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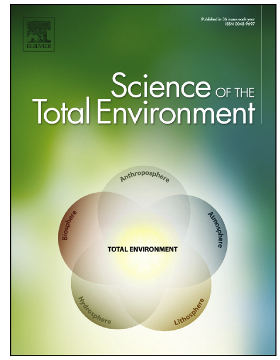

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Removal of micropollutants using a membrane bioreactor coupled with powdered activated carbon– A statistical analysis approach

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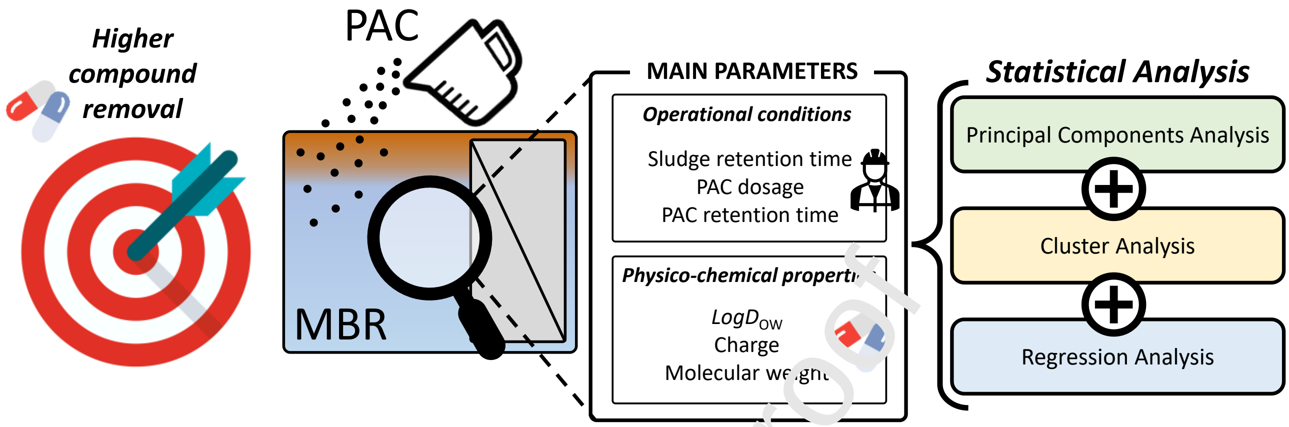
Abstract

The occurrence of micropollutants in wastewater is largely documented as well as the environmental risk posed by their residues in the aquatic environment. Many investigations have been carried out and plan to study and improve their removal efficiency in existing wastewater treatment plants. At the same time, efforts are being made to develop new technologies or upgrade existing ones to increase the removal of a selection of micropollutants. Due to the great variability in their chemical and physical properties, it would be advisable to find representative compounds or identify the factors which most influence the removal mechanisms under specific conditions. This study analyses the removal efficiencies of a great number of micropollutants in wastewater treated in a membrane bioreactor coupled with powdered activated carbon (PAC), which was the subject of a review article we have recently published. The main operational parameters (i.e. PAC dosage, PAC retention time and sludge retention time) and compound physico-chemical properties (i.e. octanol-water distribution coefficient, charge and molecular weight) were first selected on the basis of a dedicated screening step and then an attempt was carried out to clarify their influence on the removal of micropollutants from wastewater during its treatment. To this end, a statistical analysis, mainly based on exploratory methods (cluster analysis and principal component analysis) and regression analysis, was carried out to compare and discuss the different results published in the scientific literature included in the cited review article. It emerged, that, based on the collected dataset, micropollutant charge and LogD_{ow} seem to play the most important role in the removal mechanisms occurring in MBR coupled with PAC.

Keywords: Cluster Analysis; Membrane Biological Reactor; Micropollutants Removal; Powdered Activated Carbon; Principal Component Analysis; Regression Analysis.

Graphical abstract



1 Introduction

The occurrence of micropollutants in the aquatic environment has been well documented by many investigations worldwide (Wilkinson et al., 2022) and their effect on the environment as well as on human health is an issue of increasing concern. Wastewater treatment plants are considered one of the most important pathways for their immission into the environment (Ghirardini et al., 2021). Environmental quality standards and legal limits regarding treated effluent release into surface water bodies have been set for only a few of them (e.g. pesticides, plasticisers and insect repellents as in Directive 2013/39/EU of the European Parliament and of the Council (EC, 2013)) and only in some countries (e.g. some European Union member States and Switzerland). Despite this fact, great efforts are being made worldwide to test solutions that are able to improve the removal of selected micropollutants from wastewater (namely, antibiotics, analgesics and anti-inflammatory drugs, psychiatric drugs and antidiuretics). End-of-pipe treatments based on advanced oxidation processes (e.g. ozonation, $O3/H_20_2$), filtration and sorption on activated carbon (AC) are some of the options suggested for secondary effluent polishing. This is the case in Switzerland, according to their Micropol strategy (https://www.eawag.ch/en/department/eng/projects/abwasser/strategy-micropoll/). In addition, the upgrading of or changes to existing wastewater treatment steps may represent another strategy to guarantee a higher removal of a selection of micropollutants (Rizzo et al., 2019). In this context, limiting the attention to the secondary biological treatment, it was confirmed that the removal efficiencies are higher in a membrane bioreactor (MBR) than in a conventional activated sludge system for a great number of micropollutants (Choi et al., 2022; Radjenović et al., 2009; Verlicchi et al., 2013, 2012). In recent years, many, diverse attempts have been made to further improve MBR performance (Neoh et al., 2016; Woo et al., 2016) by combining MBRs with innovative treatment technologies such as consolidated ones (i.e. activated carbon and ozonation) or others that have not yet been fully implemented (i.e. advanced oxidation processes, membrane distillation bioreactors, biofilm/bio-entrapped MBRs, nanofiltration and reverse osmosis) (Rizzo et al., 2019). In all the investigations, the common aim has been to foster degradation and/or sorption removal mechanisms for a selection of micropollutants, by favouring or optimising the operational conditions. Among these modified MBRs, often called "hybrid systems" (Alvarino et al., 2017), the combination of an MBR coupled with powdered activated carbon (PAC) has attracted the interest of many researchers worldwide.

