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Prediction of the removal efficiency of emerging organic contaminants based on design and operational parameters of constructed wetlands

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Abstract

This study investigates the prediction of removal efficiency of pharmaceuticals (PhCs), personal care products (PCPs), and steroidal hormones (SHs) based on design and operational parameters (depth, area, hydraulic loading rate-HLR, organic loading rate-OLR, and hydraulic retention time-HRT) of constructed wetlands (CWs). A comprehensive statistical analysis was performed by applying principle component analysis, correlation and multiple linear regression analyses. The data used in this analysis was compiled from peer reviewed publications. The CWs design and operational parameters are good predictors of the removal efficiency of these emerging organic contaminants. Operational parameters (HLR, OLR, and HRT) are the most significant predictors and combination with design parameters (depth and area) often improved reliability of the predictions. The best predictive models for PhCs and PCPs were composed of depth, OLR, and HRT (root mean square errors-RMSEs: training set: 7-14%; test set: 22-27%). A combination of area, HLR, and OLR formed a credible model for predicting the removal efficiency of SHs (RMSEs: training set: 6%; test set: 11%). Similarly, generic models by combining data of PhCs and PCPs, PhCs and SHs, PCPs and SHs, and PhCs, PCPs, and SHs showed acceptable performance. The best performing combined model for the prediction of PhCs, PCPs, and SHs was based on area, HLR, OLR, and HRT (RMSEs: training set: 13%; test set: 22%). The information obtained by the use of these models may guide researchers, practitioners, policy makers, and citizens in enhancing knowledge and understanding for the design and operation of CWs in the field conditions.

Key words: Constructed wetlands; Design and operational parameters; Personal care products; Pharmaceuticals; Removal efficiency; Steroidal hormones.

1. Introduction

Constructed wetlands (CWs) are nature-based treatment technologies that have been extensively investigated for the removal of emerging organic contaminants (EOCs) from wastewater (Verlicchi and Zambello, 2014; Zhang et al., 2014; Verlicchi et al., 2015; Gorito et al., 2017; Vo et al., 2018). To date, a large number of individual case studies have been published in peer reviewed journals related to the removal of EOCs by CWs. Several studies indicated that design and operational parameters such as depth, area, hydraulic loading rate (HLR), organic loading rate (OLR), and hydraulic retention time (HRT) are among the major

governing factors in the removal of EOCs by CWs because these parameters considerably influence the possible removal mechanisms such as biodegradation and adsorption/sorption (e.g., Song et al., 2009; Dai et al., 2017; Vystavna et al., 2017). The design and operational factors play an important role in the treatment process in CWs for the removal of pharmaceuticals (PhCs), personal care products (PCPs), and steroidal hormones (SHs) (Ilyas and van Hullebusch., 2019, 2020a, 2020b). For instance, a significant correlation was found between the removal efficiency of some of the studied PhCs and design as well as operational parameters (depth, area, HLR, OLR, and HRT) (Ilyas and van Hullebusch., 2019).

However, the previous research did not investigate the possibility of predicting the removal efficiency by using design and operational parameters. For example, multiple linear regression analysis to develop predictive models for removal efficiency of PhCs, PCPs, and SHs with design and operational parameters was not conducted by the above-mentioned studies. Similarly, a principal component analysis (PCA) was not conducted to understand the role of different design and operational parameters of CWs in removal processes. Thus, a comprehensive statistical analysis is lacking to develop predictive models for the removal efficiency of EOCs (PhCs, PCPs, and SHs) based on design and operational parameters of CWs.

Moreover, research is needed on all aspects of modelling of EOCs removal in CWs (Yuan et al., 2020). The CWs models are broadly classified as process-based and black-box (Kumar and Zhao, 2011; Meyer et al., 2015; Yuan et al., 2020). The widely studied process-based models of CWs are RTD/GPS-X (Zeng et al., 2013), Diph-M (Petitjean et al., 2012), FITOVERT (Giraldi et al., 2010), HYDRUS-CW2D (Langergraber and Šimůnek, 2012), HYDRUS-CWM1 (Pálffy and Langergraber, 2014), CWM1-RETRASO (Llorens et al., 2011), CFD Model (Rajabzadeh et al., 2015), and BIO-PORE (Samsó and Garcia, 2013). These models mainly focus on the removal of conventional parameters such as chemical oxygen demand (COD), nitrogen, phosphorus, and ammonia. The process-based models focus on the hydraulic, chemical, and biological mechanisms occurring in CWs. While these models attempt to cover in detail the processes happening in CWs, most of them only include to model one or few processes (e.g., hydraulic, reactive-transport, biochemical, plants, and clogging), thus, partly representing several processes happening at the same times (Kumar and Zhao, 2011; Meyer et al., 2015; Yuan et al., 2020). Including more processes in available CW models is still a big challenge because it increases complexity as well as the number of parameters to quantify, and lack comprehensive experimental data for calibration and validation. On the other hand, black-box models, which are data driven models, such as regression models, first-order models, time-dependent retardation model, tank-in-series model, Monod models, neural networks, and statistical approaches, mainly focus on input and output rather than processes (Kumar and Zhao, 2011). Although these models are formed using experimental data, the application possibilities are limited to the range of data used in their development. Meyer et al. (2015) suggested that all types of models (both process-based and black-box) are valuable, although some give more understanding of the scientific processes and some are more useful for engineers to design the CW systems. In general, there is a need to include EOCs in further development of CW models.

Therefore, the main objective of this study is to comprehensively analyze the possibility of developing reliable predictive models for removal efficiency of EOCs based on design and operational parameters of CWs. The specific objectives are: (1) to develop predictive models in the form of multiple linear regression equations between removal efficiency of EOCs (PhCs, PCPs, and SHs), and design and operational parameters of CWs; (2) to develop a generic predictive model for the removal efficiencies of PhCs, PCPs, and SHs based on design and operational parameters of CWs; (3) to examine the uncertainties in the prediction process; and (4) to discuss potential applications of the developed predictive models.

2. Methodology

2.1. Data

In this study, the predictive models were formulated using data of widely studied EOCs (31 PhCs, 13 PCPs, and eight SHs) in CWs. The data were collected from the peer reviewed published sources. All the sources of data are acknowledged in the database compiled in our previous work (Ilyas et al., 2020; Ilyas and van Hullebusch, 2020a, 2020b), which formed the basis of this study. The removal efficiency is used as an independent variable to be predicted. The dependent variables were design and operational parameters: depth, area, HLR, OLR, and HRT. The final data sets used in this study are given in Supplementary materials 1: Tables S1-S3.

2.2. Statistical methods

First, PCA was performed in R software (version 3.6.2). The PCA was mainly aimed at understanding the role of different design and operational parameters of CWs in the removal efficiency. Moreover, the PCA helped to understand the key variables explaining most of the variance in the data set, and thus could be used in model building process (Supplementary materials 2 and 3: Tables S4-S11; Figures S1-S5). Second, a correlation of the removal efficiency of EOCs and design and operational parameters of CWs was estimated to select most promising variables to be used in the predictive models. Microsoft Excel software (Analysis ToolPak) was used to estimate the Pearson product moment correlation (Supplementary materials 4: Tables S12-S19).

Then, multiple linear regression analysis was carried out using Microsoft Excel software (Analysis ToolPak) (Supplementary materials 5: Tables S20-S33). The available EOCs' data sets were divided into training and test sets using a purposive sampling approach based on the number of observations in case of removal efficiency of EOCs (Tables S1-S3). For example, the data of PhCs with ≥ 15 observations was used as one set in model formulation processes. Other sets included PhCs with ≥ 20 and ≥ 25 data points, respectively. It was assumed that more observations may reduce uncertainty in the observed removal efficiency and, therefore, may results in better models (Supplementary materials 6: Tables S34-40). In the calibration process, various combinations of dependent variables were used to formulate multiple linear regression equations. For example, removal efficiency was estimated using OLR and HRT in one model. Then, other variables (e.g., depth, area, and HLR) were added into the model. The resulting regressions models were validated on an independent data (test set) (Tables S1-S3).

The difference between observed and predicted removal efficiency was used as an indicator to assess the performance of the regression models. Since these differences were both positive and negative, it was not suitable to estimate overall mean difference because of the cancelling effect. Therefore, model performance was also assessed using root mean square error (RMSE), which was estimated from the observed and predicted removal efficiency. The selection of acceptable/best performing models was based on RMSE values (lower the RMSE better the model), the difference between observed and simulated removal efficiency (lower the better), coefficient of determination (R^2) (higher the better), probability (p) value (lower the better), and the number of predictants in the equation (lower the better).

At first instance, the regression models were developed separately for each category of the EOCs, for example, separate models for PhCs, PCPs, and SHs. Then, an attempt was made to form models combining data of PhCs and PCPs, PhCs and SHs, PCPs and SHs, and PhCs, PCPs, and SHs. The similar approach of multiple linear regression was used for developing the generic models.

3. Results and discussion

3.1. Predictive models for PhCs

The first two principal components (PCs) with eigenvalue > 1.0 explained 70% variance in the data of 31 widely studied PhCs (Figure 1 and Table 1). The first PC could explain 49% variance in the data. In PC1, the high positive loadings were observed for OLR, and high negative loadings for depth, area, and HLR (Figure 2). In PC2, area indicated high positive loadings; however, HRT showed high negative loading (Figure 2 and Table 1). The removal efficiency indicated positive loadings in these two PCs. To further test the reliability of the PCA results, we also conducted PCA based on various combinations of the studied PhCs, i.e., samples with number of data points ≥ 15 , ≥ 20 , and ≥ 25 . In general, the PCA results gave similar insights as obtained using 31 PhCs for most of the parameters (Figures S1-S3 and Tables S4-S7). For example, OLR is likely to emerge as an important predictor in all cases, and is likely to show a positive correlation with removal efficiency of PhCs (Figure 3 and Tables S12-S15).

The correlation and regression outcomes were quite consistent with the PCA results (Tables S4-S7, S12-S15, and S34), although correlations were statistically non-significant in most cases. The regression models were formed by combining depth, area, HLR, OLR, and HRT, mostly with three or four variables together in one model.

Table 1. Principle component analysis (PCA) results based on widely studied 31 PhCs, 13 PCPs, and eight SHs.

Description	PhCs		PCPs			SHs	
	PC1	PC2	PC1	PC2	PC3	PC1	PC2
Eigenvalue	1.709	1.138	1.735	1.105	1.055	1.613	1.393
Proportion of Variance	0.487	0.216	0.502	0.204	0.185	0.434	0.323
Cumulative Proportion	0.487	0.703	0.502	0.705	0.891	0.434	0.757
Variables and loadings							
Depth (m)	-0.408	-0.396	-0.277	-0.716	0.121	0.547	-0.196
Area ($\text{m}^2 \text{PE}^{-1}$)	-0.501	0.337	0.378	-0.578	-0.226	0.485	0.375
HLR ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)	-0.534	-0.079	-0.509	0.082	-0.220	0.421	0.256
OLR ($\text{g COD m}^{-2} \text{d}^{-1}$)	0.438	-0.488	-0.519	0.187	-0.236	0.304	-0.603
HRT (days)	-0.223	-0.687	-0.487	-0.332	0.010	0.169	0.580
RE (%)	0.236	0.111	0.121	-0.024	-0.911	0.410	-0.236

Note: Pharmaceuticals (PhCs); Personal care products (PCPs); Steroidal hormones (SHs); Principle component (PC); **Population equivalent (PE)**; Hydraulic loading rate (HLR); Organic loading rate (OLR); Hydraulic retention time (HRT); Removal efficiency (RE).

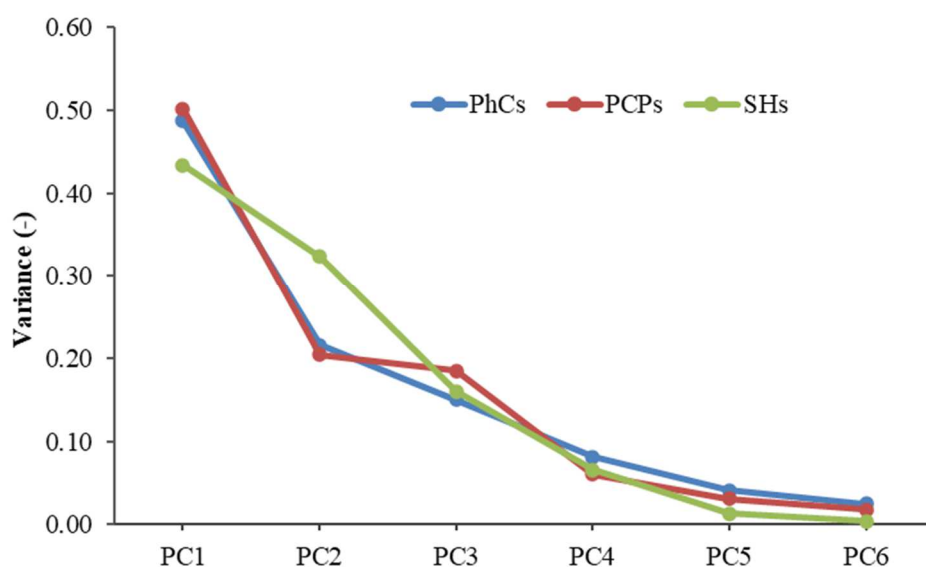


Figure 1. Scree plot indicated variance explained by each principal component (PC) for the data of widely studied 31 pharmaceuticals (PhCs); 13 personal care products (PCPs); and eight steroidal hormones (SHs).

