the diffusive flux is favourable for the system and penicillin G extraction but the convective flux has negative impact on the system in terms of penicillin G extraction. It was concluded that a hollow fibre membrane contactor has the potential for use in wastewater treatment through it is important to improve diffusive flux in the system to enhance penicillin G extraction.

1. Introduction

The world is continuously being polluted with different chemical compounds of both natural and anthropogenic origin. Growth in world population has resulted in an increase in these chemicals, and subsequently their higher concentrations in surface water, ground water, streams, and so on (Egea-Corbacho et al., 2019; Sarkar et al., 2018). Pharmaceuticals

* Corresponding author at: University of Limerick
E-mail address: shaheen.sarkar@ul.ie (S. Sarkar).
Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.arabjc.2021.103230
1878-5352

and related compounds are considered as one of the main pollutants which have caused environmental concern in recent years (Richardson et al., 2005). In pharmaceuticals wastewaters, caffeine, theophylline and theobromine, antibiotics amoxicillin and penicillin G are known as emerging contaminants (Buchberger, 2011). Antibiotics have a significant environmental influence, even at low concentrations, as they can lead to resistance to bacteria and other microorganisms (Verlicchi et al., 2012). Penicillin G (Pen G) as a representative β-lactam compound is one of the most important chemicals for production of penicillin. It is a monocarboxylic acid containing a heterocyclic ring, and has been used for treatment of many bacterial diseases (Li et al., 2008). It is imperative that it is removed from wastewater before it is discharged into the environment.

Different treatments such as sewage treatment plants (Gulkowska et al., 2008), advanced oxidation processes (Roccaro, 2018), membrane technology (Plakas et al., 2006), and reverse osmosis (Egea-Corbacho et al., 2019) have been implemented for removing penicillin G from wastewaters. Egea-Corbacho et al. (Egea-Corbacho et al., 2019) successfully used nanofiltration for removing Pen G and made it useable in many applications. Hospital and domestic wastewater in Qatar containing high concentrations of antibiotics were treated by filtration, UF and chlorination, RO and ozonation. It was found that RO and ozonation are the most effective methods for the wastewater treatment (Al-Maadheed et al., 2019). A hydrophobic PVDF-HFP hollow fiber membrane contactor was used for the elimination of Pen G from wastewater. The amount of Pen G flux obtained was 1.50×10^{-3} $kg/m^2.s$ at the optimum process conditions (Abbasi et al., 2021). Non-disperse solvent extraction of Pen-G from the aqueous phase was conducted using 5 wt% organic solution of Aliquat 336 as extractant. The optimum conditions were Pen G concentration of 218 ppm, T = 40 °C, feed flow of 51 mL/min, and organic phase flowrate of 144 mL/min (Abbasi et al., 2021).

With respect to traditional techniques, hollow fibre membrane contactor (HFMC) demonstrates great potential because of its high surface area per volume ratio and independence from aqueous and organic solutions flow rates, and has been recognised as an alternative method for wastewater treatment. Using HFMC has several benefits including prevention of foaming, channelling, entrainment and corrosion problems in the system, easy scale up, up to 500 m^{-1} surface area per unit of module volume (Pabby and Sastre, 2013). Given these advantages, it will be interesting to investigate pharmaceutical wastewater treatment using HFMCs in more detail.

Thanks to progress in computer science and software, it is possible to evaluate different separation processes by developing computational models qualitatively and quantitatively, and to facilitate the interpretation of complex data. Computational fluid dynamic (CFD) as an effective technique can provide an opportunity to investigate fluid flow, extraction or removal of contaminants, reaction kinetics in pharmaceutical wastewater treatment using HFMCs. It has been widely used for the study of different processes such as gas absorption, metal extraction, and membrane distillation. Ghadiri and co-workers used CFD methodology for investigation of CO_2 absorption using 2-amino-2-metyl-1-propanol (AMP) as solvent in HFMC (Ghadiri et al., 2017). Moreira and Puma (Peralta Muniz Moreira and Li Puma, 2021) proposed a CFD model for the investigation of pharmaceuticals and contaminants of emerging concern (CECs) removal by a UV/H_2O_2 process in helical microcapillary photoreactors. Removal of 4-chlorophenol from wastewater was evaluated by CFD technique using ANSYS Fluent software (Sandhibigraha et al., 2020). The treatment was conducted in a packed bed reactor. Through CFD simulation, the influence of the flow rate, the compound inlet concentration, and the packed bed height and its porosity on the static pressure, mass imbalance, velocity, and stress–strain field inside the packed bed reactor was studied (Sandhibigraha et al., 2020). Good agreement was found between experimental data and the developed CFD model results. Ghadiri et al. (Ghadiri et al., 2018; Ghadiri and Shirazian, 2013; Soltani et al., 2016) evaluated mass transfer or heat transfer and hydrodynamic of different liquid–liquid systems for metal extraction and phenol removal from wastewaters. The contaminant or metal distribution in organic or aqueous phases, pressure and velocity distribution were obtained at various operating parameters. However, there is little data about investigation of pharmaceutical wastewater treatment in HFMCs using a mathematical model and the current study can provide more information and understanding in this regards.