In a recent review paper (Gutiérrez et al., 2021), we presented and discussed the enhancement of the removal achieved for a multitude of MPs by the addition of PAC to the MBR or by means of a specific post-treatment using powdered or granular AC. Limiting the attention to the case of PAC added in the bioreactor, in the cited study, the removal efficiencies were related to different factors: micropollutant properties, AC characteristics, PAC addition point and duration, operational conditions (sludge and hydraulic retention times, SRT and HRT respectively) and characteristics of the wastewater under treatment (mainly dissolved organic matter, DOM). It was remarked that for weakly charged substances, the lipophilicity of a compound plays a crucial role in its adsorption to the PAC surface, while in the case of charged substances, also the electrostatic interactions between the PAC surface and the functional groups become relevant (Alvarino et al., 2017). Furthermore, DOM present in the aeration tank is likely to interfere with the PAC and the occurring micropollutants, leading to either direct competition with the micropollutants for the PAC adsorption sites or pore constriction (Delgado et al., 2012). As a result, the parameters involved in the phenomenon are manifold.

Considering the compounds, it is worth mentioning (i) the octanol-water partition coefficient (K_{OW}), or better the octanol-water distribution coefficient (D_{OW} which accounts for acid-base speciation), which provides an indication of the lipophilicity of a substance, (ii) the acid dissociation constant (pK_a), (iii) the charge and the presence of specific functional groups for its electrostatic affinities, and (iv) the molecular weight (MW) and size, which give a view of the potential to be intercepted by the PAC pores (Kovalova et al., 2013).

Otherwise, considering the adsorbent, the properties that mainly influence the fate of micropollutants in an MBR coupled with PAC regard (i) the characteristics of the adopted PAC (e.g. pore size and texture), (ii) the addition quantity and mode (PAC dosage, PAC retention time and dosage point in the reactor), and (iii) the reactor operational parameters (e.g. redox, pH, temperature, HRT, SRT, mixed liquor suspended solids) (Alvarino et al., 2018a; Mailler et al., 2016).

The cited review, which includes 64 peer-reviewed papers published between 2009 and 2020, emphasizes the complexity of the *phenomena* under study. Furthermore, it emerged that the different operational conditions and wastewater characteristics adopted in the past investigations sometimes led to different findings that, in some cases, did not coincide. As a result, a more rigorous approach to elaborate and interpret the collected data is needed to identify the main parameters affecting the removal of micropollutants in MBRs coupled with PAC. This could be useful in designing such a hybrid system or in optimising its performance. The novelty of our study consists in evaluating the joint effect of all the factors. In other words, instead of considering the predictors once at the time, we included all of them as explanatory variables. With such approach it is possible to assess the effect of each factor less other effects. Since the goal is to find new scientific results based on empirical evidence, generalizable beyond the observed cases, in our opinion, the most appropriate modeling practice is that based on inferential approach and not the one typical of machine learning. One of the goals of the paper is also to provide rigorous tools for interpreting data by providing robust modeling tools for the benefit of water treatment professionals.

In this context, the main operational parameters (i.e. PAC dosage, PAC retention time and SRT) and the physico-chemical properties of the compounds (i.e. LogD_{OW}, charge and MW) were selected on the basis of a dedicated screening step and then an attempt was made to clarify their influence on the removal of micropollutants from wastewater during its treatment. To this end, a statistical analysis, mainly based on exploratory methods (principal component analysis and cluster analysis) and regression analysis, was carried out to compare and discuss the different results published in the scientific literature included in the cited review article.

2 Material and Methods

2.1 Characteristics of the adopted dataset

The dataset adopted in this work was retrieved by Gutiérrez et al. (2021) and refers only to the data (observations) provided by 1? studies investigating the fate of micropollutants in an MBR coupled with PAC. Those referring to PAC or granular activated carbon (GAC) as a polishing treatment after an MBR were excluded. Table S1 of the Supplementary Material lists the studies and the relative observations included in the current analysis. Among these, only the observations in which all the parameters necessary for this study are available (i.e. SRT, PAC dosage, PAC retention time, D_{OW}, charge and MW) were maintained. Therefore, 26 observations (namely, the ID observations from Table S1 8–9, 37–38, 52, 57, 73–74, 89–90, 99, 102, 119–120, 125, 128–131, 138–139, 151–152, 167 and 172–174) were excluded from the original dataset (red records in Table S1). Then, the observation number 154, referring to carbamazepine, was excluded as its removal value (-90%) was considered an outlier of the dataset.

The resulting dataset includes 146 observations referring to 37 compounds (of which 6 non-steroidal anti-inflammatories drugs (NSAID), 7 antibacterials, 1 antiseptic, 5 hormones, 1 lipid regulator, 1 non-ionic surfactant, 2 pesticides, 4 psychiatric drugs, 2 stimulants, 3 synthetic musks and 5 others uncategorised compounds) collected from 7 studies (namely, Alvarino et al., 2017, 2016; Asif et al., 2020; Li et al., 2011; Nguyen et al., 2013; Serrano et al., 2011; Yu et al., 2014) (Table S1).

All the data included in the refined dataset refer to laboratory-scale plants, with the exception of the 9 observations reported by Serrano et al. (2011) which refer to a pilot-scale study. All the experimental reactors were fed with synthetic wastewater, made by adding specific compounds in water to simulate the matrix effects expected in real wastewater. Its compositions in the different studies were provided as reported in Gutiérrez et al. (2021).

The durations of the investigations range between 65 days (Asif et al., 2020) and 306 days (Nguyen et al., 2013). The configurations of the reactors adopted in the selected studies are reported schematically in Table 1. Here, in 4 out of 7 studies (providing a total of 117 observations) the membrane unit is placed in the biological reactor, while in the other 3 studies (29 observations) the membrane unit is in a separate tank (Table 1). The variability ranges of the operational conditions adopted in the studies are reported in Table 2.