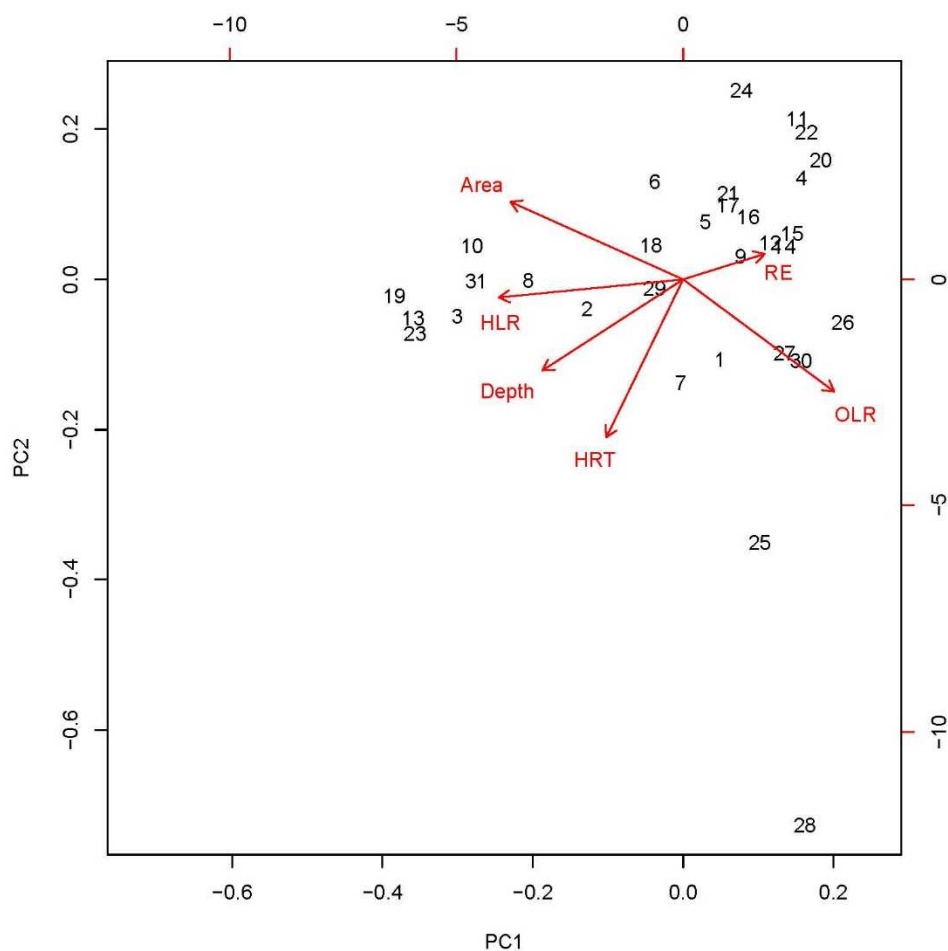


Figure 2. Byplot of PC1 and PC2 based on principle component analysis (PCA) of widely studied 31 PhCs.

Note: Hydraulic loading rate (HLR); Organic loading rate (OLR); Hydraulic retention time (HRT); Removal efficiency (RE); The widely studied 31 PhCs were: Acetaminophen (1); Atenolol (2); Bezafibrate (3); Caffeine (4); Carbamazepine (5); Clarithromycin (6); Clofibric acid (7); Codeine (8); Diclofenac (9); Diltiazem (10); Doxycycline (11); Erythromycin (12); Fexofenadine (13); Furosemide (14); Gemfibrozil (15); Ibuprofen (16); Ketoprofen (17); Metoprolol (18); Mirtazapin (19); Monensin (20); Naproxen (21); Ofloxacin (22); Ranitidine (23); Salicylic acid (24); Sotalol (25); Sulfamethazine (26); Sulfamethoxazole (27); Sulfapyridine (28); Tramadol (29); Trimethoprim (30); and Venlafaxine (31).

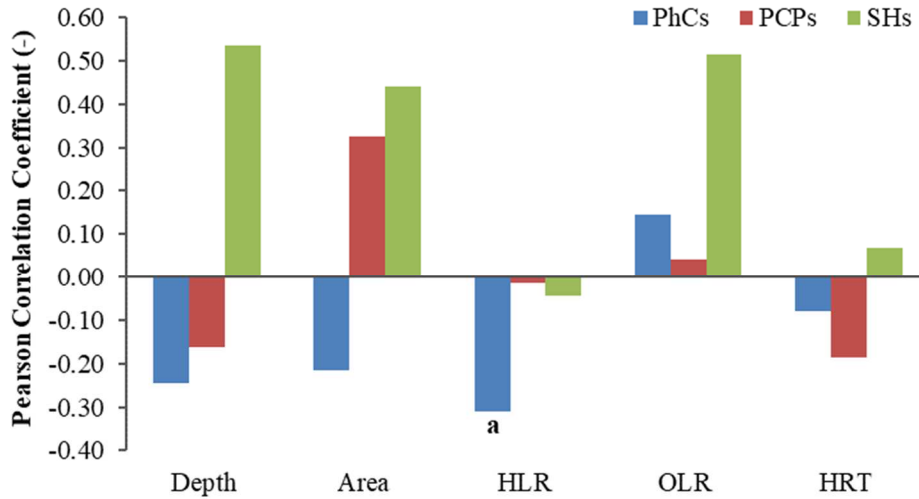


Figure 3. Pearson correlation statistics among the studied design and operational parameters and the removal efficiency of widely studied 31 PhCs, 13 PCPs, and eight SHs.

Note: 'a' shows a significant correlation between the parameters at 90% confidence level. The number of data points per pair was 31, 13, and eight in the case of PhCs, PCPs, and SHs, respectively.

For acceptable models (with RMSE < 30%), the RMSEs in training set were < 15% in most of the cases (Table S34). In general, the difference in observed and predicted removal efficiency in the test set was quite good for most of the PhCs. For example, the difference in the observed and predicted removal efficiency was < 30% in case of 14 out of 17 PhCs (82% of the cases) for the model formed based on depth, OLR, and HRT (Table S20). The difference was even < 20% for 11 of the cases indicating high level of accuracy in predication in case of ranitidine, bezafibrate, diltiazem, erythromycin, doxycycline, codeine, tramadol, clofibrac acid, gemfibrozil, furosemide, and atenolol (Figure 4). However, the removal efficiency of three PhCs (monensin, ofloxacin, and sotalol) was not well predicted, as the difference in observed and predicted removal efficiencies was quite high (ranging from 32% to 45%).

The performance of several plausible models was quite similar, as the RMSE values were not much different in most cases, and were in the range of 22% to 30% (Table S34) that implies the possibility to use any of these models for predictions. However, acceptable models were further screened to facilitate the selection of best models for application. The model given in Equation 1 is selected as the first choice, which is based on depth, OLR, and HRT (Tables S20 and S34). This model was formulated using a training set of 14 PhCs with ≥ 20 data points, and it was validated on an independent test set of 17 PhCs (Figure 4 and Table S1). The predicted removal efficiency was quite good for most of the PhCs, and the RMSE values for the training set and the test set were 14% and 22%, respectively (Table S34).

$$RE = 55.222 - 9.036 D + 0.097 OLR + 1.109 HRT \quad (1)$$

Where, *RE* is removal efficiency in %; *D* is depth in m; *OLR* is organic loading rate in g COD m⁻² d⁻¹; and *HRT* is hydraulic retention time in days.

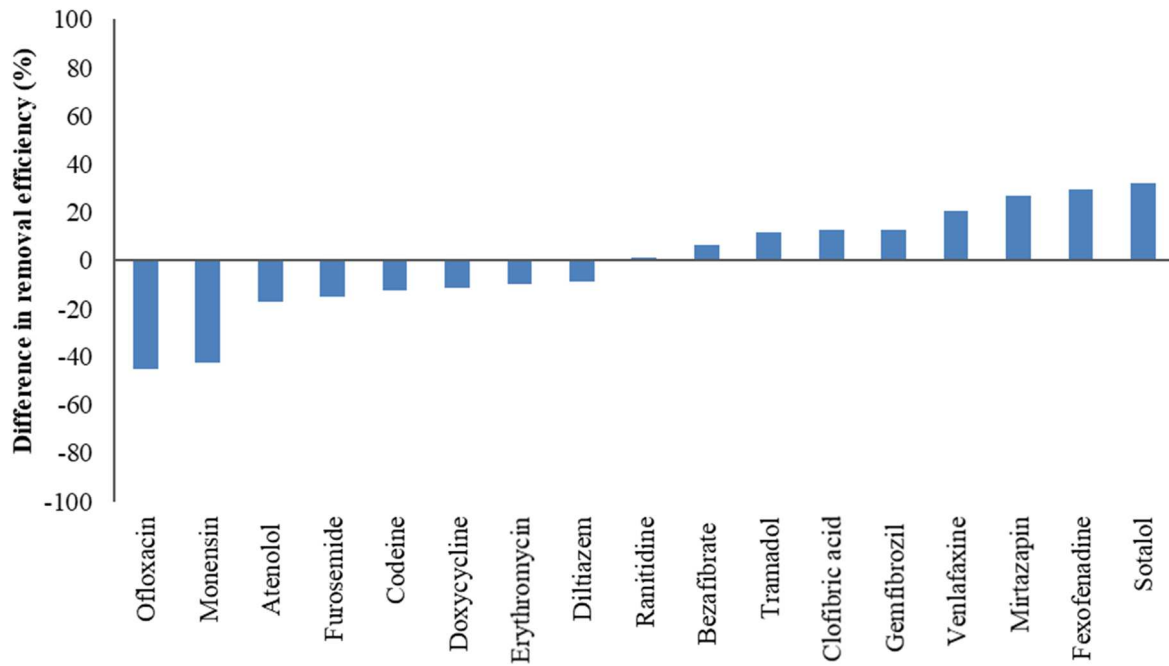


Figure 4. Difference between observed and predicted removal efficiency of test set of PhCs based on the best model with depth, OLR, and HRT.

The addition of HLR with depth and HRT resulted into the second-best model, which is given in Equation 2 (Tables S21 and S34). This model was formulated using a training set of 14 PhCs with ≥ 20 data points, and it was validated on an independent test set of 17 PhCs (Table S1). The predicted removal **efficiency was** quite good for most of the PhCs, and the RMSE values for the training set and the test set were 14% and 22%, respectively (Table S34).

$$RE = 52.725 - 2.419 D - 2.459 HLR + 1.215 HRT \quad (2)$$

Where, RE is removal efficiency in %; D is depth in m; HLR is hydraulic loading rate in $\text{m}^3 \text{m}^{-2} \text{d}^{-1}$; and HRT is hydraulic retention time in days.

3.2. Predictive models for PCPs

The first three PCs had eigenvalue > 1.0 and together could explain 89% of the variance in PCPs data (Figure 1 **and Table 1**). The first two PCs could explain 70% variance in the data (PC1: 50%; PC2: 20%). More details on PCA results with other combination of the studied PCPs are given in supplementary materials (Figure S4 **and Tables S8 & S9**). The high variance explained by three PCs in case of PCPs compared with two PCs in PhCs (89% VS 70%) (Table 1) illustrates better prospects of predictions in case of PCPs compared with PhCs. The PC1 alone explained 50% variance in the PCPs data, with the highest positive loadings of area and negative loadings of OLR, HLR, HRT, and depth. On the other hand, OLR had highest positive loadings and depth, area, and HRT indicated highest negative loadings in PC2 (Figure 5 **and Table 1**). The removal efficiency showed negative loading in case of PCPs compared with positive loadings for PhCs in PC2 and PC3 (Table 1).

