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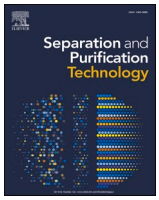
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Multivariate optimisation of norfloxacin precocentration in surface water samples: A case of polysulfone-based polymer inclusion membranes (PIMs)☆

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ABSTRACT

Norfloxacin belongs to a group of contaminants of emerging concern and its levels should be monitored in the environment. However, most conventional instruments struggle to detect trace levels of this contaminant in environmental samples. In this case, a polysulfone-based polymer inclusion membrane method was developed to enrich and separate norfloxacin in surface waters, followed by detection with HPLC UV–VIS. To achieve this, MODDE 13.1 software was used to optimise the variables crucial for the enrichment and separation of norfloxacin using a surface response methodology model with 30 experimental runs. The optimal operating conditions were predicted as pH 8.5, source solution concentration of 70 μg/L and receiver solution concentration of 0.7 M NaCl. The model predicted a maximum enrichment factor of 87.43. A test in the optimal operational conditions was conducted and the obtained experimental enrichment factor of ~ 88.14 verified the reliability and validity of the proposed model. The limit of detection for the proposed method was found to be 8.71 μg/L. Lastly, application in surface waters indicated that polysulfone PIMs have the potential to enrich, separate and monitor fluoroquinolones antibiotics.

1. Introduction

Norfloxacin is a third-generation fluoroquinolones antibiotic that is used in the management of bacterial infections including prostatitis and urinary tract infections [13,29]. It has been identified as a contaminant of emerging concern [1]. This is because of its water solubility, ecotoxicity, and non-biodegradability which lead to the emergence of antibiotic resistance, posing a threat to the environment, and human health [5,9]. Further, norfloxacin is the second most fluoroquinolone antibiotic detected in wastewater and drinking water [28]. This is concerning since it has been projected that humans will use 200 % more antibiotics in 2030 as compared to 2015 [25]. Moreover, half of the antibiotics used are excreted into the environment by metabolism through urine and faeces [6], and conventional wastewater treatment plants (WWTPs) cannot completely remove them, resulting in their release into environmental waters [7].

This suggests that we need to develop reliable analytical methods to preconcentrate norfloxacin, to enable monitoring in environmental waters. Recent studies have portrayed chemically functionalised membranes (CFMs) as an attractive tool for the separation and enrichment of antibiotics in environmental waters [8,20]. To date, polymer inclusion membranes (PIMs) are the most utilised CFMs due to their enhanced operational stability, chemical resistance and mechanical strength [30]. The membrane is made up of a base polymer, a carrier and on some occasions a plasticizer. The base polymer furnishes stability and mechanical support to the PIM [2]. Carriers serve as ion exchangers to transport targeted contaminants from the source to the receiving solution [15]. Plasticizers enhance the PIM flexibility, permeability, and compatibility of membrane components [21]. These PIM components can be tuned for analytes of interest which improve selectivity. In addition, recent advancement has demonstrated that green synthetic methods such as utilization of green solvents and the application of heat can be utilized to fabricate PIMs [3,26].

Over the years, the most utilised base polymers have been polyvinyl

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chloride (PVC) and cellulose triacetate (CTA) due to their compatibility with most of the PIM components. Nonetheless, their limited stability has led to the exploration of alternative non-conventional linear homopolymers [17]. One of the recently explored alternatives is polysulfone due to its stability over a wide range of pH, robustness at high temperatures, and exceptional oxidative resistance [10]. This polymer was used with aliquat 336 for the extraction of hexavalent chromium and demonstrated improved stability (under alkaline conditions) compared to PVC [10]. As far as we have researched, it has rarely been used to separate and/or preconcentrate organic contaminants in PIM-based separations.

The present work explored the potential of polysulfone as a base polymer for the preconcentration and monitoring of norfloxacin in aqueous solutions. Various solvents (green and toxic) were tested for the synthesis of a homogenous polysulfone-based PIM. To obtain good norfloxacin extraction efficiencies, the optimal PIM was optimized for key experimental variables (source solution pH, source solution, and receiver solution concentrations) using a multivariate approach. Lastly, the synthesized polysulfone based PIM was explored for the environmental monitoring of norfloxacin in Gauteng Province rivers (South Africa).