In the current study, non-dispersive solvent extraction of penicillin G from pharmaceutical wastewater with an organic phase of Aliquat 336 in Shellsol TK was investigated. A two dimensional model was developed using COMSOL Multiphysics software (COMSOL, Inc. software company) because of its irrefutable advantages like high precision, memory adequacy and the application simplicity. The developed model output was compared with experimental data reported in the literature (Smith and Hossain, 2007). Furthermore, the effect of operational parameters and membrane characteristics on the removal of penicillin G was evaluated.

2. Model development

The schematic of the hollow fibre membrane contactor for the non-dispersive solvent extraction is shown in Fig. 1. The organic solution containing 5% Aliquat 336 was entered through the shell side of the membrane contactor. The organic solution fills microporous membrane pores due to hydrophobic characteristic of membrane. Conversely, the aqueous solution containing penicillin G counter-currently passes through the tube side. The flow rates of the aqueous solution and organic solution were varied in the range 180–260 mL/min. The other operating conditions kept constant were: pH of 7 and concentration of penicillin G at 10 mol/m^3 in the feed solution (Smith and Hossain, 2007). The complex forms between penicillin G and Aliquat 336 in interphase of organic and aqueous solutions on the membrane surface. Then, the formed complexes penetrate through membrane pores into shell side of membrane contactor. The assumptions for the developed model were provided in Table 1.

The developed model equations are derived for three subdomains including tube side, microporous membrane, and shell side. The contactor model equations for mass transfer and momentum transfer for each of the three subdomains are given in Table 2 (Bird et al., 2002). (Bird et al., 2002). In Table 2, the symbols r, z, ρ, D, C, and V are radial direction (m), axial direction (m), fluid density, penicillin G diffusion coefficient (m^2/s) and concentration (mol/m^3), and fluid velocity (m/s) in three subdomains. Also, t, s, and m symbols are

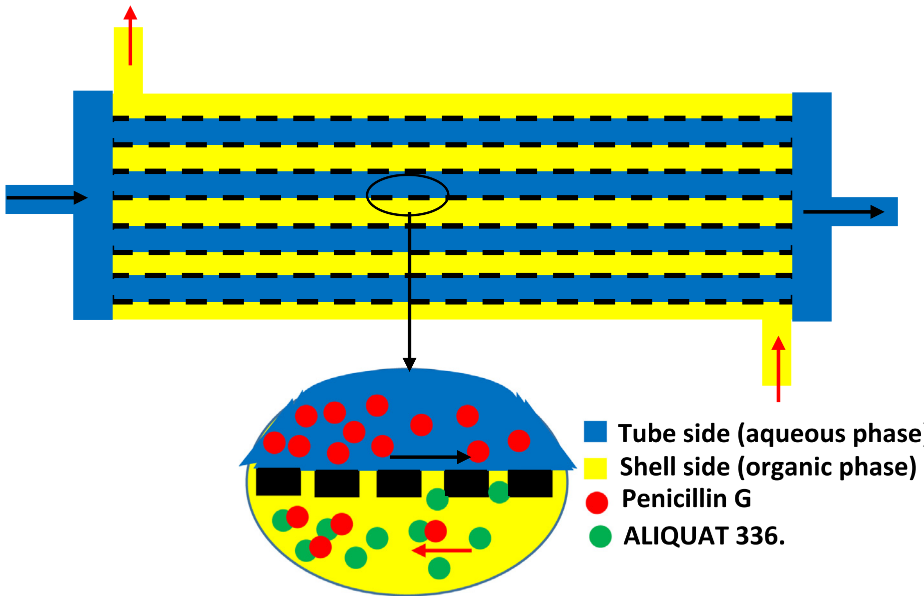

Fig. 1 Schematic of membrane contactor for extraction of penicillin G from wastewater into an organic solution.

Table 1 The developed model assumptions.

No.	Assumption
1	Fluid flow for aqueous and organic solutions is laminar.
2	Isothermal conditions as well as steady state
3	Hydrophobic membrane
4	Uniform porosity distribution in the membrane

Table 2 Model equations for penicillin G extraction in hollow fibre membrane contactor (Bird et al., 2002).