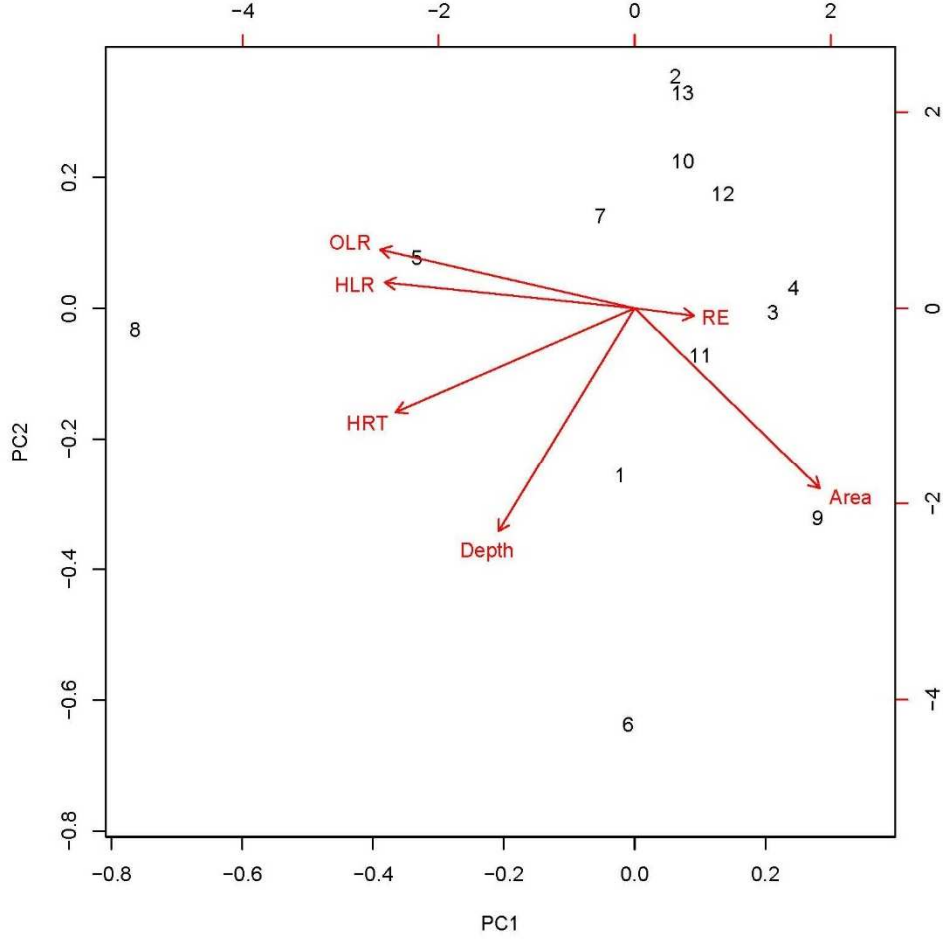


Figure 5. Byplot of PC1 and PC2 based on PCA of 13 widely studied PCPs.

Note: Acesulfame (1); Cashmeran (2); Galaxolide (3); Methyl dihydro-jasmonate (4); Methylparaben (5); N,N-diethyl-meta-toluamide (6); Oxybenzone (7); Propylparaben (8); Tonalide (9); Tributyl phosphate (10); Triclosan (11); Triphenyl phosphate (12); and Tris (2-chloroethyl) phosphate (13).

The removal efficiency indicated positive correlation with area and OLR (Tables S16 and S17), which was consistent with the PCA results (Figure 3 and Table 1). The multiple linear regression models were formed using data of training set of six PCPs with > 10 data points and was validated to predict the removal efficiency of seven PCPs (Table S2). The RMSE values of the promising models for the training set and the test set were 7% and 27%, respectively (Table S35). The best model was formed by combining depth, OLR, and HRT (Tables S22 and S35). The model is presented in Equation 3.

$$RE = 52.646 + 27.072 D + 0.641 OLR - 4.220 HRT \quad (3)$$

Where, RE is removal efficiency in %; D is depth in m; OLR is organic loading rate in $\text{g COD m}^{-2} \text{ d}^{-1}$; and HRT is hydraulic retention time in days.

The model given in Equation 4 is selected as the second-best model, which was based on two variables: OLR and HRT (Tables S23 and S35).

$$RE = 70.390 + 0.635 OLR - 3.976 HRT \quad (4)$$

Where, *RE* is removal efficiency in %; *OLR* is organic loading rate in g COD m⁻² d⁻¹; and *HRT* is hydraulic retention time in days.

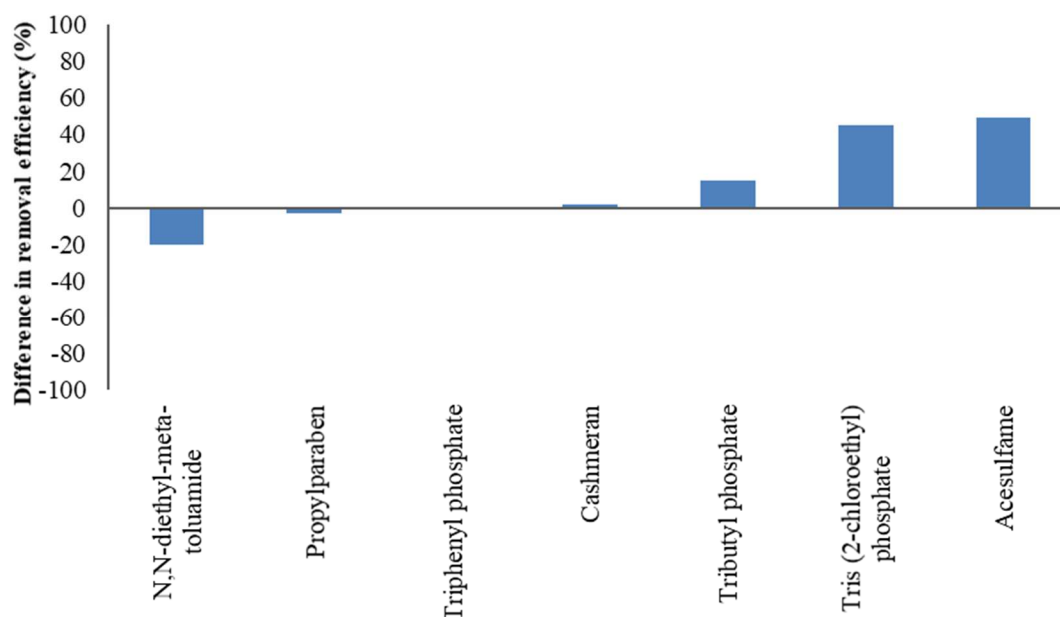


Figure 6. Difference between observed and predicted removal efficiency based on the best model for PCPs with depth, OLR, and HRT.

In most cases, the difference in observed and predicted removal efficiency was small, as illustrated for the best model by Figure 6. The difference in predicted and observed removal efficiency was < 20% in case of five out of seven PCPs in validation data set (cashmeran, N,N-diethyl-meta-toluamide, propylparaben, tributyl phosphate, and triphenyl phosphate).

3.3. Predictive models for SHs

The first two PCs had eigenvalue > 1.0 and could explain 75% of the variance in the SHs data (PC1: 43%; PC2: 32%) (Figure 1 and Table 1). In contrast with PhCs and PCPs all design and operational parameters (depth, area, HLR, OLR, and HRT) showed high positive loadings in PC1. For PC2, high positive loadings were shown by HRT, area, and HLR (Figure 7 and Table 1). More details on PCA analysis is given in supplementary materials (Figure S5 and Tables S10 & S11). The correlation (although statistically non-significant) and regression results were consistent with PCA results (Figure 3 and Tables S18 & S19), indicating the important role of these design and operational parameters in estimating the removal efficiencies of SHs in CWs.

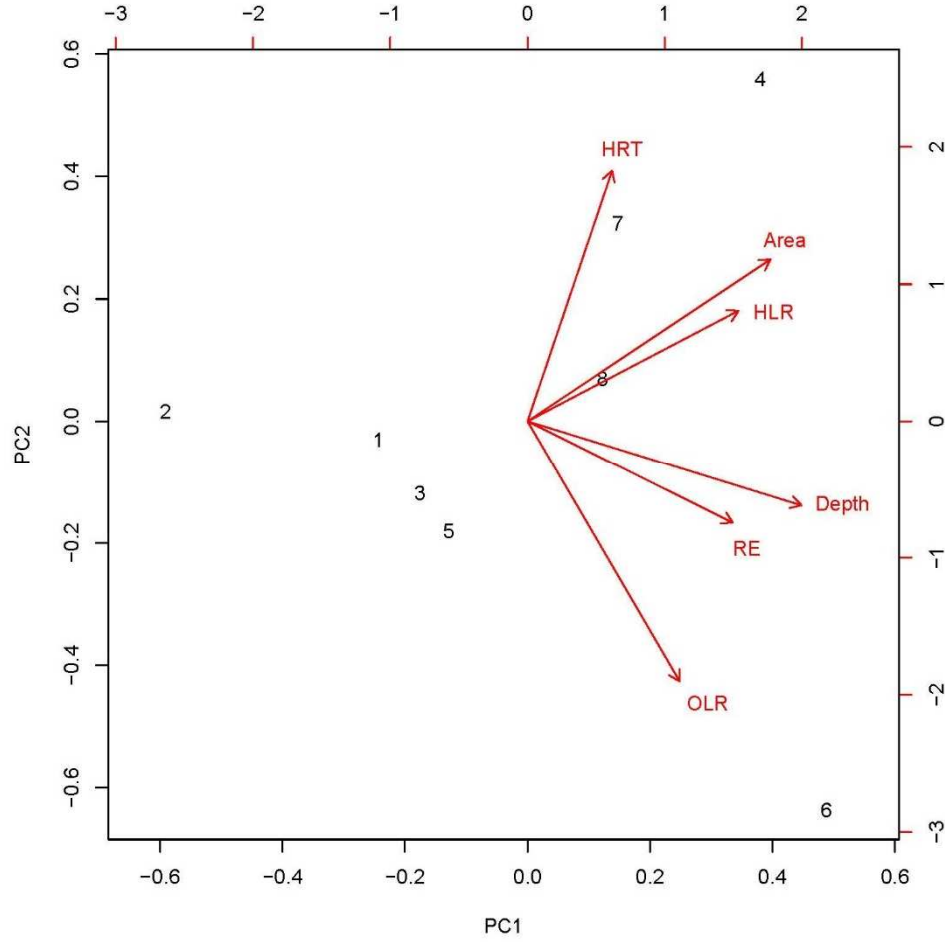


Figure 7. Byplot of PC1 and PC2 based on PCA of eight widely studied SHs.

Note: 17 β -estradiol (1); 17 α -ethinylestradiol (2); Estriol (3); Estrone (4); Levonorgestrel (5); Norethisterone (6); Progesterone (7); and Testosterone (8).

The multiple linear regression models were formed using data of training set of six SHs with > 10 data points and was tested to predict the removal efficiency of two SHs (Table S3). The resulting predictive models were very good, and are given in Table S36. The best model was formed by combining area, HLR, and OLR (Table S24), and yielded quite good performance for the training set (RMSE: 6%) and test set (RMSE: 11%) (Equation 5). The difference in observed and predicted removal efficiency of the tested SHs (norethisterone and progesterone) was only 9% and 12%, respectively (Figure 8).

$$RE = 13.779 + 16.587 A - 51.965 HLR + 0.234 OLR \quad (5)$$

Where, *RE* is removal efficiency in %; *A* is area in m² PE⁻¹; *HLR* is hydraulic loading rate in m³ m⁻² d⁻¹; and *OLR* is organic loading rate in g COD m⁻² d⁻¹.

The addition of HRT along with area, HLR, and OLR resulted in the second-best model (Table S25) with RMSE of 9% and 12% in case of training set and test set, respectively (Table S36). The model is presented in Equation 6.

$$RE = 14.932 + 16.691 A - 48.730 HLR + 0.256 OLR - 1.040 HRT \quad (6)$$

Where, RE is removal efficiency in %; A is area in $\text{m}^2 \text{PE}^{-1}$; HLR is hydraulic loading rate in $\text{m}^3 \text{m}^{-2} \text{d}^{-1}$; OLR is organic loading rate in $\text{g COD m}^{-2} \text{d}^{-1}$; and HRT is hydraulic retention time in days.

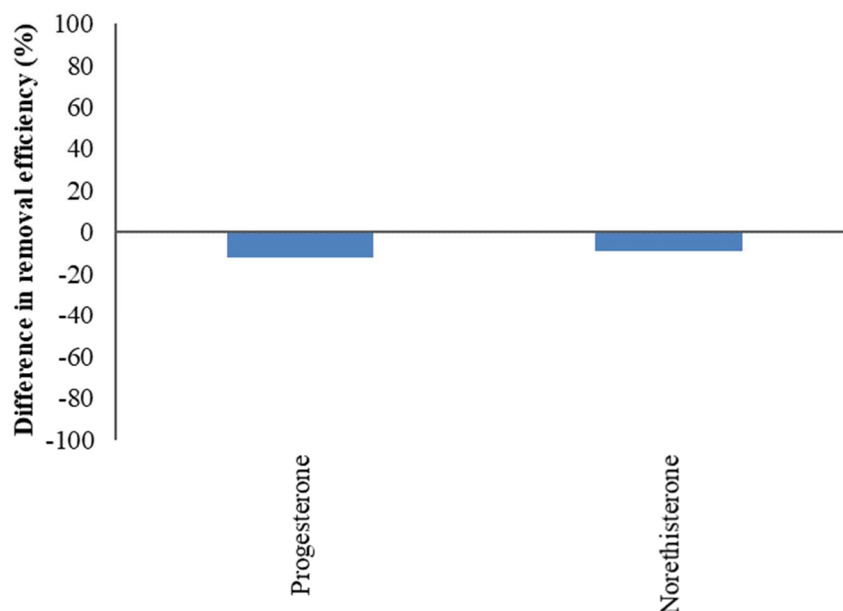


Figure 8. Difference between observed and predicted removal efficiency based on the best model for SHs with area, HLR, and OLR.