2. Methods and materials

2.1. Reagents

All chemicals used in this study were purchased as analytically pure reagents from Sigma-Aldrich (Johannesburg, South Africa) and used as received. Norfloxacin (≥98 %), N,N-dimethylformamide (≥99.5 %), ethyl acetate (98 %), dichloromethane (99 %), triethyl phosphate (≥97 %), acetone (≥99.8 %), ethyl lactate (≥98 %), N,N-dimethylacetamide (≥99.5 %), chloroform (99.9 %), aliquat 336 (≥97 %), polysulfone pellets (PSU) (MW: 35 000 g/mol), sodium chloride (99 %), sodium hydroxide (98.5 %), nitric acid (55 %), and HPLC grade methanol (≥99.8 %).

2.2. Instrumentation

A Bishoff LC-CaDI 22–14 high performance liquid chromatography (HPLC). The pH values were measured using a Mettler Toledo pH meter. Deionized water was obtained from the Milli-Q-R04 water system. An OHAUS analytical balance with up to 220 g capability was used for weighing the reagents. ROTOFIX 32 A centrifuge, EINS SCI ultrasonic cleaner, EINS SCI hot plate magnetic stirrer and a Bio base shaking hot water bath. Zeiss Evo 50, scanning electron microscope/energy dispersive X-ray (SEM/EDX) was used to acquire information on the morphology and structural configuration of the synthesized membrane. The thickness of the dry membranes was measured by an electronic outside micrometer 0–25 mm, 0.001 mm shut geometrical metrology.

2.3. Preparation of polymer inclusion membranes

Polymer inclusion membranes containing polysulfone as a base polymer were prepared using solvent evaporation (for volatile solvents) and the phase inversion method (non-volatile solvents). The following solvents were used in the preparation of the membranes: acetone, ethyl acetate, triethyl phosphate, N,N-dimethylformamide, N,N-dimethylacetamide, dichloromethane and chloroform. Polysulfone was dissolved in each solvent (0.6 g per 20 ml) to obtain a homogenous solution and the corresponding amount of aliquat 336 was added to acquire a composition of 60 w.t% PSU and 40 w.t% aliquat 336. The PIM solutions were stirred on a magnetic stirrer for approximately 3 h at room temperature. If the mixture had not dissolved, it was heated in a shaking water bath at 50 °C with the exception of acetone where 40 °C was used due to its low boiling point, for approximately 24 hrs. The homogenous PIM solution was cast in a petri dish and covered with a filter paper for the volatile solvents to evaporate overnight.

For the non-volatile solvent (N,N-dimethyl acetamide), the phase inversion method previously described by O'Brayn et al. (2016) was followed [19].

2.4. Separation and preconcentration experiments

The preconcentration experiments were performed using an in-house developed passive device. It is a system consisting of a two-compartment unit (source and receiving solutions). Circular segments of about 25 mm in diameter were cut from the polymer inclusion membranes and placed on top of the receiver solution chamber containing 5 mL of receiver solution (NaCl).

A magnetic stirrer operating at 150 rpm was used to drive the stirring magnet of about 70 mm in length and 30 mm in diameter in a 3500 mL source solution. 5 mL samples of the receiving solutions were taken at the end of the batch experiments for norfloxacin analysis. These experiments were conducted at room temperature.

The efficiency of the PIM system was determined using the enrichment factors presented by the following equation:

$$\mathrm{EF} = \frac{[NFX]_{r,t}}{[NFX]_{s,0}} \quad (1)$$

Where $[NFX]_{r,t}$ refers to the norfloxacin concentration in the receiver solution at time t and $[NFX]_{s,0}$ refers to the initial concentration of the norfloxacin in the source solution. The schematic presentation of the experimental setup is presented in Fig. 1.

2.5. Sample analysis

The norfloxacin concentrations of the source and the receiving solutions were quantified using an HPLC system with a UV–Vis detector. The procedure involved the isocratic elution of the mobile phase of 60 v/v% water and 40 v/v% methanol at a flow rate of 1 mL min^{-1}. The chromatographic separation was performed on a Kromasil C_{18} column (4.6 x 150 mm) and the injection volume was 10 μL. The absorption wavelength was set at 250 nm.

2.6. Experimental design

Various solvents were tested to form a homogenous PIM in a trial and error approach. The best PIM was chosen and surface response methodology with 3 independent variables was adopted for the optimisation of norfloxacin enrichment. MODDE Pro 13.1 (Sartorius Stedim Biotech, Malmö, Sweden) was used as the statistical software. A full factorial central composite design approach comprising of 27 experiments and 3 centre points with the same experimental conditions was used. The experiments had three replicates with the same experimental conditions (n = 3). The independent variables were pH (2–12), receiver solution concentration (0.1–1 M), and source solution concentration (10–100 μg/L). These independent variables and their levels have been chosen following most PIM studies investigating the monitoring of pharmaceuticals in aquatic systems [8,20], and have been classified as the most influential for the separation and enrichment of analytes in PIM-based separations [4]. For each experimental run, the average dependent variable [enrichment factor (EF)] of norfloxacin is presented in Table 1.