Balance equations	Mathematical expressions
Tube side	
Mass transfer	$D_{PenG,t}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{PenG,t}}{\partial r}\right)+\frac{\partial^2 C_{PenG,t}}{\partial z^2}\right]=V_{z,t}\frac{\partial C_{PenG,t}}{\partial z}$
Momentum transfer	$V_{Z,t}=2u\left[1-\left(\frac{r}{r_1}\right)^2\right]$
Shell side	
Mass transfer	$D_{PenG,s}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{PenG,s}}{\partial r}\right)+\frac{\partial^2 C_{PenG,s}}{\partial z^2}\right]=V_{z,s}\frac{\partial C_{PenG,s}}{\partial z}$
Momentum transfer	$\nabla.V_{Z,s}=0$
	$\rho\frac{\partial V_{Z,s}}{\partial t}-\nabla.\left[\eta\left(\nabla V_{Z,s}+\left(\nabla V_{Z,s}\right)^T\right)\right]$
	$+\rho\left(V_{Z,s}.\nabla\right)V_{Z,s}+\nabla p=F$
Membrane	
Mass transfer	$D_{PenG,m}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{PenG,m}}{\partial r}\right)+\frac{\partial^2 C_{PenG,m}}{\partial z^2}\right]=0$

tube, shell, and membrane sides of the contactor. The diffusion coefficient ($cm^2\ s^{-1}$) was estimated using the Wilke-Chang method (Poling et al., 2001)

2.1. Numerical solution

Suitable boundary conditions were considered for the solution of numerical equations in the developed model. At the outlet boundaries of tube and shell sides, a convective flux condition was considred in which the mass transfer of penicillin G was considered to be only a convection mechanism. The inlet penicillin G concentrations and velocities were applied as the inlet boundaries in the derived equations. In addition, a thermodynamic equilibrium was considered at the aqueous-organic interface utilizing a distribution coefficient. Furthermore, on the solid wall of fibre *No slip* condition was considered. For the numerical solution of the model's equations, a finite element method was used in COMSOL package, V5.4. The operating conditions and membrane specifications are given in Table 3.

3. Results and discussion

3.1. Effect of temperature on Pen G extraction

Fig. 2 shows the influence of temperature on the extraction of penicillin G from wastewater into organic solution. The modelling results were compared with experimental data reported in literature (Smith and Hossain, 2007). It can be seen that the amount of extraction is higher for modelling results. It could be attributed to the assumption in the developed model that fresh organic solution enters into membrane contactor while in the experimental data the organic solution is circulated in the module. Smith and Hossain (Smith and Hossain, 2007) estimated higher extraction if the system runs for a longer time. Furthermore, it should be noted that increasing temperature from 10 °C to 20 °C can increase significantly the Pen G extraction but there is a little increase in the Pen G extraction with a rise in temperature from 20 °C to 30 °C. This is because the penicillin G distribution coefficient between two phases changes slightly in the temperature range between 20 °C and 30 °C.

3.2. Effect of temperature on diffusive and convective flux distribution

The effect of temperature on diffusive flux of penicillin G in the tube side is provided in Fig. 3. It can be observed that

Table 3 The operating parameters and membrane specifications used in the simulations (Smith and Hossain, 2007).

Parameters	Unit	Values
Pen G initial concentration	mol/m^3	10
Distribution ratio (m)	–	7.5–14.7
Flow rate of aqueous phase	mL/min	180–240
Flow rate of organic phase	mL/min	180–240
Temperature	°C	10–30
Fibre type	–	Polypropylene
Fibre inside diameter	μm	240
Contactor inside diameter	cm	6
Effective fibre length (L)	m	0.15
Fibre thickness	μm	30
Porosity of the fibre (ε)	vol%	0.4
Tortuosity of the fibre (τ)	–	2.5
Number of fibres	–	10,000
Operation mode	–	Counter-current and once through

an increase in temperature from 10 °C to 30 °C increases diffusive flux of penicillin G along the membrane contactor. In fact, it is directly related to the distribution coefficient of penicillin G between two phases. The maximum penicillin G diffusive flux was obtained at slightly more than 2.5e^{-3} mol/m^{2}s at 30 °C and at bottom section of membrane contactor. Moreover, a rise in temperature increases the diffusion coefficient of penicillin G inside the pores of the membrane. The profile of convective flux of penicillin G in the middle of tube side is demonstrated in Fig. 4. A change in the system temperature in the range of 10–30 °C has been used in the simulation to study the influence of temperature on convective flux. According to Fig. 4, it can be seen that the convective flux decreases along the tube side of the membrane contactor. It means that the Pen G extraction happens along membrane contactor and the convective flux that is in the Z direction decreases. The penicillin G convective flux decreased from 0.134 mol/m^{2}s to 0.095 mol/m^{2}s, and reached 0.065 mol/m^{2}s at temperature of 30 °C. Furthermore, it should be pointed out that the contribution of penicillin G convective flux in the *z*-direction is 100 times higher than axial the diffusive flux. This is because the aqueous solution velocity is considerably high in the z direction which leads to higher penicillin G convective flux.