Six parameters were chosen on the basis of a dedicated screening of data availability. In addition they were selected only if they present a wide and heterogeneous variability range~~, six parameters were chosen~~. Their influence on the micropollutant removal mechanism during treatment in an MBR coupled with PAC is well known (Gutiérrez et al., 2021). Other variables which could affect the removal (e.g. membrane shape, pore size, biomass characteristics) were not considered as the investigations available in the literature do not provide the full set of data to be included in the dataset or few data were found.

Table 1.

Table 2.

2.2 Statistic tools

A univariate linear regression analysis was initially carried out to predict average removal as a function of the other considered variables. To test the Goodness of Fit, both the parametric and non-parametric ANOVA were applied. In both the cases the *p*-value indicated no significance. After that, non-linear relationships were considered through the application of linear models to transformed variables. In particular, it was taken into account the logit of average removal as dependent variable, the inclusion of the squared explanatory variables and of the interactions in the set of predictors, the logarithmic transformation of the explanatory variables and combinations of this modifications of the original model. Then, the same previous attempts were done with the bivariate model, considering the average of removal and the standard deviation of removal as response variables and finally it was repeated the analysis on a multivariate version of the model with average, standard deviation, minimum and maximum of removal as dependent variables. In no case the Goodness of Fit tests were significant. Finally, the univariate two-sample NPC test approach was applied. The logit of average removal took the role of response and logD_{ow} as a "treatment". Again there was not empirical evidence of a significant effect of the factor on the dependent variable. Based on these results other tools were considered.

2.2.1 Principal Component Analysis

Principal Component Analysis (PCA) was applied in order to reduce the dimensionality of the dataset. The application of PCA aims to reduce the number of variables by eliminating a small proportion of data variability. PCA transforms the original correlated observed variables into new uncorrelated variables (Principal Components), with minimum loss of the original information represented by the observed variability. The principal components (PCs) are linear combinations of the original observed variables. The first component is the linear combination with maximum variance. It corresponds to the dimension along which the dispersion of data is maximum. The second component is the linear combination with maximum variance among those corresponding to orthogonal directions with respect to the first component. The subsequent components are detected in a similar way, considering orthogonal directions and maximising the variance. Hence, the resulting PCs are uncorrelated themselves and represent a new set of variables, related to the original variables by a defined linear combination (Lever et al., 2017).

The loadings are the correlations between the principal components and original variables. They correspond to the weights of the linear combinations explaining the variables by the components. The scores of the principal components map the different samples in the new dimensional space of the principal components facilitating the investigation of the different relationships between the variables (Vasilaki et al., 2018).

In this study, PCA was performed using R software ((Beiras, 2018), (software available at https://www.r-project.org). Then, Varimax orthogonal rotation was applied for the PCA axes and to reduce the contribution of the less relevant parameters within each PC (Jollife and Cadima, 2016).

2.2.2 Cluster analysis

Clustering techniques are widely applied in order to identify and group underlying patterns in high dimensional datasets. It is not easy to categorize them clearly, nevertheless they can be classified into four classes: partitioning, hierarchical, density-based and grid methods. Cluster Analysis (CA) aims to group datapoints (or equivalently statistical units) into homogeneous groups (clusters). Therefore, in the current study it was used to analyse the similarities among the different observations and gather potential relationships between them and their removal. The latter then were investigated better using the regression analysis.

In this study, CA was carried out adopting the *K*-means method which is one algorithm of the partitioning method. *K*-means is a partitional clustering algorithm which creates a defined number (K) of groups (also called clusters, c_k) of datapoints x_i. The within-cluster sum of squares S between the datapoints and the cluster empirical mean (i.e. the centroid, μ_k) (which measures the within-cluster heterogeneity) between the datapoints is minimised (Hennig et al., 2016), according to eq. 1:

$$S = \min \sum_{k=1}^{K} \sum_{x_i \in c_k} \| x_i - \mu_k \|^2 \quad \text{(eq. 1)}$$

In particular, this algorithm begins by fixing the number of clusters K and their corresponding centroids. Then, each statistical unit is included in the cluster with the nearest centroid. Once all the units have been classified, every centroid is recalculated as the value providing the lowest distance to all the members of its class. As the centroids have changed, the distance between each datum and the centroids must be calculated again so that the units are reassigned to the closest cluster. The process is repeated until no improvement in the classification process is obtained (de la Vega and Jaramillo-Morán, 2018).

As this algorithm needs a fixed number of clusters prior to starting the clustering process, in some cases several possible K values must be tested and evaluated to find out which one provides the best classification. The number of clusters must not be too high in order to guarantee that the classification obtained is both useful and meaningful (de la Vega and Jaramillo-Morán, 2018).

The number of clusters (K) which better describes the similarities within the dataset is often tricky to evaluate and there is no predefined criterion for its evaluation (Jain, 2010). In this work, the well-known Elbow and Silhouette methods were adopted to overcome this issue (Kassambara, 2017). The first was used to identify a range of K graphically which may be adopted for the analysis. In the former method, the sum of squares for each possible number of clusters is calculated and plotted, in order to detect an evident slope change point (a bend) that corresponds to the optimal number of clusters. The latter method provides a measurement of the similarity of each unit with those inside its own cluster compared with those outside the cluster. Now, if the silhouette of each datum inside a cluster is represented in decreasing order, a graphic representation of the quality of the allocation of data inside them is provided for all the clusters. The mean value of the silhouettes for all the clusters will provide a measurement of the quality of the clustering carried out, so that the higher the value, the better the classification. Therefore, the different clustering configurations were compared based on their average Silhouette value (Sil_{ave}) in order to assess the consistency of the solutions proposed by the graphical interpretation of the Elbow method results. Before the analysis, the dataset values were standardised to reduce outliers which may drive the grouping (Mohamad and Usman, 2013).

2.2.3 Regression analysis

Finally, regression analysis was used to investigate the influence of the selected parameters on the removal of micropollutants in an MBR coupled with PAC.

The regression analysis was conducted to find a possible relationship between average removal (response of the model) and some explanatory variables in order to predict the response values. The function *lm* in the R software environment was used to carry out the analysis, with a significance level α=0.05.