2.7. Model fitting

The multiple linear regression was used to calculate the fitting model and the response surface. The model suitability was evaluated by the lack of fit test, R^2, Adj-R^2 and Q^2 values. The model fit is given by R^2-Adj-R^2 and the Q^2 value provides an estimate of the future prediction precision [18]. Moreover, the observed vs. predicted plot was drawn and coefficient plots were obtained.

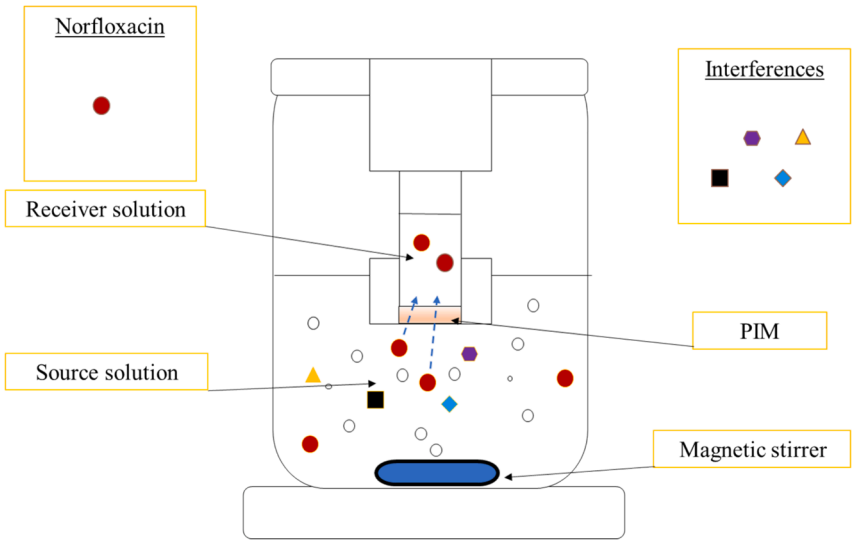


Fig. 1. Schematic presentation of the separation and preconcentration experiments.

Table 1
Experimental conditions with the corresponding norfloxacin enrichment factor (EF).

Exp No	pH	Source Concentration (μg/L)	Receiver Concentration (M)	EF
1	3	10	0.1	24
2	7.5	10	0.1	30
3	12	10	0.1	41
4	3	55	0.1	39
5	7.5	55	0.1	48
6	12	55	0.1	43
7	3	100	0.1	45
8	7.5	100	0.1	34
9	12	100	0.1	63
10	3	10	0.55	50
11	7.5	10	0.55	61
12	12	10	0.55	70
13	3	55	0.55	52
14	7.5	55	0.55	58
15	12	55	0.55	93
16	3	100	0.55	54
17	7.5	100	0.55	63
18	12	100	0.55	84
19	3	10	1	43
20	7.5	10	1	52
21	12	10	1	70
22	3	55	1	54
23	7.5	55	1	63
24	12	55	1	77
25	3	100	1	59
26	7.5	100	1	63
27	12	100	1	81
28	7.5	55	0.55	68
29	7.5	55	0.55	74
30	7.5	55	0.55	83

2.8. Validation and application of the polysulfone-based PIM technique

The applicability of the optimized polysulfone-based PIM to monitor norfloxacin in surface water was investigated by water samples from the Hennops and the Jukskei Rivers (Gauteng, South Africa). Water samples were collected in 5 L bottles from various locations across the river and transported to the lab in coolers. The physicochemical parameters are presented in Table 2. These were immediately filtered through 0.22 μm filters before analysis. Norfloxacin was extracted (using the PIM method) from surface water blanks and spiked samples (10 μg/L norfloxacin spiked) before HPLC UV–VIS analysis. Extraction efficiency (percentage ratio of the amount spiked versus the amount recovered) was used to determine the applicability of the method for the determination of norfloxacin.

Table 2
Physicochemical parameters of environmental samples.