3.4. Predictive models for EOCs combining PhCs, PCPs, and SHs

3.4.1. Predictive models combining PhCs and PCPs

The consistency in PCA and correlation results (Figure 3 and Table 1) contributed in forming acceptable predictive models with combined data of PhCs and PCPs (Tables S26, S27, and S37). The models were formed by combining area, OLR, HLR, and HRT mostly with three or four variables together in one model. For acceptable models, the RMSEs in training set were < 15% in all the cases. The best model given in Equation 7 was formed by combining area, HLR, OLR, and HRT (Table S26), which yielded satisfactory results for the test set (RMSE: 22%) (Table S37). The difference in observed and predicted removal efficiency of 20 out of 24 tested PhCs and PCPs was < 30%. The difference in predicted and observed removal efficiency was quite small (< 15%) in the case of doxycycline, tramadol, ranitidine, erythromycin, gemfibrozil, cashmeran, diltiazem, tributyl phosphate, bezafibrate, clofibric acid, triphenyl phosphate, and codeine (Figure 9). However, four out of 24 PhCs and PCPs had quite high difference in observed and predicted removal efficiency (ranging from 32% to 47%).

$$RE = 22.966 + 2.582 A - 7.217 HLR + 0.593 OLR + 0.588 HRT \quad (7)$$

Where, RE is removal efficiency in %; A is area in $\text{m}^2 \text{PE}^{-1}$; HLR is hydraulic loading rate in $\text{m}^3 \text{m}^{-2} \text{d}^{-1}$; OLR is organic loading rate in $\text{g COD m}^{-2} \text{d}^{-1}$; and HRT is hydraulic retention time in days.

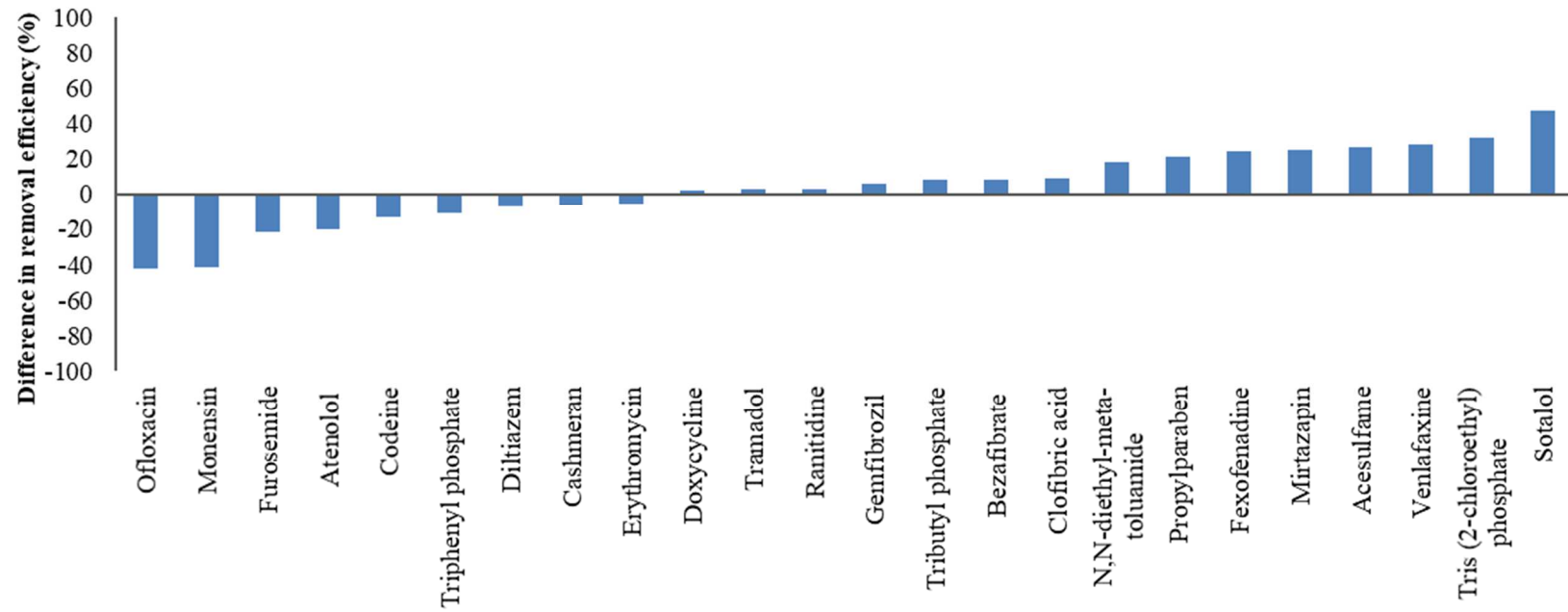


Figure 9. Difference between observed and predicted removal efficiency based on the best model for combined PhCs and PCPs with area, HLR, OLR, and HRT.

The model given in Equation 8 is selected as the second-best model, which was based on three variables: area, HLR, and OLR with RMSE of 14% and 22% in case of training set and test set, respectively (Tables S27 and S37).

$$RE = 23.588 + 2.592 A - 4.419 HLR + 0.686 OLR \quad (8)$$

Where, RE is removal efficiency in %; A is area in $m^2 PE^{-1}$; HLR is hydraulic loading rate in $m^3 m^{-2} d^{-1}$; and OLR is organic loading rate in $g COD m^{-2} d^{-1}$.

3.4.2. Predictive models combining PhCs and SHs

The consistency in PCA and correlation results (Figure 3 and Table 1) contributed in forming acceptable predictive models with combined data of PhCs and SHs (Tables S28, S29, and S38). The models were formed by combining depth, area, OLR, HLR, and HRT, with two, three or four variables together in one model. For acceptable models, the RMSEs in training set were $\leq 15\%$ in all cases (Table S38). The best model given in Equation 9 was formed by combining depth and OLR, which yielded satisfactory results for the training set (RMSE: 14%) and the test set (RMSE: 21%) (Tables S28 and S38). The difference in observed and predicted removal efficiency of 15 out of 19 tested PhCs and SHs was $\leq 25\%$ (Figure 10). However, three out of 19 PhCs and SHs had quite high difference in observed and predicted removal efficiency (ranging from 35% to 43%).

$$RE = 49.122 + 4.280 D + 0.240 OLR \quad (9)$$

Where, RE is removal efficiency in %; D is depth in m; and OLR is organic loading rate in $g COD m^{-2} d^{-1}$.

The addition of HRT along with depth and OLR resulted in the second-best model (Table S29) with RMSE of 14% and 22% in case of training set and test set, respectively (Table S38). The model is presented in Equation 10.

$$RE = 51.944 - 8.051 D + 0.250 OLR + 0.905 HRT \quad (10)$$

Where, RE is removal efficiency in %; D is depth in m; OLR is organic loading rate in $g COD m^{-2} d^{-1}$; and HRT is hydraulic retention time in days.

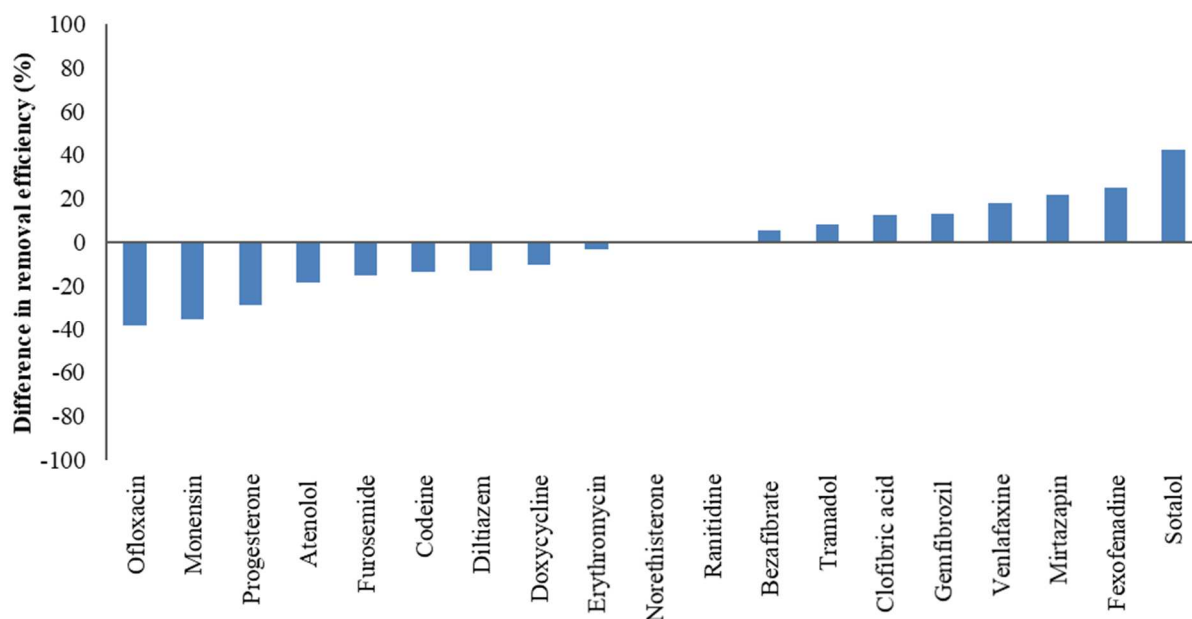


Figure 10. Difference between observed and predicted removal efficiency based on the best model for combined PhCs and SHs with depth and OLR.

3.4.3. Predictive models combining PCPs and SHs

In case of PCPs and SHs, the models were formed by combining area, OLR, HLR, and HRT, mostly with two or more variables together in one model. For acceptable models, the RMSEs in the training set were 11% in all the cases (Table S39). The differences in observed and predicted removal efficiencies were not very large in most models, as illustrated by the results of the best model (Figure 11). The best performing model given in Equation 11 was formed by combining area, OLR, and HRT (Table S30). This model yielded quite good results for both the training set (RMSE: 11%) and test set (RMSE: 20%) (Table S39). The difference in the observed and predicted removal efficiency of six out of nine PCPs and SHs (N,N-diethyl-meta-toluamide, cashmeran, norethisterone, triphenyl phosphate, propylparaben, and tributyl phosphate) was < 15% (Figure 11). This indicate that the removal efficiency of these compounds could be adequately predicted by the proposed models. However, in the case of three compounds (acesulfame, progesterone, and tris (2-chloroethyl) phosphate) the difference in observed and predicted removal efficiency was higher than 30%.

$$RE = 49.470 + 2.001 A + 0.279 OLR - 1.515 HRT \quad (11)$$

Where, RE is removal efficiency in %; A is area in $m^2 PE^{-1}$; OLR is organic loading rate in $g COD m^{-2} d^{-1}$; and HRT is hydraulic retention time in days.

The addition of HLR along with area and OLR resulted in the second-best model (Table S31) presented in Equation 12, which yield almost similar results for the training and test sets (RMSEs: 11% and 22%, respectively) (Table 39). However, this model was not able to explain more variance compared with the best model. Nevertheless, the differences in observed and predicted removal efficiency was somewhat similar to the best model.

$$RE = 45.145 + 1.892 A - 9.096 HLR + 0.285 OLR \quad (12)$$

Where, RE is removal efficiency in %; A is area in $\text{m}^2 \text{PE}^{-1}$; HLR is hydraulic loading rate in $\text{m}^3 \text{m}^{-2} \text{d}^{-1}$; and OLR is organic loading rate in $\text{g COD m}^{-2} \text{d}^{-1}$.