3.3. Effect of feed solution pH on Pen G extraction

The effect of feed solution pH on the penicillin G extraction using Aliquat 336 extractant in Shellsol TK solvent is shown in Fig. 5. The penicillin G extraction rates obtained were 34.7%, 25.1%, and 45.8% at pH of 5.5, 6.5, and 7, respectively. It can be seen that the pH of feed solution is important parameter and there is an optimum pH to achieve the highest extraction of penicillin G in the system. Formation of complex between penicillin G and Aliquat 336 is the highest according to distribution coefficient values at the organic–aqueous interface which results in higher extraction into organic phase in the shell side of membrane contactor (Smith and Hossain, 2007). The reaction between amine group of extractant and Pen G ion can be written as follows (Reschke and Schügerl, 1984):

$$A(org) + H^+_{(aq)} + P^+_{(aq)} \rightarrow AHP_{(org)} \tag{1}$$

where A denotes amine, P$^-$ refers to penicillin anion, and AHP denotes the complex formed in the interphase between organic and aqueous phases. Also, the pH of solution (H$^+$) has influence on the reaction rate and distribution of Pen G between two phases based on the reaction (Reschke and Schügerl, 1984; Yang and Cussler, 2000). It was reported that the reaction at pH of 7 has the highest distribution ratio (Smith and Hossain, 2007).

3.4. Effect of feed solution pH on flux distribution

The diffusive flux of penicillin G at different pH of feed solution in the middle of the tube side is shown in Fig. 6. There was an increase in penicillin G diffusive flux until reaching a maximum, then, it was decreased until leaving the tube side of the membrane contactor. The highest diffusive flux was obtained at pH of 7 while the lowest was at pH of 6.5. Furthermore,

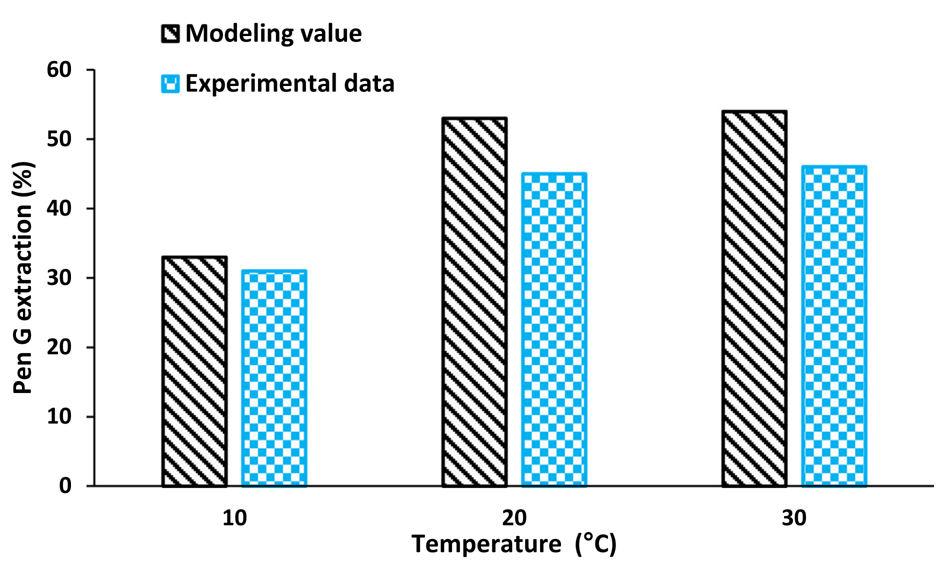

Fig. 2 Effect of temperature on the Pen G extraction.