Parameter	Hennops river	Jukskei river
pH	9.86	6.57
Conductivity (μS cm^{-1})	924	371
Chloride (mg/L)	92.08	39.10
Fluoride (mg/L)	0.16	0.18
Nitrate (mg/L)	3.37	9.53
Phosphate (mg/L)	11.10	0.94
Sulfate (mg/L)	47.79	24.68

3. Results and Discussion

3.1. Solvent screening for a homogeneous polymer inclusion membrane (PIM)

A recent study has shown that a compatible solvent is crucial for the formation of a homogenous PIM that is flexible with enhanced mechanical strength [3]. This is because PIM homogeneity and composition have a central role in the transport process of the target analyte(s). Polysulfone (PSU) has good solubility with polar aprotic solvents [27]. In this study, acetone, ethyl acetate, dichloromethane (DCM), N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF), chloroform, ethyl lactate and triethyl phosphate were tested for homogeneous PSU-based PIM formation.

For all the screened solvents, 60 w.t% PSU and 40 w.t% aliquat 336 was used as the baseline composition. This composition has previously been classified as the most common ratio between the base polymer and the carrier in PIM studies [16]. In this case, aliquat 336 was used as a cationic carrier of choice as it has previously been explored to extract antibiotics such as tetracyclines and fluoroquinolones in aqueous solutions[8,20]. For the sake of clarity, a visual inspection was used to differentiate between homogenous, rigid and soft membranes. This was done by assessing any visual defects such as cracks, tears or holes. The PIMs were also assessed to ensure that the colour and texture was uniform. In addition, the surface finish was also inspected for any defects. Table 3 represents the suitability of the different solvents for PIMs formation. The green solvents (non-hazardous) were unable to form a homogeneous PIM. Acetone formed a rigid PIM that could not be applied, this effect has been observed in a Poly(vinylidene fluoride-

Table 3
Suitability of solvents for homogenous PIM formation.

Solvent	Solvent type	Dissolution condition	Homogenous, flexible, and mechanically strong PIM?
Acetone	Green polar aprotic	Dissolved at 40 °C	No (rigid)
Ethyl acetate	Green polar aprotic	Dissolved at 50 °C	No (too soft)
DCM	Polar aprotic	Dissolved at RT	Yes
DMA	Polar aprotic	Dissolved at RT	No (too soft)
DMF	Polar aprotic	Dissolved at RT	No (too soft)
Chloroform	Polar aprotic	Dissolved at RT	Yes
Ethyl lactate	Polar protic	Did not dissolve	–
Triethyl phosphate	Polar	Did not dissolve	–

RT, room temperature

hexafluoropropylene)-based PIM and was attributed to the high volatility of acetone, which results in quick evaporation of the solvent that causes a non-homogenous PIM [3]. Ethyl acetate formed a PSU-based PIM that was too soft to apply. For the toxic solvents (DCM, DMA, DMF, and chloroform), DCM and chloroform were the two solvents which resulted in homogenous, flexible, and mechanically strong PIMs. DMA and DMF dissolved PIMs were too weak for usage. As expected, the polar protic solvents (ethyl acetate and tri ethyl phosphate) could not dissolve PSU even at elevated temperatures since this polymer is dissolved by polar aprotic solvents.

As such DCM and chloroform synthesized PIMs were evaluated for the enrichment of norfloxacin. The source solution consisted of 10 mg/L of norfloxacin at pH 9. This was to ensure that norfloxacin exists in its anionic phase to form an ion pair with aliquat 336. The receiving solution consisted of 1 M NaCl. These enrichment experiments were conducted for 24 hrs (n = 3, RSD). The enrichment factor (EF) of the DCM dissolved PSU PIM was 73.14 ± 2.67, while the EF of the chloroform dissolved PIM was 67.03 ± 0.08. As such, the DCM dissolved PIM was used to optimise the variables (source solution pH, receiver solution concentration and source solution concentration) crucial for the transport of norfloxacin across the PIM using surface response methodology.

Scanning electron microscopy (SEM) was used to investigate the structural and morphological difference between the DCM and chloroform-synthesised PSU-PIMs. The SEM images indicated a smooth surface with small pores on both PIMs surfaces despite dissolving the membrane components using different solvents (Fig. S1). This suggests that the dissolution solvent may not have much influence on the PIM morphology. As such we can propose that the PIM surface morphology only depends on membrane components and their compositions.