We performed two equations: the first, with data in three out of the four identified clusters (e.g. Cluster A, B and D), in which the response variable is the average removal and the explanatory variables are SRT, PAC retention time, PAC dosage, logD_{ow}, charge and MW; in the second, concerning only two clusters (Cluster B and D), we have the same response variable and the explanatory variables are SRT, PAC retention time, PAC dosage, logD_{ow} and MW.

In the current study, the analysis was carried out considering two different sub-datasets. The first one included all the observations except for the seven provided by the study by Asif et al. (2020), which were considered outliers due to the especially high PAC dosage adopted (20 g L^{-1}, compared to 0.1 to 1 g L^{-1} in the other studies). In this context, although the influence of PAC is not proportional to the added dosage, as discussed in Section 4.1, the especially high dosage may result in different *phenomena* in the reactor (e.g. changes in the rheological properties of the mixed liquor) which make the experiment difficult to compare to the others. Accordingly, the differences between these seven observations and the others were observed also in the exploratory data analysis (Sections 3.1 and 3.2).

Otherwise, the regression analysis was conducted considering only the observations related to negatively charged and neutral compounds (which correspond to clusters B and D, respectively, as defined in Section 3.2), in order to investigate their expected behaviour in the reactor, as suggested by different studies (such as Alves et al., 2018, Kovalova et al., 2013, and Mailler et al., 2016, to name just a few). A variable was considered significantly correlated to the removal when the *p*-value was less than 0.05.

Finally, regression analyses were always completed with diagnostic assessments on residuals (see Figure S2 in Supplementary Materials)

3 Results

3.1 Principal Component Analysis

The results of the PCA in terms of loadings of the considered variables are reported in Table 3, while biplots of the first 4 principal components are shown in Figure 1. These biplots of the PCs two by two were used to visualise the combined behaviour of the significant variables that affect the system. The biplots enable the simultaneous visualisation of the variable loadings and scores of the principal components (Vasilaki et al., 2018).

The dimensionality of the dataset was reduced to 4 principal components (hereinafter PC1, PC2, PC3 and PC4) explaining the 87% of the total cumulative variance (27% up to PC1, 50% up to PC2, 70% up to PC3 and 87% up to PC4. For PC1, the highest loadings were exhibited by charge (0.901), followed by MW (0.804). As a result, high positive values of PC1 in Figure 1 represent high values of the physico-chemical properties charge and MW of the compounds. SRT and the opposite of the PAC dosage are mostly represented in PC2 (0.844 and -0.788, respectively) which mainly describes the variation of the operational conditions under study, as no considerable values of the physico-chemical property-related loadings emerged (Table 3). High positive values of PC2 in Figure 1 correspond to high values of SRT, while negative values of PC2 represent high PAC dosages. PC3 and PC4 mainly represent the PAC retention time operational conditions (0.962) and the physico-chemical property D_{OW} (0.962), respectively. These two variables appear to be represented only by the respective principal components, with negligible loadings in the others (Table 3).

Table 3.

Figure 1.

3.2 Cluster analysis

The result of the elbow method is represented in Figure S1 of the Supplementary Material. The obtained curve suggests an optimal number of clusters (K) ranging between 3 and 5. The highest Sil_{ave} for these different clustering configurations was found for K=4 (Sil_{ave}=0.44). Therefore, the dataset was partitioned in 4 clusters.

The centroids of the clusters obtained in terms of SRT, PAC dosage, PAC retention time, LogD_{OW}, charge and MW, together with the number of observations included in each cluster and their corresponding average removal efficiency after the treatment, are reported in Table 4.

As shown in Table S2 of the Supplementary Material, it emerges that while clusters A, B and D include datapoints from various studies, cluster C grouped the observations of the only investigation conducted by Asif et al. (2020). This can be explained by the fact that cluster C grouped the observations characterised by an extremely high PAC dosage value (Table 4), of which the centroid shows the highest value (20 g L^{-1}) compared to the other clusters in which the centroids are centred around a similar value of mean PAC dosage (0.4 to 0.6 g L^{-1}). This reflects the particular experimental features of the investigation conducted by Asif et al. (2020), in which the adopted PAC dosage (20 g L^{-1}) was considerably higher than those added in the other studies (0.03 to 1 g L^{-1}, as shown in Table 2). For this reason, the relevant distance between the observations included in cluster C and all the others points in Figures 1a, 1d and 1e is not surprising, due to the high relevance of the PAC dosage in PC2. Furthermore, cluster C also exhibited the lowest average value of SRT (30 days). Indeed, with the exception of the 6 observations by Yu et al. (2014) referring to PFOA and PFOS (with an SRT of 30 days), the experiment conducted by Asif et al. (2020) was the only one in which an SRT lower than 92 days was adopted (as better described below). The combination of a different PAC dosage and SRT make it an outlier, in terms of operational conditions.

The other clusters (A, B and D) are characterised by greater heterogeneity in terms of included studies and compounds as well as a higher number of included observations (Table S2). Clusters A and B are characterised by the highest and the lowest average charge value (0.9 and -0.9, respectively). In particular, cluster B includes observations regarding mainly anionic compounds, grouping the majority of them (59 out of 62) among the whole dataset. In detail, the datapoints grouped in B refer to the anionics sulfamethoxazole (11 values), diclofenac (10), ibuprofen (10), naproxen (10), PFOA (3), PFOS (3), 17β-estradiol-acetate (2), fenoprop (2), gemfibrozil (2), ketoprofen (2), pentachlorophenol (2), salicylic acid (2) but also the neutrals metronidazole (2), primidone (2) and paracetamol (2). On the contrary, cluster A grouped only cationic substances, including erythromycin (8 values) and roxithromycin (8), which represent the majority of cationic substance-related observations in the dataset (16 out of 27).

Finally, cluster D mainly grouped neutral or zwitterionic compounds (48 observations out of 57 of the whole dataset), with the only exception being the neutral/cationic trimethoprim (8 values) and the cationic fluoxetine (2). The compounds included in D refer to carbamazepine (13), 17β-ethinylestradiol (8), estrone (8), 4-n-nonylphenol (2), 4-tert-butylphenol (2), 4-tert-octylphenol (2), 17β-estradiol (2), bisphenol A (2), diazepam (2), estriol (2), triclosan (2), celestolide (1), galaxolide (1) and tonalide (1) (Table S2). This cluster is not only characterised by the neutral average charge, but also for the highest LogD_{OW} (= 3.3, Table 4), which drove its partitioning.