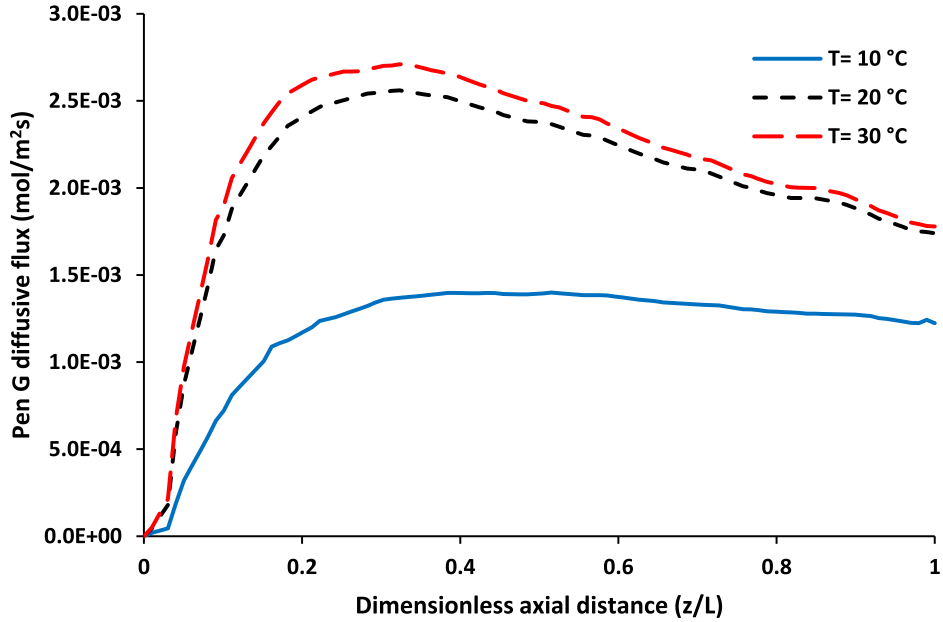

Fig. 3 Influence of temperature on diffusive flux of penicillin G along the membrane contactor, Qorg = 240 mL/ min, Qaq = 240 mL/ min.

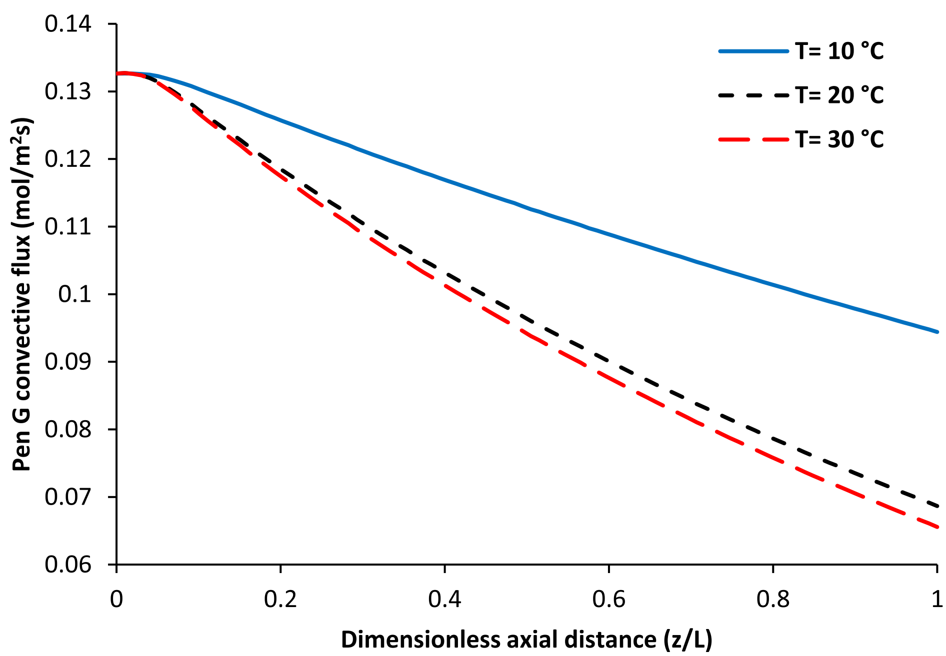

Fig. 4 Influence of temperature on convective flux of penicillin G along the membrane contactor. Q_{org} = 240 mL/ min, Q_{aq} = 240 mL/min.

based on Fig. 7, the convective flux of penicillin G decreased along the membrane contactor. In order to achieve the greatest extraction, the diffusive flux should be at its highest while the convective flux should be at its lowest. For example, the maximum extraction was obtained at pH of 7 (Fig. 5) which the diffusive flux related to this pH is highest (Fig. 6) where the convective flux is lowest (Fig. 7).