3.2. Effect of the selected variables for the enrichment of norfloxacin

Three independent variables were tested for their influence on norfloxacin enrichment to enable detection by a less sensitive analytical instrument (i.e., HPLC UV–Vis). These variables (source solution pH, source, and receiver solution concentrations) are vital for the transport of the target analyte from the contaminated source into the receiving solution. In most studies, including the current study where an anionic exchanger (aliquat 336) is used as a carrier, when the source solution pH is basic, norfloxacin will exist in its anionic form which can form an ion pair with the aliquat 336. This will diffuse into the PIM/receiving phase interface where norfloxacin is released into the receiver and then replaced by the chloride ion from the sodium chloride solution. This has been termed facilitated transport and is driven by the high concentration of the receiving solution that enables the transport of norfloxacin from a lower concentration solution to a higher concentration solution [8]. Other variables that could potentially influence the transport of the analyte were kept constant (i.e., stirring rate 150 rpm, temperature 25 °C, membrane thickness 100 μm, and extraction time 24 hrs).

The coefficients plot (Fig. 2) shows that all the selected variables (source solution pH, source (Cs), and receiver solution (Cr) concentrations) had a significant positive effect on the enrichment of norfloxacin with p-values < 0.05 (Table S1). These linear factors had a direct proportionality effect on the enrichment of norfloxacin as indicated by the positive regression coefficient. However, the regression coefficients of the quadratic form of the source concentration (Cs*Cs) and the receiver concentration (Cr*Cr) had a strong negative effect on the enrichment factor.

The response contour plots were used to describe the relationship between varying the variables (within the experimental range) while one variable was kept constant at the center point. Fig. 3 indicates that there was an increase in the enrichment factor of norfloxacin with an increase in the source solution concentration and pH. This is expected for an aliquat 336 based extraction of an anionic analyte such as norfloxacin since alkaline conditions are favourable.

Similar to the source concentration, increasing the receiver solution concentration and the pH results in an increase of the enrichment factor (Fig. 4). This occurs because there should be a sufficient concentration of the receiver to facilitate the back extraction at the PIM/receiving solution boundary layer.

Additionally, there was also an increase in enrichment factor when the concentrations of both the source and the receiving solutions were increased (Fig. 5). However, there was a threshold with which the source concentration could be increased. This is because a high concentration of the target analyte in the source has the potential to accumulate into the membrane surface which hinders transport efficiency [14], this then limits the enrichment factor.

3.3. Model fitting and predictive efficacy

Table S2 provides the model parameters. With p < 0.05, they demonstrate that the model was significant. Further, the lack of fit test was not significant which is promising for surface response methodology. The values of the R^2 and Adj-R^2 were 0.85 and 0.82 respectively (Table S3). Q^2 value was 0.77 with a model validity of 0.97. However, the model reproducibility was a bit lower at 0.61. The Box-Cox plot (Fig. 6) suggested that the model required a modification with a value of 0.5 obtained for Lambda (λ).

To this end, the power transformation was employed to develop a more reliable and accurate model with improved values of R^2, Adj-R^2, Q^2 and model reproducibility (Table 4). As expected, the transformed model had more accuracy than the initial model. This transformed model can be represented by Equation (2).

$$(EF)^{\frac{1}{2}} = 7.348 + 0.642A + 0.361B + 0.675C - 0.321B^2 - 0.893C^2 \quad (2)$$

In the above equation, A, B and C represent pH, source concentration and receiver concentration respectively.

The observed vs predicted plot was assessed for the model abilities (Fig. 7). The data set has some deviations between the observed and the predicted values. However, an outlier test was conducted and there were none, thus indicating the model validity. The optimum operating conditions were predicted as source solution pH 8.5, source solution concentration of 70 μg/L and receiver solution concentration of 0.7 M NaCl.

3.4. Method validation and application

To validate the method, the surface response methodology central composite design model was analysed with the optimum conditions (pH 8.5, source solution concentration of 70 μg/L and receiver solution concentration of 0.7 M NaCl). It was found that the maximum enrichment factor (EF) predicted by the model was 87.43 (Table 5). The