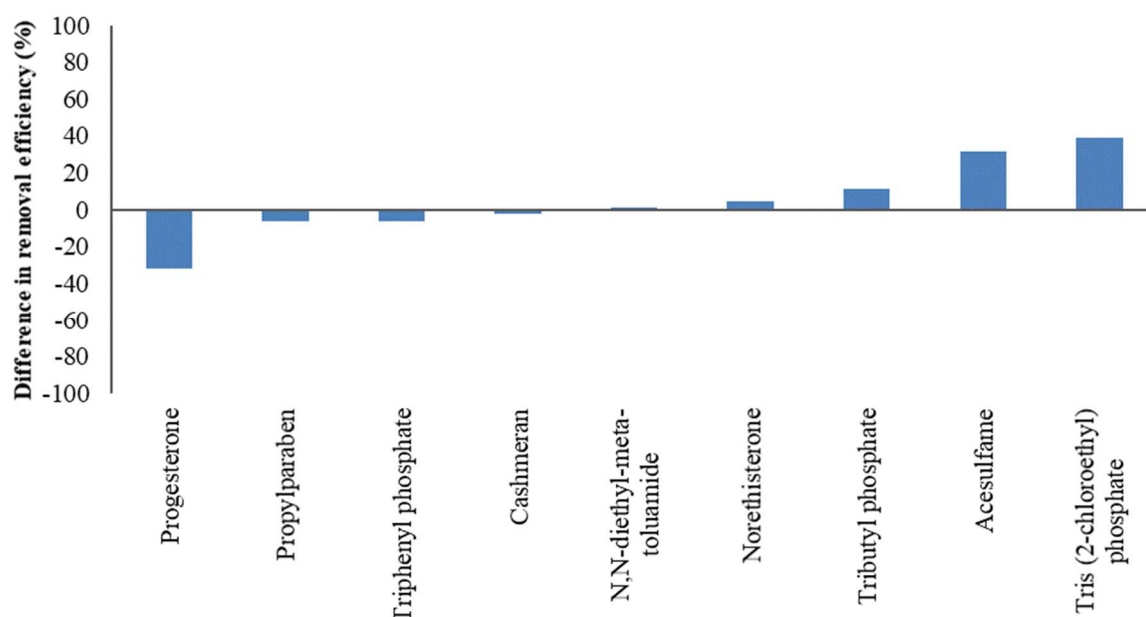


Figure 11. Difference between observed and predicted removal efficiency based on the best model for combined PCPs and SHs with area, OLR, and HRT.

3.4.4. Predictive models combining PhCs, PCPs, and SHs

The generic models of PhCs, PCPs, and SHs were formed by combining area, OLR, HLR, and HRT, mostly with three or more variables together in one model. For acceptable models, the RMSEs in the training set were 13% in all the cases (Table S40). The differences in observed and predicted removal efficiencies were not very large in most models, as illustrated by the results of the best model (Figure 12). The best performing model given in Equation 13 was formed by combining area, HLR, OLR, and HRT (Table S32). This model yielded quite good results for both the training set (RMSE: 13%) and test set (RMSE: 22%) (Table S40). The difference in the observed and predicted removal efficiency of 20 out of 26 EOCs (77% of the cases) was < 30% (Figure 12). The difference was even < 20% for more than half of the cases (17 out of 26 EOCs) indicating high level of accuracy in predication in case of doxycycline, diltiazem, cashmeran, tramadol, ranitidine, gemfibrozil, erythromycin, codeine, tributyl phosphate, triphenyl phosphate, norethisterone, clofibric acid, bezafibrate, atenolol, propylparaben, furosemide, and N,N-diethyl-meta-toluamide. This indicate that the removal efficiency of these compounds could be adequately predicted by the proposed models. However, in the case of six compounds the difference in observed and predicted removal efficiency was higher than 30% (Figure 12).

$$RE = 28.539 + 2.275 A - 6.968 HLR + 0.411 OLR + 0.797 HRT \quad (13)$$

Where, RE is removal efficiency in %; A is area in $\text{m}^2 \text{PE}^{-1}$; HLR is hydraulic loading rate in $\text{m}^3 \text{m}^{-2} \text{d}^{-1}$; OLR is organic loading rate in $\text{g COD m}^{-2} \text{d}^{-1}$; and HRT is hydraulic retention time in days.

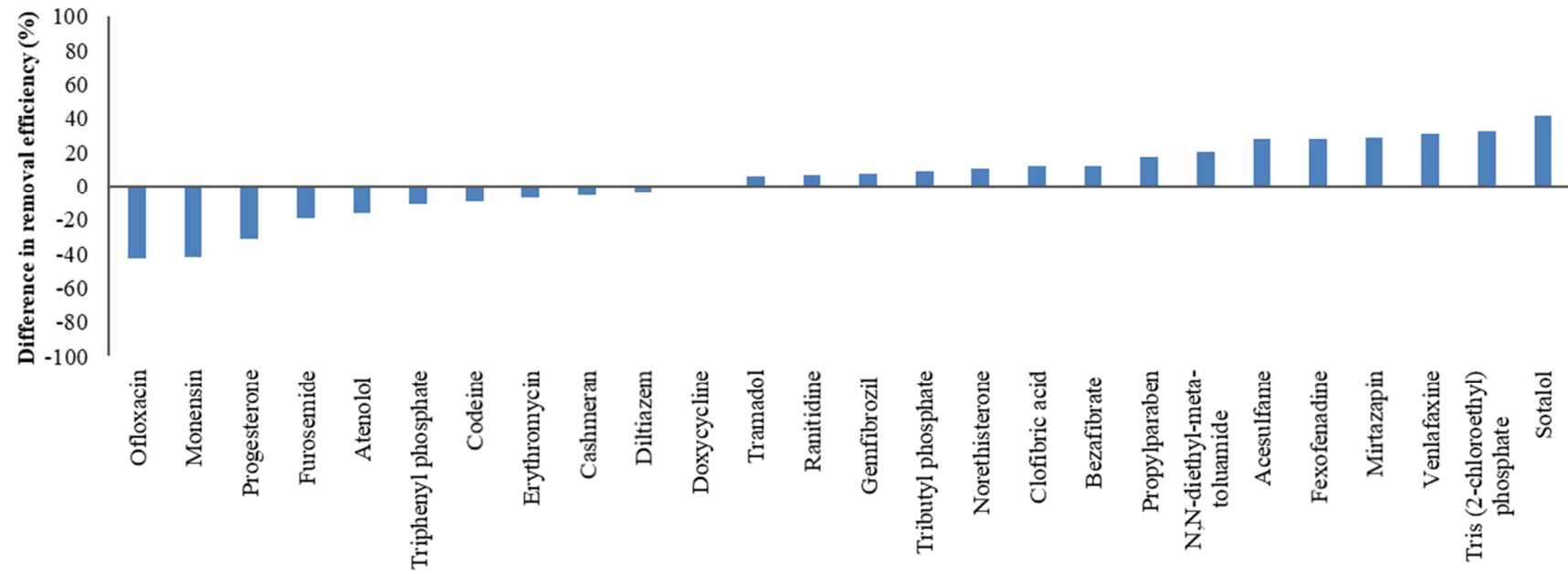


Figure 12. Difference between observed and predicted removal efficiency based on the best model for combined PhCs, PCPs, and SHs with area, HLR, OLR, and HRT.

The second-best model presented in Equation 14 is also possible with the three variables: area, OLR, and HRT (Table S33), which yield almost similar results for the training and test sets (RMSEs: 13% and 24%, respectively) (Table S40). However, this model was not able to explain more variance compared with the best model. Nevertheless, the difference in observed and predicted removal efficiency was somewhat similar to the best model.

$$RE = 23.743 + 2.573 A + 0.439 OLR + 0.718 HRT \quad (14)$$

Where, *RE* is removal efficiency in %; *A* is area in m² PE⁻¹; *OLR* is organic loading rate in g COD m⁻² d⁻¹; and *HRT* is hydraulic retention time in days.

3.5. Role of design and operational parameter in EOCs removal mechanisms

The adequate predictive power of the models formed to predict the removal efficiency of PhCs, PCPs, and SHs individually as well as the combined models developed for EOCs based on design and operational parameters of CWs showed that these parameters play a fundamental role in the establishment of suitable conditions required for the removal of different types of EOCs. For example, the biodegradation (aerobic and anaerobic) is the most dominant removal mechanism for PhCs and SHs removal in CWs (e.g., Rühmland et al., 2015; Choi et al., 2016; Dai et al., 2017; Herrera-Melián et al., 2018; Chen et al., 2019; Nivala et al., 2019; Ilyas et al., 2020; Ilyas and van Hullebusch, 2020b) and PCPs have adsorption onto the substrate and sorption onto organic surfaces as their major removal mechanisms (e.g., Carranza-Diaz et al., 2014; Matamoros et al., 2016; Vymazal et al., 2017; Vystavna et al., 2017; Wang et al., 2019; Ilyas and van Hullebusch, 2020a).

Few experimental studies have investigated the effect of depth of CWs on the removal efficiency of PhCs (Rühmland et al., 2015) and SHs (Song et al., 2009). Rühmland et al. (2015) achieved almost similar removal efficiency of some of the studied PhCs at all water depths and attributed the removal of those PhCs to biodegradation. Song et al. (2009) reported the reduction in removal efficiency of SHs by increasing the depth of CWs and emphasized the importance of maintaining sufficient aerobic conditions in shallow CWs for efficient removal of estrogens (SHs). Several studies reported that longer HRT improves the removal efficiency of PhCs (Dordio and Carvalho, 2013; Herrera-Cárdenas et al., 2016; Auvinen et al., 2017; Vystavna et al., 2017), PCPs (Herrera-Cárdenas et al., 2016; Vystavna et al., 2017; Salcedo et al., 2018), and SHs (Chen et al., 2014; Vystavna et al., 2017; Campos et al., 2019) because most of the mechanisms contributing to the removal of these EOCs such as adsorption onto the substrate media, sorption onto carbon-rich surfaces, plant uptake, anaerobic biodegradation, and photodegradation are slow processes (Auvinen et al., 2017; Vystavna et al., 2017; Petrie et al., 2018) and requires longer HRT for their completion. On the other hand, some studies did not observe a significant difference in the removal efficiency of some of the studied PhCs with the increase in HRT (Zhang et al., 2011, 2012a, 2012b). Zhang et al. (2012b) reported that the non-significant differences ($p > 0.05$) in the removal of carbamazepine, clofibrac

acid, and naproxen at different HRT might be due to that these PhCs are recalcitrant (carbamazepine), very persistent, refractory and non-biodegradable (clofibric acid). The non-significant difference in the removal efficiency of naproxen between batch (83% and 91%) and continuous modes (81% and 93%) at HRT of two and four days might be that naproxen is readily biodegradable and substrate aeration by the plants was sufficient for its complete biodegradation at the studied HRTs. Although the shorter HRT reduced the land area requirement of CWs (Zhang et al., 2011, 2012a; Herrera-Cárdenas et al., 2016), the removal of PhCs should be sufficient to significantly reduce the toxicity of the effluent after treatment with CWs (Herrera-Cárdenas et al., 2016). The removal efficiency of EOCs is also affected by different HLR (Matamoros et al., 2007; Dan et al., 2013; Ávila et al., 2014a; Sharif et al., 2014) and OLR (Sharif et al., 2014; Matamoros et al., 2017) of CWs. Although the HLR of systems is positively correlated with OLR, the organic matter increases the microbial activity and promotes the degradation of pollutants up to a certain HLR. The further increase in HLR reduces the contact time of EOCs with microbes (e.g., Dan et al., 2013) and continuous operation of the system at high HLR for a longer period of time significantly reduces the removal efficiency of EOCs, which are removed by aerobic biodegradation and adsorption onto particles (e.g., Dai et al., 2017).

In addition to the above-mentioned design and operational parameters of CWs, suitable type of plants and support matrix in CWs also play a pivotal role to enhance the performance of the system for the removal of EOCs. For instance, plants play a considerable role in the removal of PhCs, PCPs, and SHs by direct uptake and their indirect positive effects such as degradation by enzymatic exudates and aerobic biodegradation (e.g., Li et al., 2014; Dai et al., 2017; Lee et al., 2018; Nuel et al., 2018). The effect of plants in CWs by considering the removal of these EOCs in planted CWs by using large variety of plants depending upon their availability in different climatic regions and unplanted CWs have been investigated by several individual studies. It is reported that the biotic pathways such as plant uptake and microbial degradation are the feasible degradation mechanisms for these types of EOCs in CWs (Kumar et al., 2011; Li et al., 2014; Dai et al., 2017; Hakk et al., 2017; Lee et al., 2018; Nuel et al., 2018). Similarly, the role of support matrix in the removal of EOCs have been examined by using the substrate material of high adsorption capacity, rich in organic/inorganic surfaces, and high surface area. This indicated that adsorption to the substrate media and/or sorption onto organic/inorganic surfaces is an important removal mechanism to reduce PhCs (Dan et al., 2013; Chen et al., 2016; Huang et al., 2017; Park et al., 2018; Nivala et al., 2019), PCPs (Ávila et al., 2014b; Salcedo et al., 2018; Xie et al., 2018), and SHs (Herrera-Melián et al., 2015, 2018; Hakk et al., 2018; Campos et al., 2019) from wastewater. Ilyas and van Hullebusch (2019, 2020a, 2020b) conducted a comprehensive and critical review of the performance and a comparison of all types of planted and unplanted CWs for the removal of PhCs, PCPs, and SHs based on available literature. The role of support matrix in the removal of these categories of EOCs by using the substrate material of high adsorption capacity, rich in organic/inorganic surfaces, and high surface area is also summarized in these studies. Several researchers suggest that physicochemical properties of EOCs play a crucial role in their removal mechanisms in CWs (e.g., Hakk et al., 2018;

Nuel et al., 2018; Petrie et al., 2018; Chen et al., 2019). The physicochemical properties of EOCs, which play considerable role in the removal processes, are governed by molecular weight/structure, water solubility, dissociation constant (pKa), cationic or anionic nature (charge), presence of certain elements (e.g., chlorine), organic carbon sorption coefficient (Log K_{oc}), octanol-water partition coefficient (Log K_{ow}), and distribution coefficient (Log D_{ow}). Ilyas et al. (2020) and Ilyas and van Hullebusch (2020b, 2020c) conducted a comprehensive analysis on the role of physicochemical properties in the removal mechanisms of PhCs, PCPs, and SHs. The prediction of removal efficiency of EOCs based on their physicochemical properties is explored by developing the novel predictive models, in the form of multiple linear regressions in Ilyas et al., under review in *Journal of Environmental Management*.