3.5. Effect of feed solution flow rate on the Pen G extraction

Fig. 8 shows the effect of the feed solution flow rate on the extraction of penicillin G at various pH of the feed solution. Generally, the amount of penicillin G extracted decreases with an increase in the flow of the aqueous solution containing penicillin G in the tube side of the membrane contactor. This is due

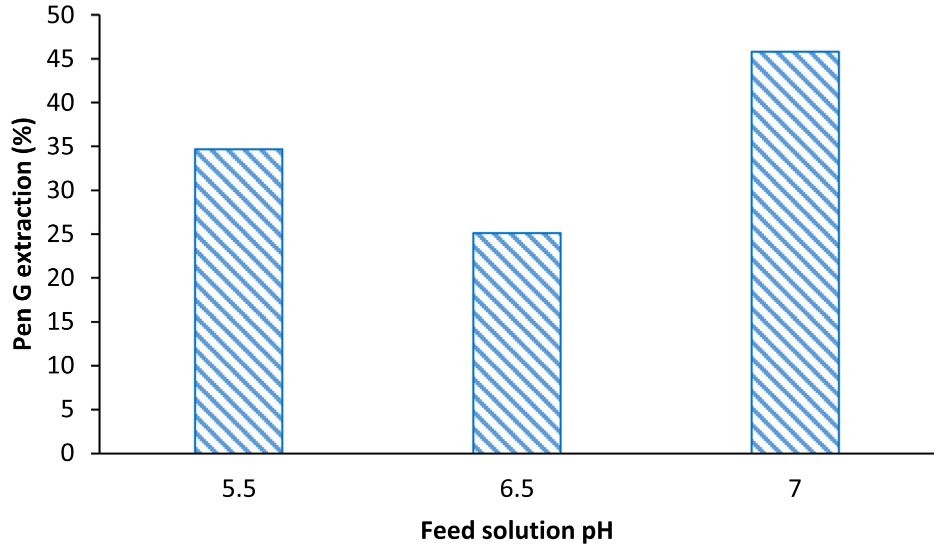

Fig. 5 Effect of aqueous solution pH on the Pen G extraction.

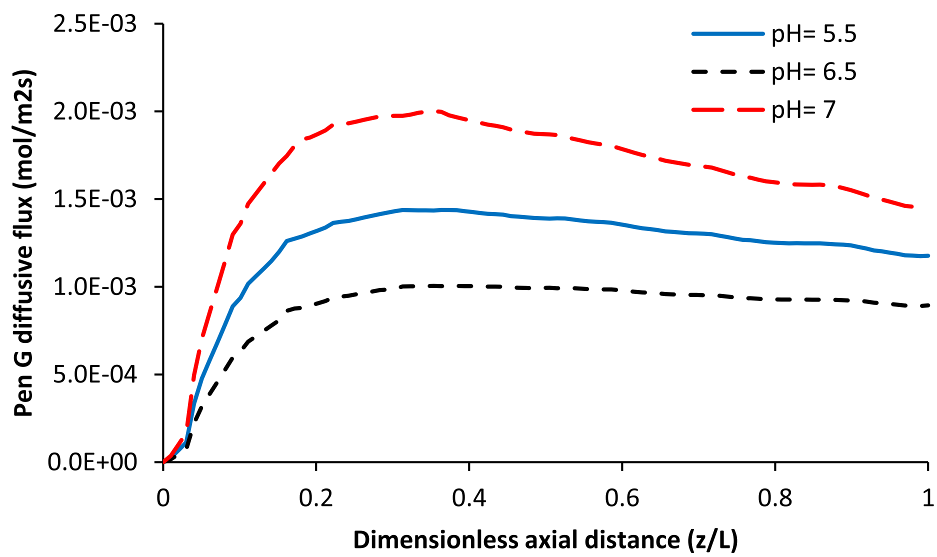

Fig. 6 Influence of feed solution pH on diffusive flux of penicillin G along the membrane contactor, Q_{org} = 220 mL/ min, Q_{aq} = 220 mL/min.

to the aqueous solution residence time in the contactor. Furthermore, it should be noted that the amount extracted was 40.1%, 29.4%, and 52.1% at the lowest flow rate and pH of 5.5, 6.5, and 7, respectively, but only 30.7%, 22%, and 41% at the highest feed flow rate and pH of 5.5, 6.5, and 7, respectively.