The stratification of charge is clearly visible in Figures 1a, 1b and 1c, in which PC1 is displayed. It is also interesting to observe that for similar values of charge, clusters B and D are well differentiated by their LogD_{OW} values represented by PC4 (Figure 1c).

Table 4.

3.3 Regression analysis

The results of the regression analysis are reported in Table S3 and S4.

We carried out a multiple linear regression analysis with parameter estimates based on the ordinary least squares method. Given the outcome of the diagnostic analysis in which we have no evidence supporting the assumption of normality of the errors, instead of the classic parametric t or F tests, we applied the permutation test on the coefficients' significance and the permutation ANOVA, which are more flexible and robust with respect to the departure from normality (see Bonnini and Cavallo, 2022).

In the first regression, considering Clusters A, B and D, we obtain an Adjusted R-squared equal to 0.1299, while in the second regression in Cluster B and D we have an Adjusted R-squared equal to 0.0984. Considering the dataset in which all the observations except the seven provided by Asif et al. (2020) were included (for a total of 139 observations), it emerged that the removal of micropollutants in an MBR coupled with PAC was significantly correlated to their charge (p = 0.049 < 0.05). Here, also LogD_{OW} appears to be important in the removal process, albeit the corresponding coefficient estimate appears weakly significant (p = 0.088 < 0.10). According to the estimates of the coefficients, a +1 increase in LogD_{OW} determines a variation of +2.23 in average removal, while a +1 variation in charge corresponds to a change equal to +3.13 in the response. No significance was observed for MW or any of the operational condition-related variables (p > 0.1) (Table S3).

The results of the regression analysis conducted when considering the dataset in which there were 123 observations of clusters B and D revealed that, when excluding the effect of the charge, the LogD_{OW} has a strongly significant effect on removal (p < 0.001) and MW gains importance in the removal process, although its regression coefficient is weakly significant (p = 0.076 < 0.10). The expected variation of removal when LogD_{OW} and MW increase by one is +4.16 and +7.36, respectively. None of the three operational condition-related variables resulted in significantly affecting the removal of micropollutants in the MBR coupled with PAC (p > 0.1).

However, given the small values of the coefficients of determination, the results of the regression analysis should be evaluated prudently because the goodness-of-fit of the model is low. This may be because other explanatory variables (e.g. redox potential, biomass concentration and membrane pore size) not included in the model could be more important than those considered as predictors of removal. Another possible reason for the low goodness-of-fit could be the non-linear relationship between the variables under study and the consequent incorrect specification of the model. In other words, the reasons why the Adjusted R-square is low and therefore we do not have very satisfactory results can be: (a) the specification of the model is not appropriate (perhaps the relationship is not linear and a different specification of the equation of the regression model should be considered) or (b) important explanatory variables are missing in the model as predictors of the response. Since, as also mentioned in Section 2.2, we tested various model specifications that also include nonlinear relations, we can say that most likely the Adjusted R-squared is low because important explanatory variables are missing. Hence, in future studies, better models could be obtained by adding new predictors. Anyway, even if from the descriptive point of view the goodness-of-fit is not high because the specification of the model could be improved, from the inferential point of view, we have significances indicating non-null effects of some predictors on the response.

4 Discussion

4.1 Influence of the operational conditions

Taken together, the collected results provide interesting insights regarding the main factors involved in the removal of micropollutants during wastewater treatment by an MBR coupled with PAC.

The high average removal efficiency of the datapoints grouped in cluster C (97%) suggests that the PAC dosage may play an important role in micropollutant removal, especially when a particularly high quantity is added in the bioreactor (20 g L^{-1}, as in the case of Asif et al., 2020). Indeed, it is well known that the presence of PAC improves the physico-chemical properties of the sludge (i.e. it promotes floc growth and structure strength) entailing increased adsorption and, potentially, biodegradation (Alvarino et al., 2020; Hu et al., 2015). On the other hand, the variability in the average removal obtained by more commonly adopted values of PAC dosages (0.03 to 1 g L^{-1}) ranging from 84% (cluster B) to 98% (cluster A) seems to downsize the relevance of this factor. Moreover, the results of the regression analysis that was conducted taking into account all the datapoints with the exception of those of cluster C, considered as outliers, showed that selected PAC dosages, alone, do not significantly influence the removal of micropollutants during the treatment (p = 0.115, Table S3). This result may be due to different factors. Although different studies highlighted that the PAC dosage is a crucial operational condition with respect to micropollutant removal (among them Alvarino et al., 2017 and Li et al., 2011), its activity may be influenced by (i) PAC addition timetable (and therefore PAC aging in the reactor); (ii) wastewater matrix effect (as it affects the micropollutant saturation rate and floc biological activity (Alvarino et al., 2018b; Paredes et al., 2018)); (iii) characteristics of the selected PAC (mainly, pore size, specific surface area and bulk density (Alves et al., 2018; Mailler et al., 2016)); and (iv) physico-chemical characteristics of the micropollutants (Alvarino et al., 2018b). Furthermore, although not found in the selected studies, also (v) PAC potential losses due to excess sludge withdrawal, and vi) PAC addition point (e.g. in the anoxic tank as done by Remy et al., 2012, or in the aerobic tank as done by Asif et al., 2020 and Echevarría et al., 2019, to name just a few), may influence the sorption on the PAC surface. Therefore, the sum of all these factors makes it difficult to discuss statistically the significance of the PAC dosage on micropollutant removal efficiency.

Nevertheless, dedicated works (among them Cecen and Aktas, 2011; Loos et al., 2013 and Yu et al., 2014) highlighted that, strongly limiting the influence of the six above listed factors, the positive influence of the PAC dosage becomes statistically significant. In this regard, Mailler et al. (2016) observed that the positive correlation between the PAC dosage and removal efficiency follows a logarithmic pattern. Therefore, the addition of particularly high dosages of PAC may not entail proportional benefits.