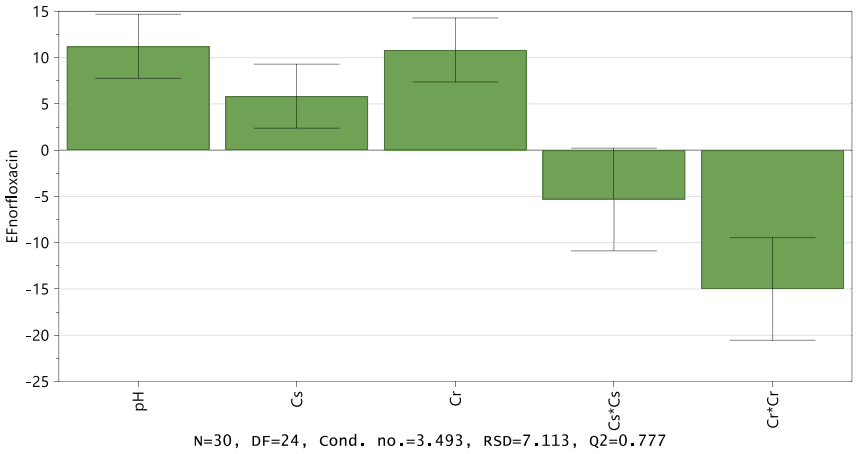


Fig. 2. Coefficients plot of the investigated variables for the enrichment of norfloxacin.

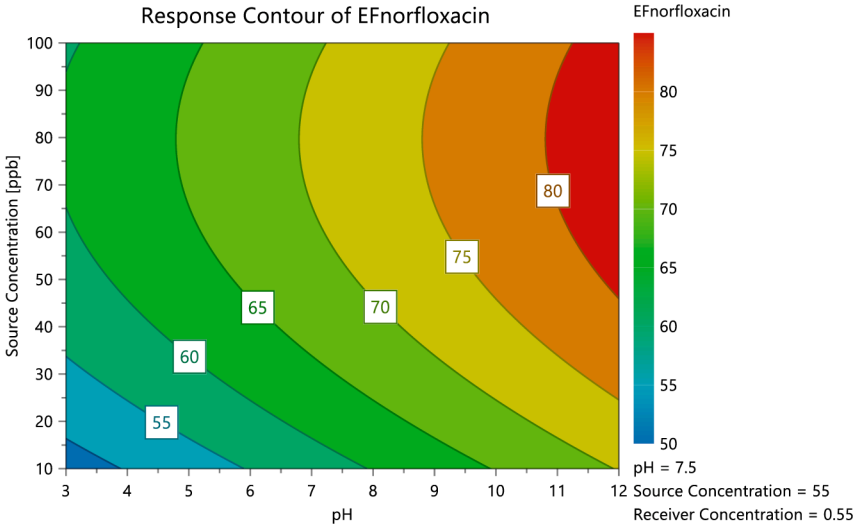


Fig. 3. Contour plot of source solution concentration vs pH.

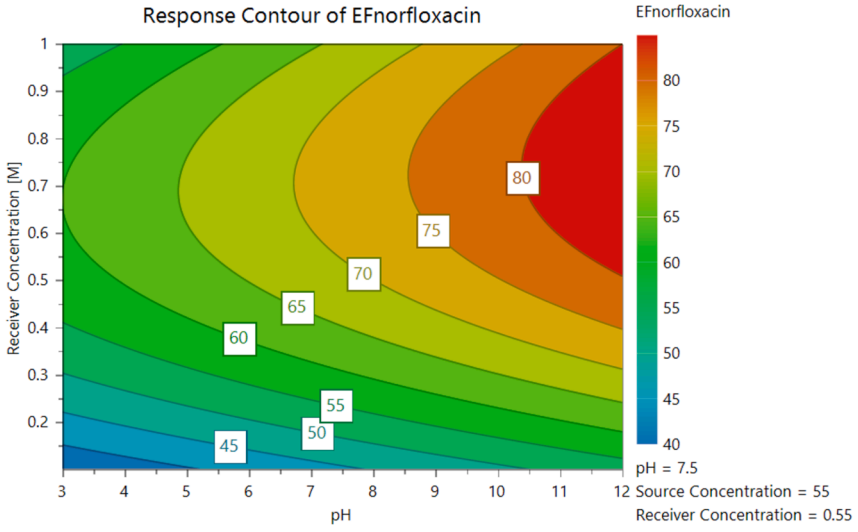


Fig. 4. Contour plot of receiver solution concentration vs pH.