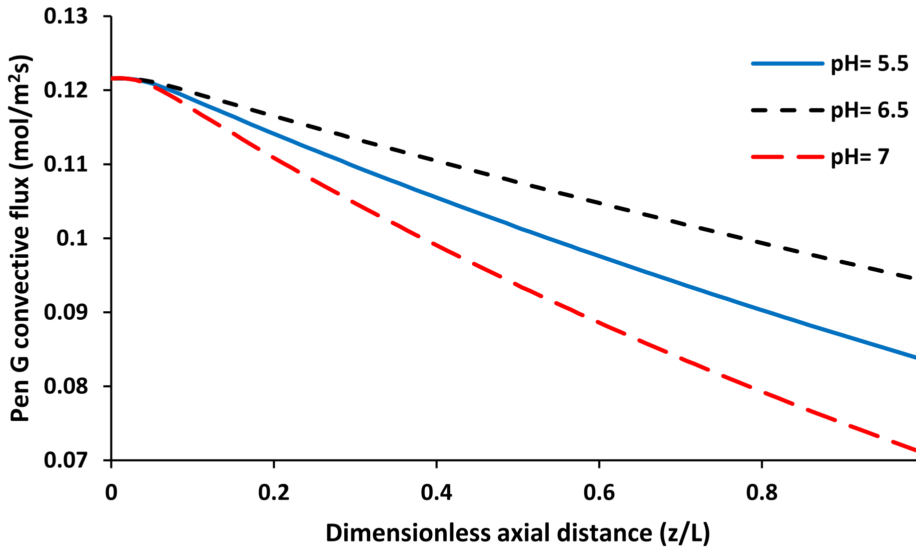

Fig. 7 Influence of feed solution pH on convective flux of penicillin G along the membrane contactor. Q_{org} = 220 mL/ min, Q_{aq} = 220 mL/min.

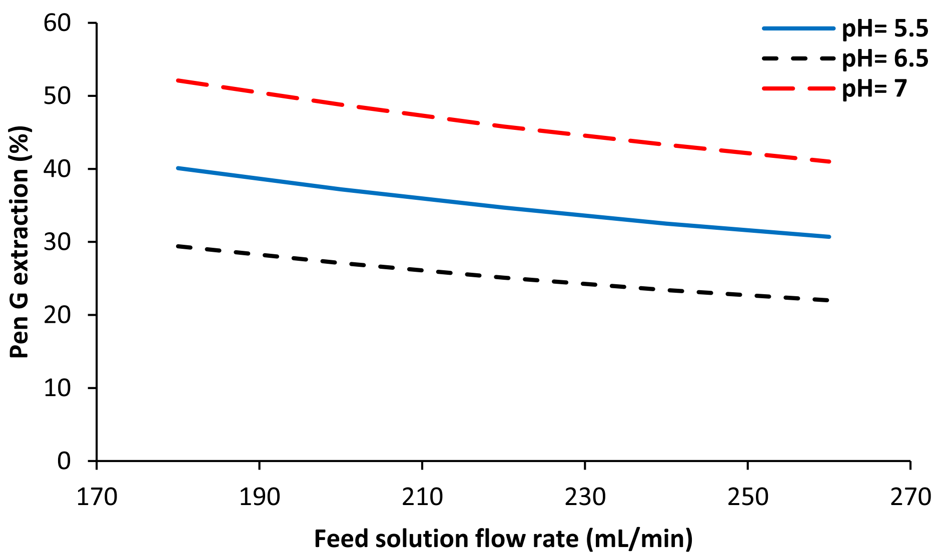

Fig. 8 Effect of feed solution flow rate on the Pen G extraction at different pH of feed solution.

4. Conclusion

A two dimensional mathematical model was developed for the investigation of penicillin G extraction from pharmaceutical wastewater using a Shellsol TK containing 5% Aliquat 336. The feed solution was passed through the tube side of a membrane contactor and the organic solution entered in shell side of contactor counter-currently. Based on the obtained results, the temperature has a positive impact on the penicillin G extraction especially when it was increased from 10 °C to 20 °C; there was no great increase in penicillin G extraction between 20 °C and 30 °C. The optimum pH for penicillin G extraction was found to be pH = 7. Moreover, the diffusive flux was increased at the entrance of the membrane contactor and, having reached a maximum, it decreased until the end of membrane contactor. There was a decrease in convective flux along the membrane contactor at all operating conditions. Finally, a decrease in penicillin G extraction was observed as the feed flow rate increased at all three different pH levels.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

Afrasyab Khan is thankful to the Russian Government and Institute of Engineering and Technology, Department of Hydraulics and Hydraulic and Pneumatic Systems, South Ural State University, Lenin prospect 76, Chelyabinsk, 454080, Russian Federation for their support to this work through Act 211 Government of the Russian Federation, contract No. 02. A03.21.0011.

References

Abbasi, F., Jazebizadeh, M.H., Mansourizadeh, A., Hojjati, M.R., 2021. Extraction of penicillin-G from pharmaceutical wastewaters via a developed hydrophobic PVDF-HFP hollow fiber membrane contactor and process optimization. Environ. Technol. Innovation 22, 101406.