3.6. Uncertainty Analysis

It is important to acknowledge the uncertainty associated with observed and predicted removal efficiencies. Therefore, we did uncertainty analysis by comparing the mean and standard deviation of the removal efficiency of the examined EOCs in case of observed and predicted values. The results are shown by Figures 13-19. The analysis reveals that there is a quite high standard deviation in case of observed removal efficiencies. This indicates considerable differences in removal efficiencies under different environmental, design and operational conditions of CWs. On the other hand, the mean of predicted removal efficiency is in close agreement with the observed values, as it falls well within the range of standard deviation in most cases. Furthermore, the predictions made by various regression models is not much different from each other, as indicated by small standard deviation of the predicted values (< 5% in most cases). Therefore, the removal efficiencies can be predicted with reasonably good accuracy by using the proposed individual models or by estimating mean and standard deviations based on all plausible models. The second option is preferred one because it includes uncertainty into the predicted results, and hence include uncertainty in the decision-making process. Moreover, it is recommended to consider the uncertainties associated with observed and predicted removal efficiencies, and take caution in interpreting and using these estimates in decision making process. Additionally, a main assumption is that the proposed models are applicable within the range of data used in their development (Supplementary materials 1: Tables S1-S3). It is assumed that the proposed models are applicable under wide range of design and operation conditions (e.g. temperature, plants, and support matrix) because these are developed based on global data set. Nevertheless, the predications made by using the data beyond the input ranges is likely to be more uncertain. Despite this limitation, the models are assumed to work well for wide range of environmental, design and operational conditions.

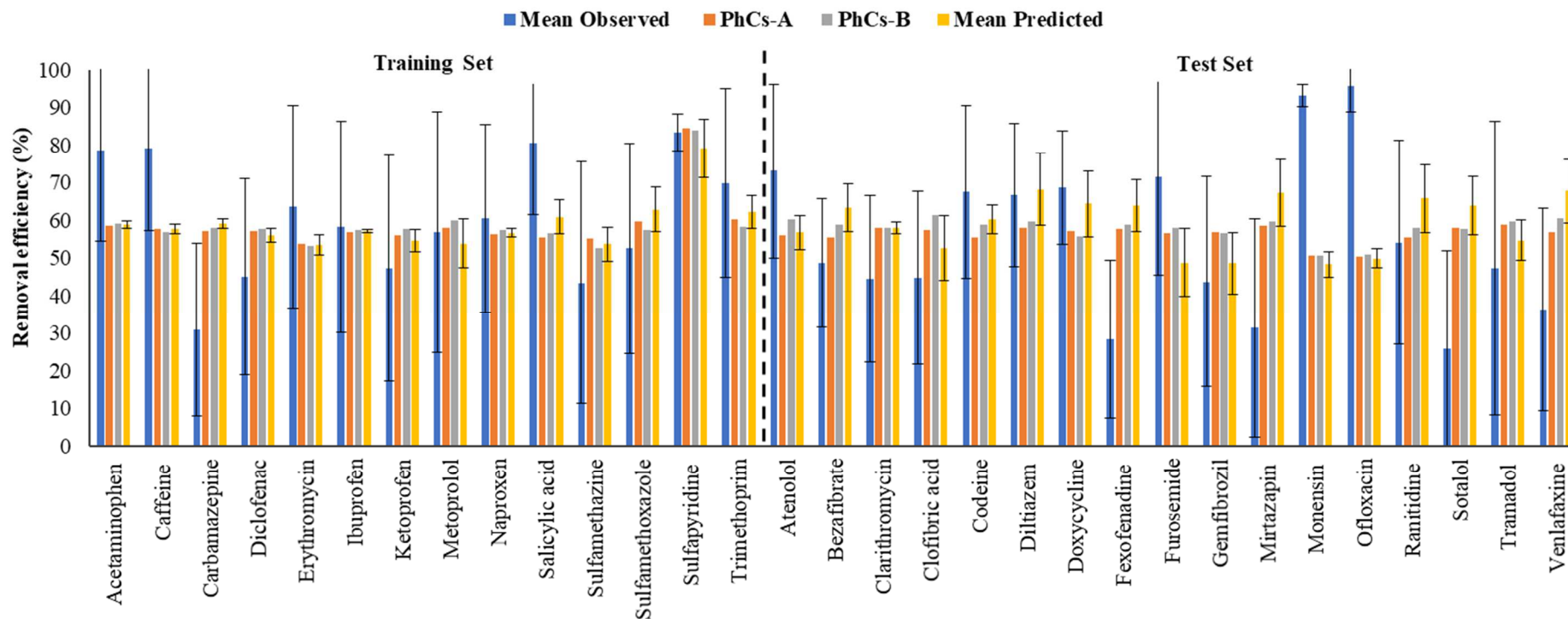


Figure 13. Difference between observed and predicted removal efficiency based on six acceptable models formed using data of 14 PhCs with ≥ 20 data points. Note: “A” and “B” represent first- and second-best models. Standard deviation values were capped at 100 to improve the readability of the graph. Actual values can be found in REOCW-DOP.

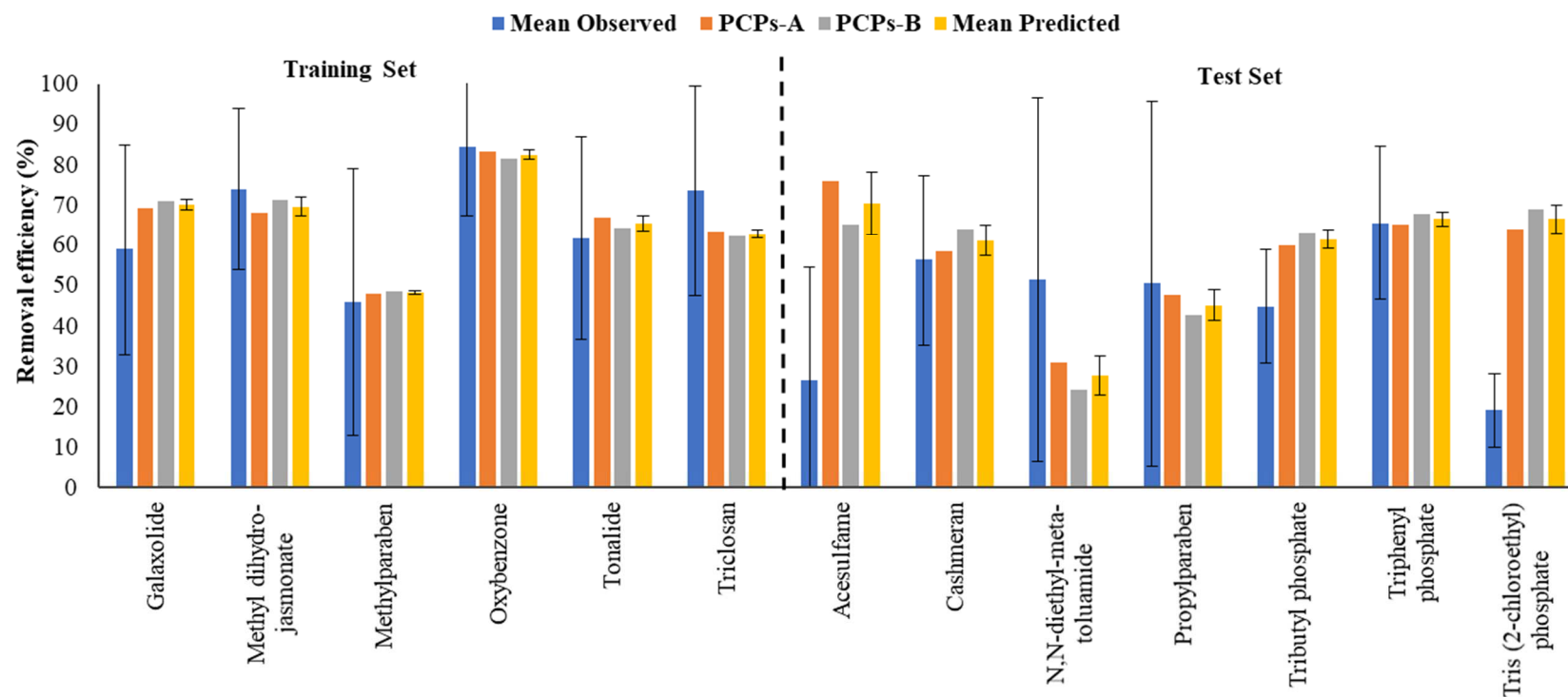


Figure 14. Difference between observed and predicted removal efficiency based on two acceptable models formed using data of six PCPs with > 10 data points.

Note: “A” and “B” represent first- and second-best models. Standard deviation values were capped at 100 to improve the readability of the graph. Actual values can be found in REOCW-DOP.

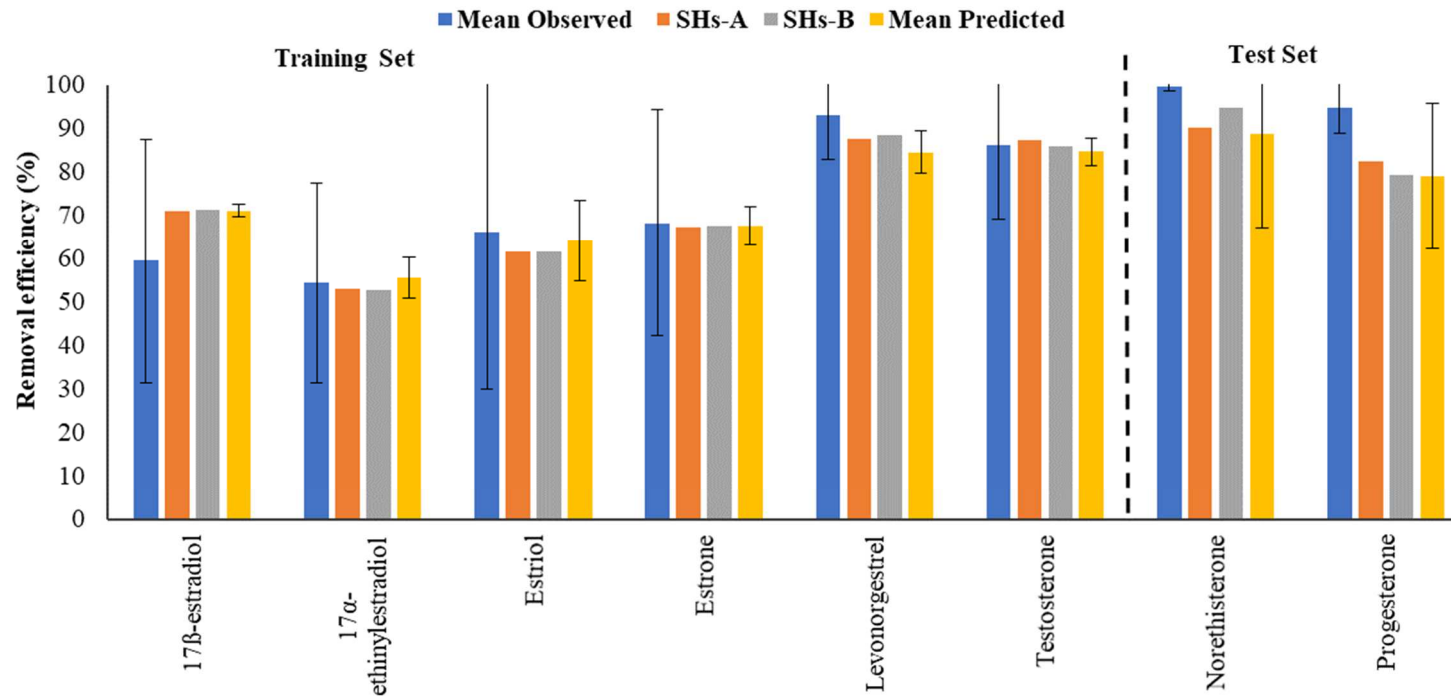


Figure 15. Difference between observed and predicted removal efficiency based on six acceptable models formed using data of six SHs with > 10 data points. Note: “A” and “B” represent first- and second-best models. Standard deviation values were capped at 100 to improve the readability of the graph. Actual values can be found in REOCW-DOP.