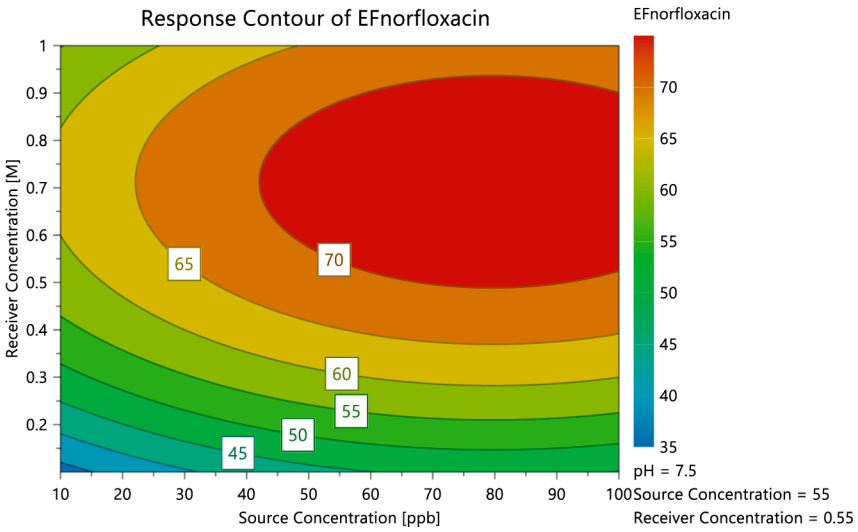


Fig. 5. Contour plot of source solution concentration vs receiver solution concentration.

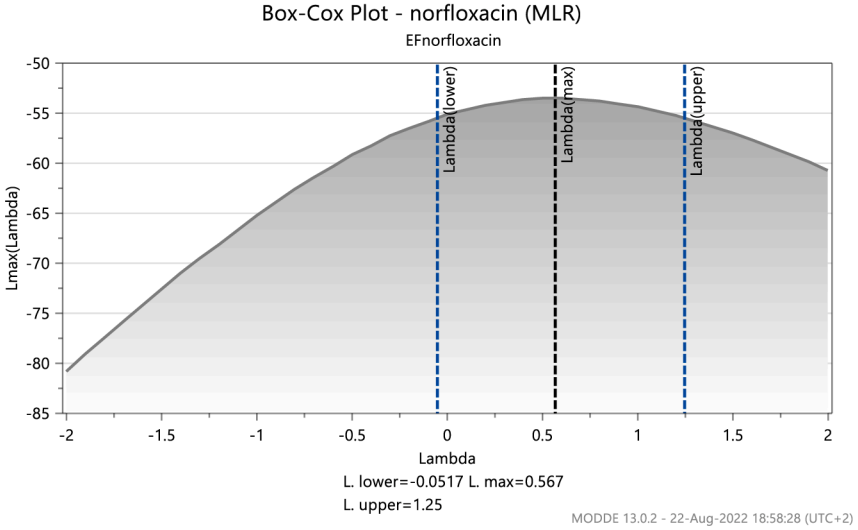


Fig. 6. Box-Cox plot for power transformation.

Table 4
Summary of fit values for the transformed model.

	R^2	R^2 Adj.	Q^2	Model Validity	Reproducibility
EFnorfloxacin~	0.87	0.84	0.80	0.97	0.70

enrichment experiments were then carried out three times under the models optimum conditions. The results from the three repeat studies revealed an average EF of 88.14 ± 0.54, which is considerably closer to the predicted value. As a result of a small percentage error between the observed and predicted values, the model had the ability to enrich norfloxacin concentrations in aquatic environments. In a comparative study a cellulose tri-acetate based PIM was used to preconcentrate six antibiotics where a maximum EF of 70 was achieved which is slightly comparative to the current study[8].

Due to the validity of the model, the PSU-based PIM method was applied in environmental water samples (Hennops and Jukskei Rivers). The observed transport efficiencies (Table 6) did not differ significantly even though the water samples had different physicochemical properties. This suggests that the sample matrix did not affect the PIM performance, indicating that norfloxacin had a higher extraction constant compared to the anionic species present in the water samples (Table 2). As such, the proposed PIM-based approach has a promising potential for the enrichment and transport of antibiotics of the fluoroquinolones family in environmental waters. However, efforts should be taken to improve the observed low transport efficiencies which could hinder large-scale applications. In addition, a comprehensive study should be conducted to investigate the stability of the polysulfone-based PIMs. Nonetheless, a previous study has demonstrated that polysulfone has a comparable stability to PVC in acidic conditions and more stable than PVC in alkaline conditions as demonstrated by mass loss over 24 hrs exposure to these conditions[10].