Al-Maadheed, S., Goktepe, I., Latiff, A.B.A., Shomar, B., 2019. Antibiotics in hospital effluent and domestic wastewater treatment plants in Doha, Qatar. J. Water Process Eng. 28, 60–68.

Bird, R., Stewart, W., Lightfoot, E., 2002. Transport phenomena. John Wiely and Sons. Inc., Hoboken, NJ.

Buchberger, W.W., 2011. Current approaches to trace analysis of pharmaceuticals and personal care products in the environment. J. Chromatogr. A 1218 (4), 603–618.

Egea-Corbacho, A., Gutiérrez Ruiz, S., Quiroga Alonso, J.M., 2019. Removal of emerging contaminants from wastewater using nanofiltration for its subsequent reuse: Full–scale pilot plant. J. Cleaner Prod. 214, 514–523.

Ghadiri, M., Marjani, A., Shirazian, S., 2017. Development of a mechanistic model for prediction of CO2 capture from gas mixtures by amine solutions in porous membranes. Environ. Sci. Pollut. Res. 24 (16), 14508–14515.

Ghadiri, M., Mohammadi, M., Asadollahzadeh, M., Shirazian, S., 2018. Molecular separation in liquid phase: Development of mechanistic model in membrane separation of organic compounds. J. Mol. Liq. 262, 336–344.

Ghadiri, M., Shirazian, S., 2013. Computational simulation of mass transfer in extraction of alkali metals by means of nanoporous membrane extractors. Chem. Eng. Process. Process Intensif. 69, 57–62.

Gulkowska, A. et al, 2008. Removal of antibiotics from wastewater by sewage treatment facilities in Hong Kong and Shenzhen. China. Water Research 42 (1), 395–403.

Li, D. et al, 2008. Determination of penicillin G and its degradation products in a penicillin production wastewater treatment plant and the receiving river. Water Res. 42 (1), 307–317.

Pabby, A.K., Sastre, A.M., 2013. State-of-the-art review on hollow fibre contactor technology and membrane-based extraction processes. J. Membr. Sci. 430, 263–303.

Peralta Muniz Moreira, R. and Li Puma, G., 2021. CFD modeling of pharmaceuticals and CECs removal by UV/H2O2 process in helical microcapillary photoreactors and evaluation of OH radical rate constants. Chemical Engineering Journal, 415: 128833.

Plakas, K.V., Karabelas, A.J., Wintgens, T., Melin, T., 2006. A study of selected herbicides retention by nanofiltration membranes—The role of organic fouling. J. Membr. Sci. 284 (1), 291–300.

Poling, B.E., Prausnitz, J.M., O'Connell, J.P., 2001. The properties of gases and liquids. McGRAW-HILL, New York, USA.

Reschke, M., Schügerl, K., 1984. Reactive extraction of penicillin I: Stability of penicillin G in the presence of carriers and relationships for distribution coefficients and degrees. The Chemical Engineering Journal 28 (1), B1–B9.

Richardson, B.J., Lam, P.K.S., Martin, M., 2005. Emerging chemicals of concern: Pharmaceuticals and personal care products (PPCPs) in Asia, with particular reference to Southern China. Mar. Pollut. Bull. 50 (9), 913–920.

Roccaro, P., 2018. Treatment processes for municipal wastewater reclamation: The challenges of emerging contaminants and direct potable reuse. Current Opinion in Environmental Science & Health 2, 46–54.

Sandhibigraha, S., Sasmal, S., Bandyopadhyay, T.K., Bhunia, B., 2020. Computational fluid dynamics analysis of flow through immobilized catalyzed packed bed reactor for removal of 4-chlorophenol from wastewater. Environ. Eng. Res. 25 (6), 878–889.

Sarkar, B. et al, 2018. Designer carbon nanotubes for contaminant removal in water and wastewater: A critical review. Sci. Total Environ. 612, 561–581.

Smith, E., Hossain, M.M., 2007. Extraction and recovery of penicillin G in a hollow-fiber membrane contactor. Asia-Pac. J. Chem. Eng. 2, 455–459.

Soltani, H., Pelalak, R., Heidari, Z., Ghadiri, M., Shirazian, S., 2016. CFD simulation of transport phenomena in wastewater treatment via vacuum membrane distillation. J. Porous Media 19 (6), 515–526.

Verlicchi, P., Al Aukidy, M., Zambello, E., 2012. Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment—A review. Sci. Total Environ. 429, 123–155.

Yang, C., Cussler, E.L., 2000. Reactive extraction of penicillin G in hollow-fiber and hollow-fiber fabric modules. Biotechnol. Bioeng. 69 (1), 66–73.