In accordance with the findings of different studies (among them Alvarino et al., 2017, Löwenberg et al., 2014, and Wei et al., 2016), the PAC retention time appeared to be non-significantly correlated to the removal of the investigated micropollutants in both the regression analyses conducted (p = 0.745

considering the whole dataset with the exception of cluster C, and p = 0.592 considering only the neutral and anionic substances of clusters B and D). Briefly, once PAC is added in the bioreactor, its porous surface is entirely available, while after a period of time, its active sites start to be occupied by the sorbed micropollutants and the competitor DOM, which are present in the mixed liquor. This leads to a decrement of PAC potential sorption capacity, but at the same time, it provides an environment suitable for the development of a microbial community in the sludge flocs where the PAC is embedded. A more complex and heterogeneous microbial community can potentially enhance the biodegradation processes (Baresel et al., 2019). In other terms, the removal mechanisms of the substances may differ based on PAC age, promoting the removal of recalcitrant compounds that are more prone to be sorbed in/on fresh PAC (e.g. carbamazepine), or those which are more likely to be sorbed and biodegraded in the PAC-sludge floc complex. As a result, the effect of the PAC retention time on the removal of micropollutants strongly depends on their corresponding physico-chemical properties. In this regard, to achieve a good performance of PAC during the treatment for both cited types of substances, which are more prone to be sorbed or bio-transformed, Alvarino et al. (2017) recommend a dosage of 0.2 g L^{-1} added every 35 days.

Similar considerations may be applied to the SRT. As shown by Ng et al. (2013), low SRT values (i.e. 10 days) implies the addition of fresh PAC, providing a higher sorption of compounds which are prone to be sorbed on the PAC surface. On the contrary, high SRTs (> 100 days) promote the development of different species in the biomass, entailing a better bio-transformation of the compounds (Alvarino et al. 2018). In accordance with these considerations, both regression analyses conducted showed that the SRT is not significantly correlated with the removal (p > 0.465). Nevertheless, except for the 7 observations related to Asif et al. (2020) in which the SRT was 30 days, SRTs in the dataset are always particularly high (from 92 in Alvarino et al., 2017 to 288 days in Serrano et al., 2011) compared to those expected in common conditions adopted in MBR reactors (20–50 days, Metcalfe and Eddy, 2014). Indeed, compounds with low biodegradability are not expected to increase their removal at high SRTs (Yu et al., 2014) and therefore an exhaustive conclusion cannot be provided due to the lack of heterogeneity of the values.

4.2 Influence of the physico-chemical characteristics of the micropollutant

Concerning the physico-chemical characteristics of the compounds, it is interesting to observe that the highest and lowest average removal efficiencies refer to the observations grouped in clusters A and B, respectively (98% and 84%). These are also distinguishable by the highest and the lowest average charge values. This evidence suggests that the removal of micropollutants is positively correlated to their corresponding charge.

Though this may seem counterintuitive, as the surface of the PAC added in the experiments is generally neutral to positively charged at a pH higher than 7, this fact was observed in many studies (among them Boehler et al., 2012; Loos et al., 2013; Mailler et al., 2016; Margot et al., 2013). This can be explained bearing in mind that the covering of the DOM, typically negatively charged at neutral pH, on the PAC surface entails a consistent decrease in its overall charge (Yu et al., 2012). As a result, a high *adsorption* (indicating the potential of electrostatic interactions, according to Ternes et al., 2004) of positively charged micropollutants (i.e. cationic) and the negatively charged PAC-DOM complex surface is expected, as well as for repulsion in the case of anionic compounds (de Ridder et al., 2011).

The reduced average removal efficiency (84%) characterising the observations grouped in cluster B is not surprising, as it mostly refers to anionic compounds which are, additionally, also characterised by a low Log$D_{OW,}$ and therefore characterised by a low lipophilicity. Hereinafter they are referred to as compounds with low *absorption* potential (Ternes et al., 2004). However, for these compounds, removal may be driven by biotransformation and can be enhanced by the presence of the specific functional groups of the compound which interact between the PAC-DOM complex, explaining an average removal of 84% (Alvarino et al., 2017).

On the contrary, even if the particularly high average removal efficiency characterising the observations of cluster A seems to reflect the same behaviour, this might also be due to other reasons. Indeed, cluster A grouped the observations related to 2 substances (namely, erythromycin and roxithromycin) which have been demonstrated to be readily biodegradable in bioreactors in which high nitrification is reached, making their removals only slightly influenced by the addition of PAC in such reactors (Alvarino et al., 2017).

The results of the regression analysis confirmed the importance of the role of the charge in the removal of micropollutants during wastewater treatment. Excluding the 7 observations related to the study by Asif et al. (2020), the removal of the compounds under study showed to be significantly correlated to their charge ($p = 0.049$).

Despite this, as mentioned above, the sorption of micropollutants on the PAC surface is not only driven by adsorption due to electrostatic interactions by their functional groups and the PAC surface. On the contrary, especially in the case of non-charged substances, the adhesion of the micropollutants in the PAC-sludge floc complex may also be due to absorption and, therefore, to compound lipophilicity (Mailler et al., 2015).

The results of the statistical analysis that was conducted confirm these considerations. A relatively high average removal efficiency was found for the observations grouped in cluster D (91%) in which the high presence of non-charged compounds is counteracted by a high average value of LogD_{OW} (= 3.3, Table 4).

In addition, it is interesting to observe that the removal efficiency appears to be significantly correlated to LogD_{ow} only when considering the neutral and anionic compounds ($p < 0.001$). On the contrary, considering the whole dataset, no significance was observed ($p = 0.088$), suggesting that in the absence of strong electrostatic interactions, the lipophilicity of a compound plays a crucial role in the sorption mechanism.