3.5. *Figures of merit and comparison to literature*

The linearity of the PIM-based preconcentration method was assessed in the range of 10 – 100 μg/L. The R^2 value for the linear plot was 0.9963 while the matrix matched limit of detection (LOD, S/N = 3) was 8.71 μg/L. These results indicate a highly sensitive analytical methods with acceptable linearity. Table 7 compared the findings of the PIM method with literature data. Many of the studies involved the preconcentration of norfloxacin in other sample matrices. This study is

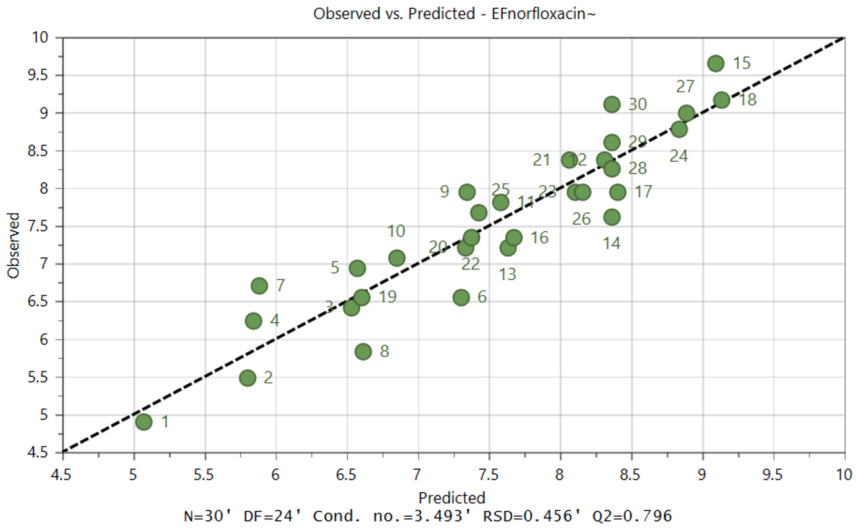


Fig. 7. Observed vs predicted values plot.

Table 5
Observed vs. predicted results of the enrichment factor.

Pharmaceutical	Predicted results	Observed results (n = 3, RSD)
Norfloxacin	87.43	88.14 ± 0.54

Table 6
Evaluation of sample matrix on the enrichment of norfloxacin in environmental waters (n = 3, RSD).

Sample ID	Enrichment factor (EF)	%Transport efficiency
Hennops River	56 ± 3	78 ± 4
Jukskei	61 ± 2	81 ± 3

Table 7
Comparison of the PIM based method with studies from literature.

Utilized method	R^2	LOD (μg/L)	Reference
PIM-based	09,963	8.71	This study
Electrochemical cell, voltammetry	–	3.20	[22]
Voltammetry	0.998	2.10	[24]
Liquid phase microextraction chip	0.999	10.0	[23]
Magnetic solid-phase extraction	0.999	0.0085	[11]
Molecular imprinted solid phase extraction	–	0.0270	[12]

LOD: limit of detection, LOQ: limit of quantification, –: not reported

one of the first attempts to preconcentrate norfloxacin in river water samples using a PIM-based method. The method was highly sensitive and able to eliminate matrix effects. However, more work should be conducted to improve the LOD of the proposed method. Nonetheless, PIMs have a future potential to preconcentrate and monitor antibiotics in environmental samples considering that a less sensitive analytical instrument was utilized in the current study.

4. Conclusion

An effective method utilizing a polysulfone-based PIM was developed for the preconcentration of norfloxacin in surface waters. This was followed by the detection by HPLC UV–VIS. As expected, the study confirmed that polar aprotic solvents have good solubility for polysulfone. Response surface methodology central composite design (RSM-CCD) model was used to optimise the experimental conditions for the enrichment of norfloxacin. Three independent variables crucial for the enrichment factor namely, pH (2–12), source concentration (10–100 μg/L) and receiver concentration (0.1–1 M) were tested within the specified ranges. The model indicated that all the variables had a significant positive effect on the enrichment of norfloxacin. However, the model had to be modified with a power transformation ($\lambda = 0.5$) to improve its reproducibility. Under the optimum enrichment conditions, the predicted enrichment factor of 87.43 predicted by the model was in agreement with the experimental results of ~ 88.14, thus validating the model generated by RSM-CCD. The polysulfone-based PIM was then applied in surface waters. It was interesting to note that the effect of sample matrix does not influence the extraction efficiencies of the polysulfone-based PIM. However, more studies need to be conducted to improve the transport efficiency, this is in addition to evaluating the stability of polysulfone-based PIMs. Nonetheless, there is a promising potential for polysulfone-based PIMs for the enrichment and separation of organic contaminants in surface waters.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.131063.

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