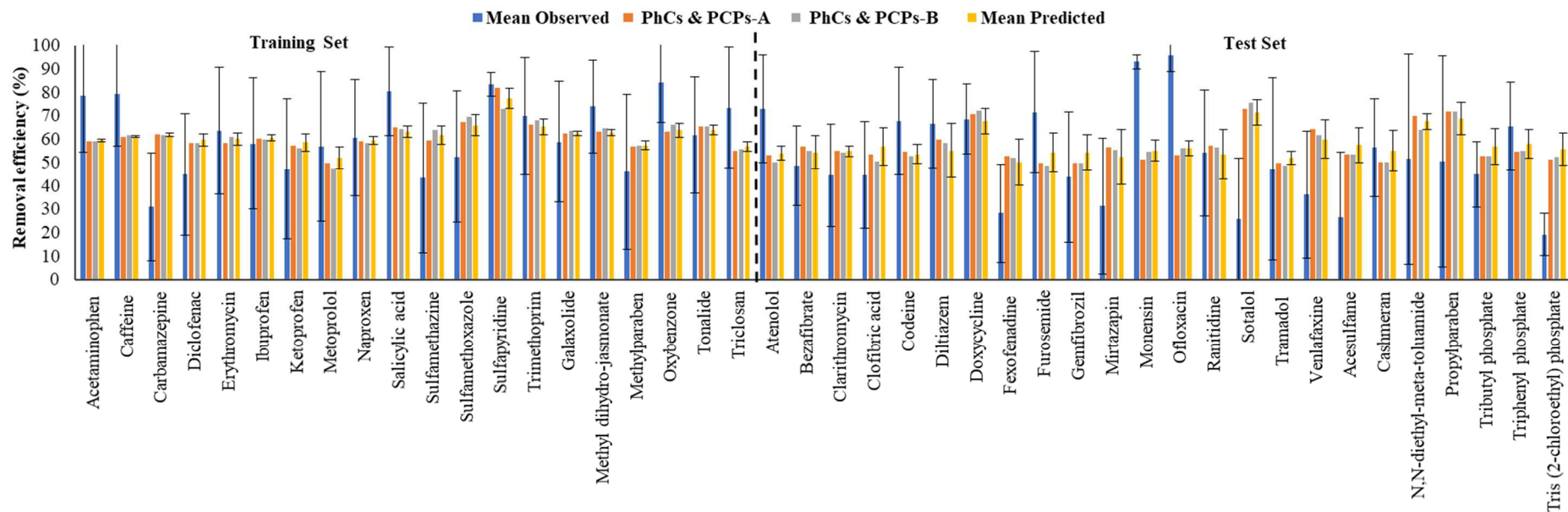


Figure 16. Difference between observed and predicted removal efficiency based on seven acceptable models formed using data of 14 PhCs and six PCPs with data points ≥ 20 and > 10 , respectively.

Note: "A" and "B" represent first- and second-best models. Standard deviation values were capped at 100 to improve the readability of the graph. Actual values can be found in REOCW-DOP.

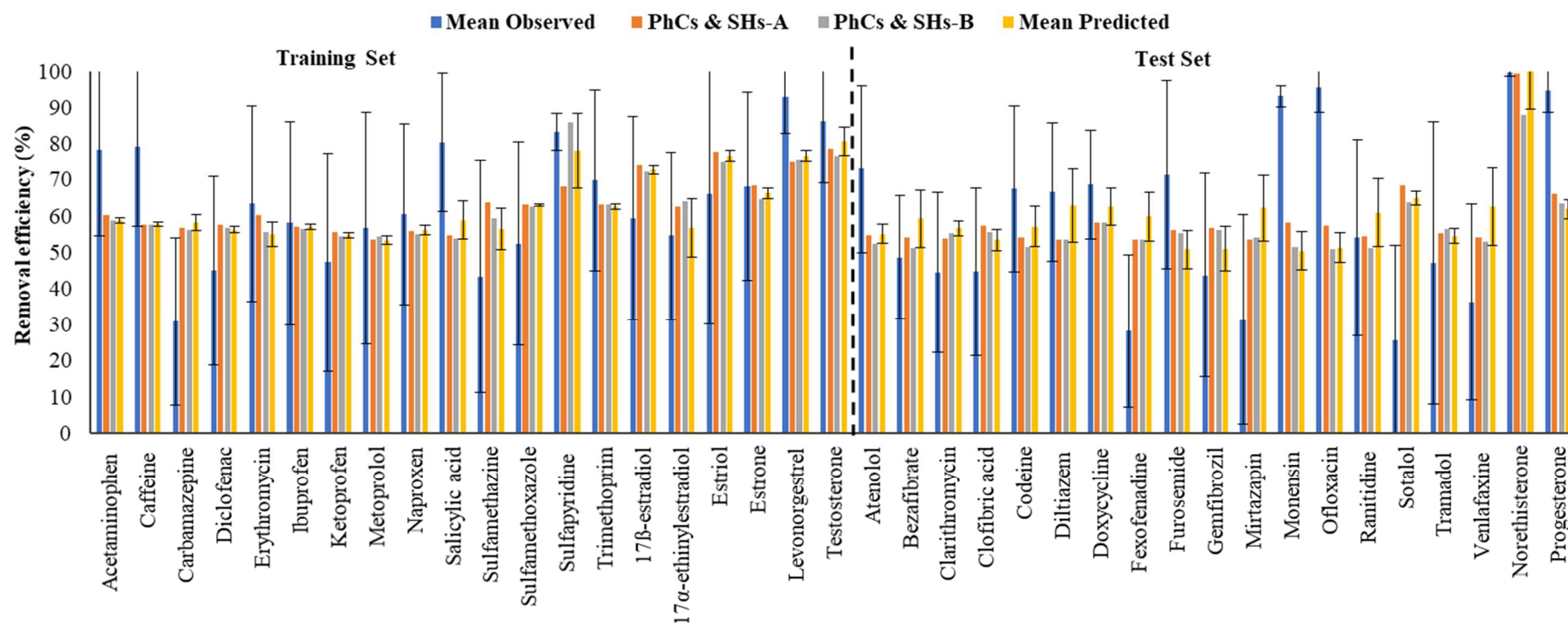


Figure 17. Difference between observed and predicted removal efficiency based on six acceptable models formed using data of 14 PhCs and six SHs with data points ≥ 20 and > 10 , respectively.

Note: “A” and “B” represent first- and second-best models. Standard deviation values were capped at 100 to improve the readability of the graph. Actual values can be found in REOCW-DOP.

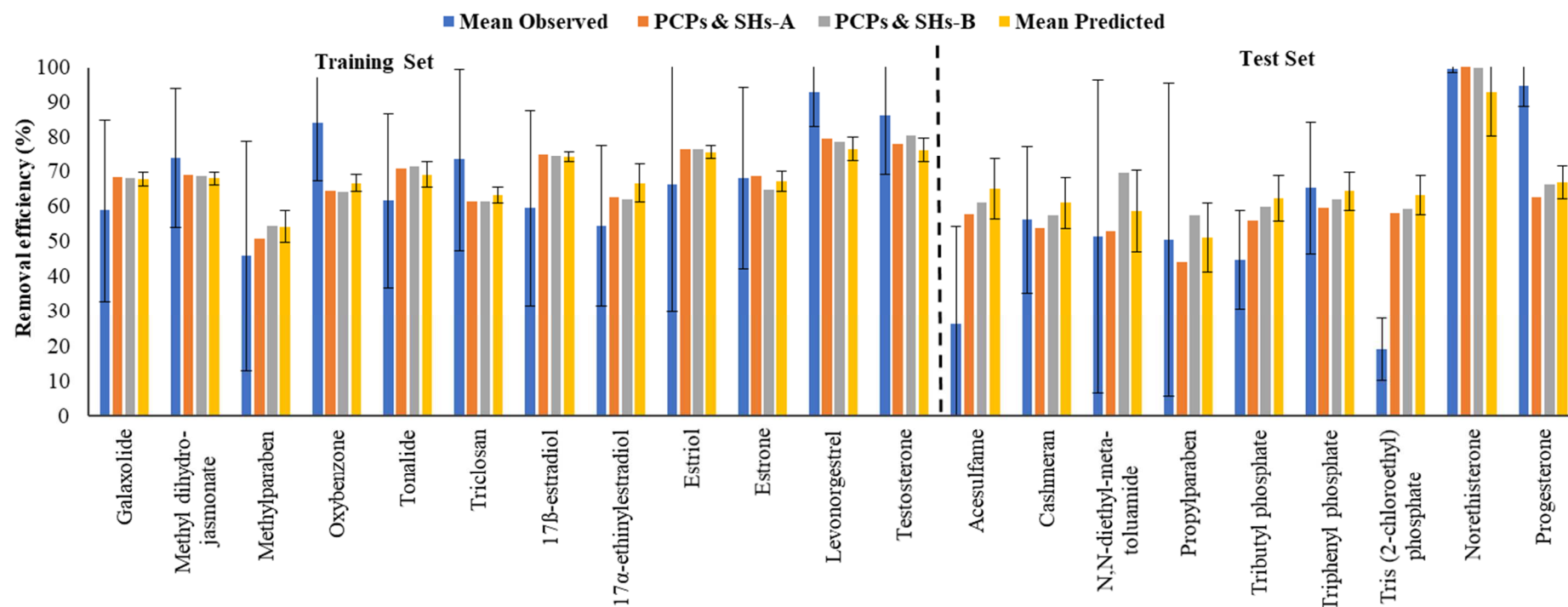


Figure 18. Difference between observed and predicted removal efficiency based on twelve acceptable models formed using data of six PCPs and six SHs with data points > 10 in both cases.

Note: "A" and "B" represent first- and second-best models. Standard deviation values were capped at 100 to improve the readability of the graph. Actual values can be found in REOCW-DOP.

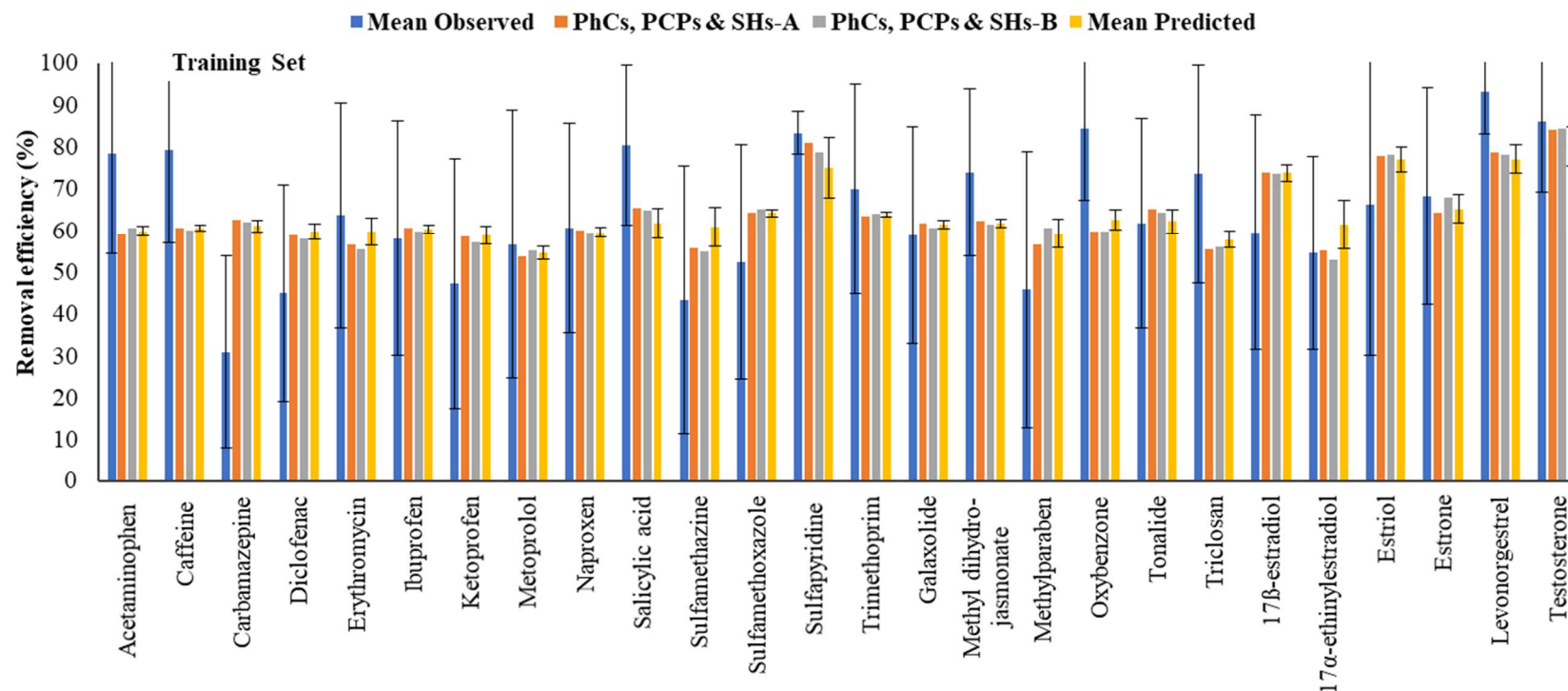


Figure 19a. Difference between observed and predicted removal efficiency of training set based on ten acceptable models using data of 14 PhCs, six PCPs, and six SHs with data points ≥ 20 , > 10 , and > 10 , respectively.