Finally, the outcomes of the statistical analysis suggest that the molecular weight does not play a crucial role in the fate of micropollutants in an MBR coupled with PAC. Considering the whole dataset, with the exception of cluster C, the regression analysis shows that MW is not significantly correlated to the removal efficiency data (p = 0.453). Nevertheless, considering only the negatively charged and neutral compounds (clusters B + D), MW gains relevance in the removal process, albeit remaining non-significant (p = 0.076). This suggests that in absence of strong electrostatic interactions, MW may moderately influence the removal of compounds with high MW (and therefore high molecular size). These findings are in line with those shown in the investigation conducted by Alves et al. (2018) who found that, considering weakly charged compounds, a slight positive correlation between the adsorption potential and MW occurs. Furthermore, Tadkaew et al., (2011) noted that compounds with relatively high MW may be more prone to biodegradation processes, as they present more branches susceptible to be attacked by specialised microorganisms developed on the PAC-sludge floc complex, especially in the case of high lipophilic compounds. It is important to remark that the cited study refers to MBR. On its basis, it seems that there is a *weak* correlation between the removal efficiencies and MWs. In particular, compounds with higher MWs resulted to be more lipophilic (e.g. with higher LogD_{ow}). These findings are in agreement with our statistical analyses, confirming that in the case of a lack of strong electrostatic interactions between cationic MPs and negatively charged PAC-sludge complex, MW gains importance. Tadkaew et al. (2011) also suggested that the presence of a specialized biomass in the MBR could justify the increased biodegradation. In our selected studies, biomass characterization was not investigated and therefore no specific conclusions about the specialized microorganisms can be obtained.

5 Final remarks and further research

The statistical analysis highlights and suggests interesting conclusions regarding the fate of micropollutants in MBR treatments coupled with PAC.

No significant correlation was found between PAC dosage and micropollutant removal efficiency in the studied range of PAC concentrations (0.03 – 1 g/L). Nevertheless, the complexity of the factors influencing the sorption of micropollutants on the PAC surface during treatment (e.g. PAC addition timetable and point, compounds characteristics and matrix effect), and the difficulty in comparing observations provided by different experimental conditions, prevent a clear view in this regard. Further research is needed to clarify the role of the PAC dosage on micropollutant removal, as well as to investigate the good practices (e.g. timetable and point of addition) leading to a better exploitation of the potential of PAC in the reactor, instead of only the variation in the PAC dosage.

The same applies to the PAC retention time, the relevance of which appears to be strongly related to the micropollutant physico-chemical properties. The adoption of a short PAC retention time may enhance the removal of those substances which are more prone to be sorbed on PAC-sludge flocs complex, while a long

PAC retention time may entail an increased biotransformation of the compounds due to a more complex and heterogeneous microbial community in the reactor.

Inconclusive results were found for the SRT as it generally varied between very high values (92 and 288 days) and an exhaustive interpretation of all the expected values was not possible.

Considering the physico-chemical properties, the charge demonstrated to be significantly correlated to the removal of micropollutants in an MBR coupled with PAC. This can be explained by the electrostatic interactions between the positively charged substances and the negatively charged surface of the PAC covered by DOM.

In addition, LogD_{OW} showed to be significantly correlated to the removal of neutral and anionic substances, suggesting that the absence of electrostatic interactions, or even the repulsion to the flocs for the anionic compounds, is counteracted by the high relevance of the compound lipophilicity.

Similar behaviour was observed concerning the MW of the substances, which showed to gain importance for neutral and anionic compounds, although not being as statistically significant as LogD_{OW}.

Overall, the results of this study suggest that the variation of the defined operational conditions (i.e. SRT, PAC retention time and PAC dosage) does not always entail a better removal efficiency of a broad spectrum of micropollutants. On the contrary, confirming the scientific literature on the topic, the specific physico-chemical characteristics (in particular, charge and LogD_{OW}) of each compound seem to play the most important role in such a complex process.

Nevertheless, precise management of the operational conditions may significantly entail the removal of specific micropollutants or groups of them.

The results obtained may provide a better understanding of the role played by the selected factors in the removal of micropollutants in an MBR coupled with PAC.

It is important to underline that most of the observations included in the dataset referred to lab scale studies and synthetic wastewater. This implies that the useful considerations suggested by the results of the current statistical analysis should be strengthened by dedicated experiments in full scale plants according to (O'Flaherty and Gray, 2013).

The findings mentioned above may help in the management of such advanced biological treatment in view of achieving a higher removal efficiency of the compounds considered in this study, as well as others that were not included but that exhibit similar physico-chemical characteristics, and thus behaviour. In addition, this study showed that basic statistic means and exploratory data analysis applied to the results of different investigations may be an effective tool to elucidate the influence of the main parameters involved in the complex *phenomena* behind the removal of micropollutants in MBR systems coupled with PAC. As remarked above, future investigations on this type of upgraded MBR should include other parameters including membrane shape, pore size, biomass characteristics, reactor configurations in order to allow a more complete statistical analysis.

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FIGURE Caption

Figure 1. Biplots of the principal components (PCs) with a representation of the PCA scores (referring to the experimental observations) included in each cluster (A-D, according to the results of Section 3.2). The vectors represent the loadings of the PCA (i.e. how strongly each variable influences a PC).