Note: “A” and “B” represent first- and second-best models. Standard deviation values were capped at 100 to improve the readability of the graph. Actual values can be found in REOCW-DOP.

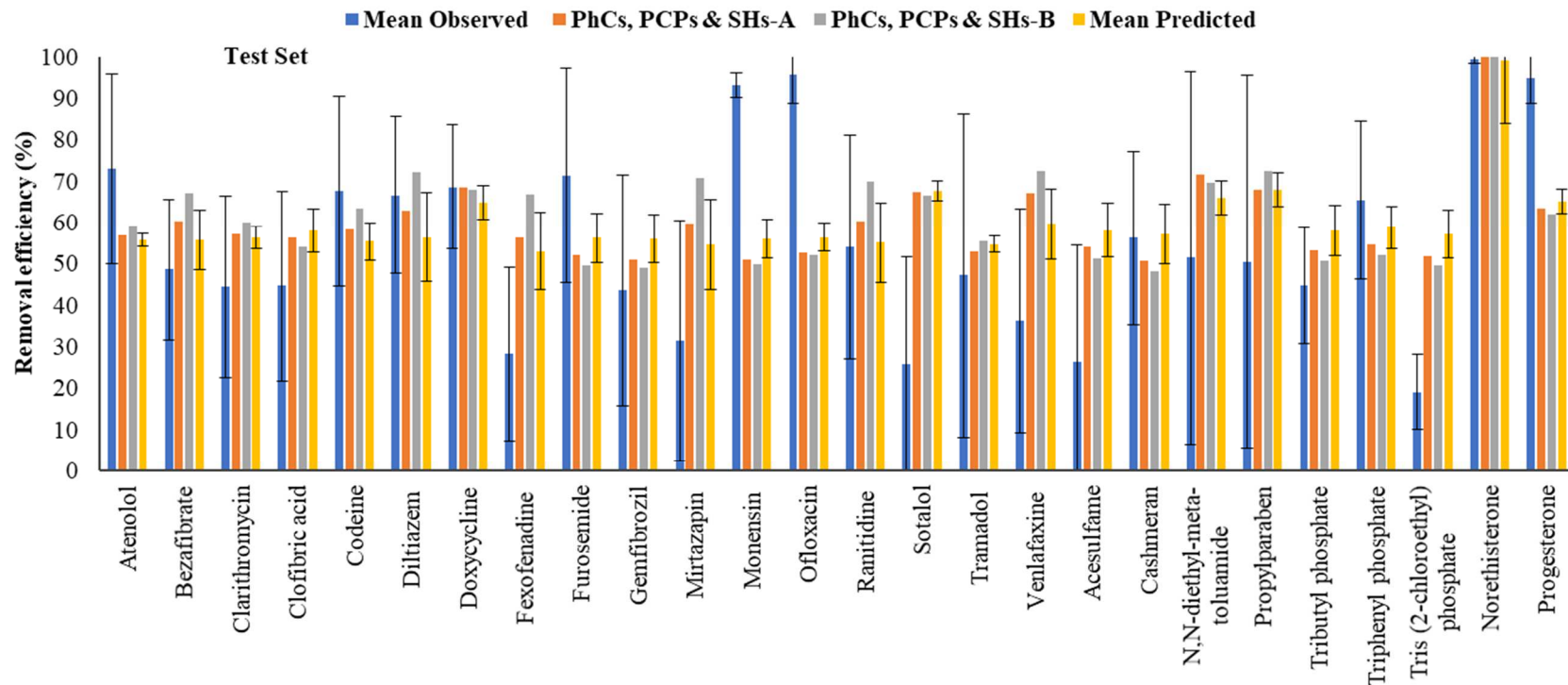


Figure 19b. Difference between observed and predicted removal efficiency of test set based on ten acceptable models using data of 14 PhCs, six PCPs, and six SHs with data points ≥ 20 , > 10 , and > 10 , respectively.

Note: “A” and “B” represent first- and second-best models. Standard deviation values were capped at 100 to improve the readability of the graph. Actual values can be found in REOCW-DOP.

4. Further development and applications

The predictive models developed in this study could provide useful information in the decision-making process. For example, initial estimates of removal efficiencies could be generated using design and operational parameters of a CW system. Thus, the developed models could serve as useful screening tools to provide first-hand information on the expected removal of PhCs, PCPs, and SHs in CWs. Similarly, preliminary values of design and operational parameters can be generated from the proposed models and experimental data sets. Furthermore, the plausible models could be used in developing and upgrading different decision-making tools. For instance, we developed a decision support tool based on this research work, which could provide an easy way of estimating removal efficiency of PhCs, PCPs, and SHs based on design and operational parameters of CWs. The tool could be used by various stakeholders such as researchers, practitioners, policy makers, and citizens. The developed decision support tool (DST) is named as REOCW-DOP. REOCW-DOP mainly follows the concept we developed in our previous work (Ilyas et al., under review in Journal of Environmental Management). The key features of the tool are schematized in Figure 20 and outlined below. REOCW-DOP was developed using Microsoft Excel 2016, and is provided as a supplementary material (Excel file: DST-REOCW-DOP-secure, along with the user manual).

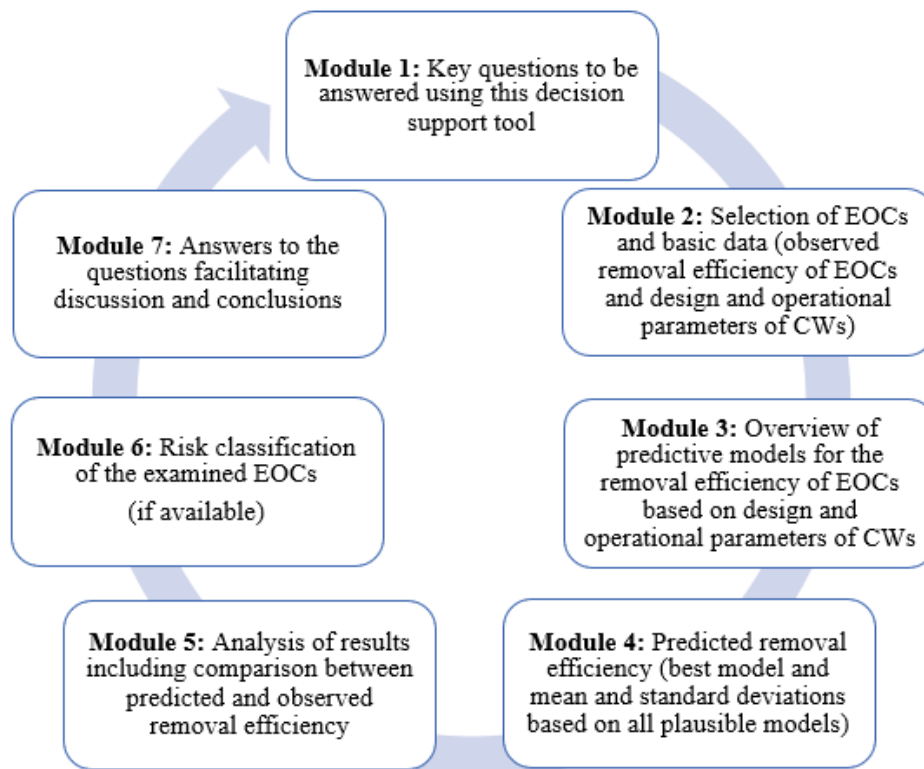


Figure 20. A schematic diagram illustrating the main steps of the developed DST-REOCW-DOP.

The REOCW-DOP consists of seven modules. The users are advised to follow a step by step process, and sequentially follow the modules. The first module contains information on the design of REOCW-DOP. It also provides few key questions that could be answered by using the tool. REOCW-DOP can be used by an individual user or multiple users in the form of a group of different stakeholders (e.g., policy/decision makers, wastewater managers, design engineers and operators of CW systems, researchers/scientists, and citizens). The following main questions are enlisted under module 1.

1. What could be the removal efficiency of a certain EOC in CWs?
2. What is the likelihood of removal efficiency in falling under a certain quartile range (e.g., Q1: 0-25%; Q2: 26-50%; Q3:51-75%; Q4: 76-100%)?
3. Which design and operational parameters are better predictor of removal efficiency for a certain EOC?
4. How the predicted and experimental removal efficiencies differ from each other?
5. What is the range of uncertainty in the available predictions and field observations?
6. What is the potential environmental risk posed by the EOCs of interest?
7. What lessons could be drawn based on the predictions and observations?

In the second module, basic data of EOCs is given, which include name and observed removal efficiency (mean and standard deviation) of EOCs under study, and the mean values of design and operational parameters compiled from the peer reviewed published sources in our previous research (Ilyas et al.,2020; Ilyas and van Hullebusch, 2020a, 2020b). The user will be able to select specific EOCs or all of them during a simulation process. If more than one stakeholder is involved in using the tool, they need to agree on the list of EOCs to be examined.

In the third module, we include the novel predictive models developed in this research. Based on these models, the removal efficiencies of the EOCs are predicted, and information is generated to answer the above-mentioned questions. The results of these predictions are shown in the fourth module. The estimates are given for the first- and second-best models as well as mean and standard deviation based on all plausible models. Under the fifth module, a comparative analysis is done between the predicted and observed removal efficiency. Additionally, module six provides information on environmental risk posed by EOCs, which was estimated in our previous research (Ilyas et al., 2020; Ilyas and van Hullebusch, 2020b, 2020c). In the seventh module, the information is summarized (in Tabular and Graphical forms) to provide answers to all the above-mentioned questions. This information could serve as the basis of an informed discussion and, consequently contribute to the informed decision-making process. After evaluating information given in module 7, the users may end the simulation session or run another round of simulation using a different set of EOCs.

5. Conclusions

The following conclusions are drawn from this study:

1. The design and operational parameters of CWs are good predictors of the removal efficiency of EOCs in CWs. Operational parameters, HLR, OLR, and HRT are the most significant predictors followed by design parameters (depth and area). Thus, plausible predictive models were formulated by combining these parameters, and acceptable models contained two-four of these parameters.
2. The removal efficiency of PhCs, PCPs, and SHs in CWs could be predicted reasonably well using design and operational parameters of CWs: depth, area, HLR, OLR, and HRT. The plausible models for PhCs were formed by including three-four of these parameters, and the best model was based on depth, OLR, and HRT (RMSEs: training set: 14%; test set: 22%). The best models for PCPs were developed with OLR and HRT or adding depth (RMSEs: training set: 7%; test set: 27%). Similarly, the removal efficiency of SHs was predicted very well with the model including HLR, OLR, and area (RMSEs: training set: 6%; test set: 11%).
3. A generic model by combining data of PhCs, PCPs, and SHs also showed acceptable performance; the best model was formed by combining area, HLR, OLR, and HRT (RMSEs: training set: 13%; test set: 22%). Similarly, the combined models for the prediction of removal efficiency of PhCs and PCPs, PhCs and SHs, and PCPs and SHs were also possible. The adequate predictive power of the combined models based on design and operational parameters of CWs showed that these parameters play a crucial role to establish suitable conditions required for the removal of different types of EOCs. For example, the biodegradation (aerobic and anaerobic) is the most dominant removal mechanism for PhCs and SHs removal in CWs, and PCPs have adsorption onto the substrate and sorption onto organic surfaces as their major removal mechanisms.
4. It is recommended to examine uncertainties associated with the prediction process. The uncertainties could be present due to limitations related to experimental data and statistical analyses. Therefore, it is important to include uncertainties in the decision-making process. Thus, it is preferable to use more than one predictive model (when available), and include the uncertainty range, for example, by assessing the mean and standard deviations of predicted and observed removal efficiencies.
5. The novel models developed in this study could serve as useful screening tools in the decision-making process by providing initial estimates of the possible removal efficiency of PhCs, PCPs, and SHs in CWs with specific design and operational conditions. Using the promising results of this study, a decision support tool (DST-REOCW-DOP) was developed, which could be easily used by different stakeholders such as researchers, policy makers, design engineers and operators of the CW systems.

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Graphical abstract

Prediction of the removal efficiency of emerging organic contaminants based on design and operational parameters of constructed wetlands