Figures

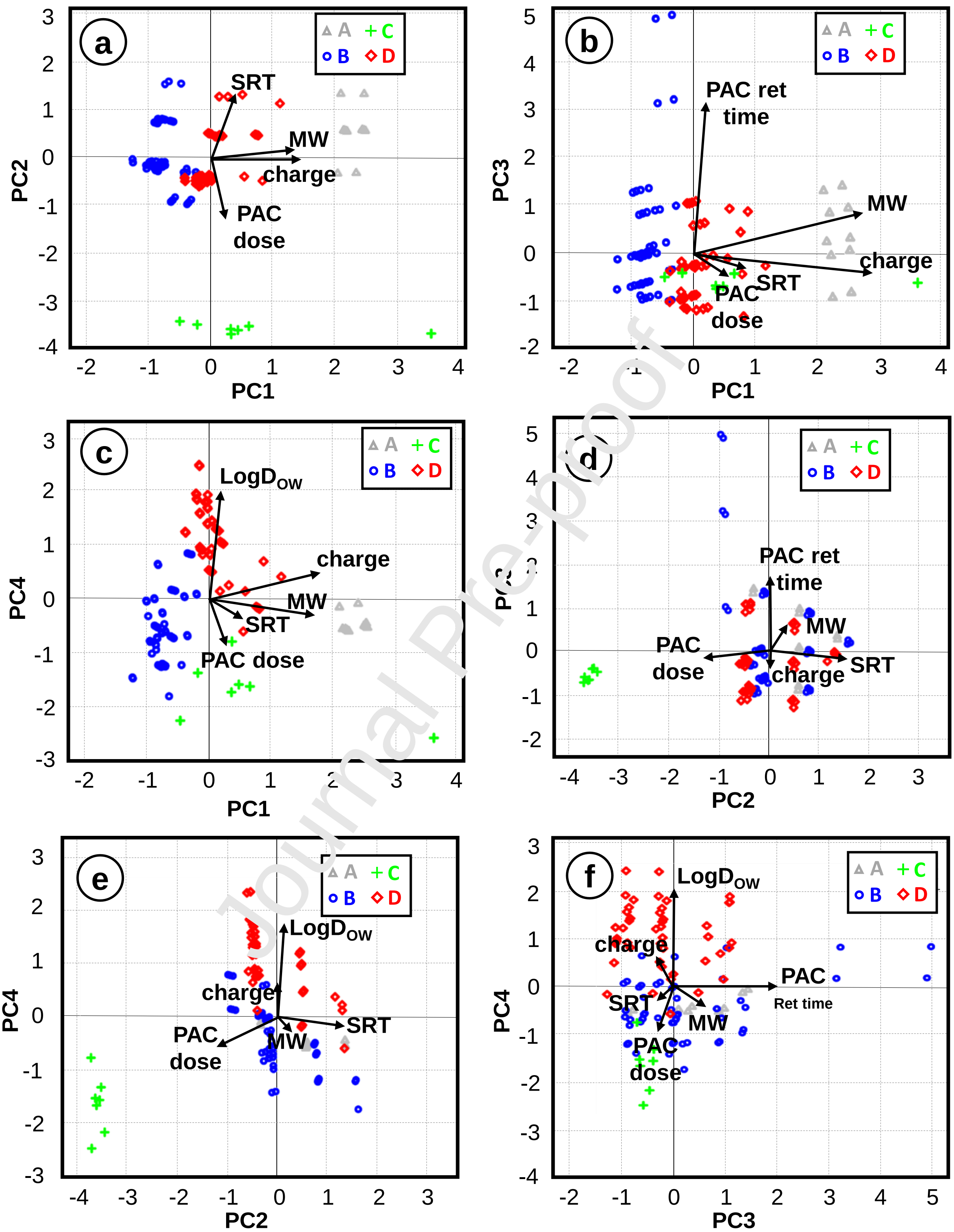


Figure 1.

TABLES

Table 1. The two configurations of MBR coupled with PAC together with the corresponding references included in this study.

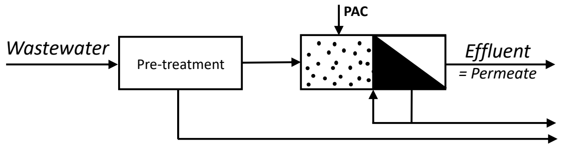
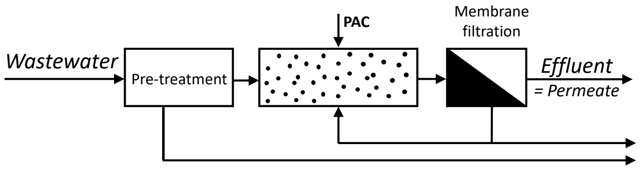
Configuration scheme	Description	Referring studies (number of observations)
 	Submerged MBR: The membrane is placed in the biological reactor, where PAC is added.	Alvarino et al. (2017) (60); Li et al. (2011) (7); Nguyen et al. (2013) (44); Yu et al. (2014) (6).
 	Side-stream MBR: The membrane is placed in a separated tank. PAC is added in the biological reactor.	Alvarino et al. (2016) (13); Asif et al. (2020) (7); Serrano et al. (2011) (9).

Table 2. Selected operational conditions and corresponding values in the included investigations.

References (no. of observations)→ Operational conditions ↓	Alvarino et al. (2016) (13)	Alvarino et al. (2017) (60)	Asif et al. (2020) (7)	Li et al. (2011) (7)	Nguyen et al. (2013) (44)	Serrano et al. (2011) (9)	Yu et al. (2014) (6)
SRT [d]	118	200	30	92	100	288	30
PAC dosage [g L^{-1}]	1	0.25 – 0.75	20	0.1 – 1	0.1 – 0.5	1	0.03 – 0.1
PAC retention time [d]	118	35 – 105	65	28 – 60	37 – 63	86	88 – 246

Table 3. Details of the PCA loadings. The numbers in parenthesis represent the percentage of variance explained by each component.

Variable	**PC1 (27%)**	**PC2 (23%)**	**PC3 (19%)**	**PC4 (18%)**
SRT	0.253	0.844	-0.112	-0.147
PAC dosage	0.164	-0.788	-0.127	-0.375
PAC retention time	<0.10	<0.10	0.962	<0.10
LogD_{OW}	<0.10	<0.10	<0.10	0.962
Charge	0.901	<0.10	-0.131	0.253
MW	0.852	0.126	0.239	-0.137

Table 4. Characteristics of the clusters, in terms of number of observations included in each cluster, average removal efficiency and centroids of each of the six selected variables.

Cluster ID	Number of observations included	Average removal [%]	SRT [d]	PAC dosage [g L^{-3}]	PAC retention time [d]	LogD_{OW}	Charge	MW
A	16	97.9	200.7	0.6	78.0	1.39	0.95	785.5
B	65	84.4	139.7	0.4	73.9	0.69	-0.90	261.5
C	7	97.4	30.0	20.0	65.0	-0.56	-0.07	286.3
D	58	91.0	156.1	0.5	67.8	3.35	0.12	261.8

Highlights

- Main factors influencing micropollutant removal in an MBR coupled with PAC
- The main operational conditions and physico-chemical properties were considered
- Comparison of the influence of the selected factors based on statistical analysis
- Principal Component Analysis, Cluster analysis and Regression Analysis were done
- Micropollutant charge and log D_{ow} result significantly correlated to the removal