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Pollution parameters evaluation of wastewater collected at different treatment stages from wastewater treatment plant based on E-nose and E-tongue systems combined with chemometric techniques

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Abstract

Wastewater contains harmful chemicals and heavy metals that are known to cause various environmental and health problems. Therefore, the water quality control using sensitive, simple, fast, accurate, and portable tools is of great importance. In this study, an electronic nose (E-nose) and an electronic voltammetric tongue (E-tongue) combined with chemometric methods were used for qualitative analysis of water samples collected from a wastewater treatment plant (WWTP) that treats domestic and industrial wastewaters. Quantitative determination of pollution parameters of water and wastewater samples were performed in BAM, Berlin. The inductively coupled plasma optical emission spectrometry was used for cations determination. Analysis of anions was carried out by ion chromatography with a Metrosep A Supp 5 - 100/4.0 column. Chemometric methods, such as Principal Component Analysis (PCA), Discriminant Function Analysis (DFA), Support Vector Machines (SVMs), and Hierarchical Cluster Analysis (HCA), were used to process the E-nose and E-tongue data to describe the similarities between the samples. In addition, Partial Least Squares Regression (PLSR) model was constructed using the E-nose and E-tongue data to simultaneously predict the levels of physicochemical parameters. Indeed, the PLSR analysis is performed generating a correlation coefficient, for the training and testing sets, higher than 0.91 for the prediction of the concentration of all physicochemical parameters, except for iron (Fe) which remains 0.84. These results suggest that simple, portable, and inexpensive tools such as electronic noses and tongues are suitable for wastewater analysis.

Keywords: Wastewater, Electronic nose, Voltammetric electronic tongue, Water quality control, Chemometric methods.

I. Introduction

Detecting and controlling chemical pollution in the environment has become a major challenge for developed and emerging countries in the modern world. Every year, great quantity of organic and inorganic chemical pollutants are released into the air, sea, and soil, posing potential health risks to plants, animals, and humans [1,2]. The pollution of natural water resources by heavy metals is one of the most worrying issues [3,4]. Environmental pollution monitoring is necessary to protect the public and mitigate the many potential negative effects on environmental quality and human health. The unpleasant odor of wastewater and its negative impact on aquatic ecosystems has even led to strict requirements for wastewater treatment [5].

Conventionally, wastewater quality is generally determined by the levels of various factors related to the main pollutants, including chemical oxygen demand (COD), biological oxygen demand (BOD), ammonium, orthophosphate, nitrate, conductivity, and pH [6-8]. These parameters provide essential information on wastewater quality. They are useful for demonstrating that wastewater meets discharge requirements [9,10]. Chromatographic techniques such as high performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS) are most commonly used for the determination of compounds in wastewater [11]. However, some of these techniques are time consuming and most of them require considerable economic resources. Some wastewater parameters, such as BOD, require 5 to 20 days to obtain measurement results, making these tests unsuitable for automated monitoring and control [12]. Thus, operating costs may somewhat limit the applicability of these traditional techniques.

For these reasons, portable, easy-to-use, and inexpensive systems are in high demand to monitor and control processes, increase their pollutant removal capacity and achieve consistent and stable operation. This would allow meeting the requirements of wastewater treatment at minimal cost. Due to the simplicity and portability of E-noses and E-tongues, as well as the

possibility of implementing them in on-line automated equipment, they can be used as complementary systems to analytical methods. According to the definition of the International Union of Pure and Applied Chemistry (IUPAC), an E-nose and E-tongue are multi-sensory systems, which consist of a number of sensors and use advanced mathematical procedures for signal processing, based on multivariate analysis techniques [13-15]. They use semi-selective sensors that produce a signal that can be associated either with a specific compound or with a qualitative aspect of the samples [16]. Despite the use of non-specific sensors, their combination offers enormous potential for information [17]. When these systems are subjected to a sample containing different compounds, they generate an output pattern that represents a synthesis of all the components contained in the analyte [18].

Considerable research efforts have been devoted to the development of E-noses and E-tongues as well as their application in various fields, including the environment, agriculture, biomedicine, cosmetics, food, military, pharmaceuticals, and various areas of scientific research [19-22]. There are several potential applications of E-noses in environmental pollution monitoring. They are used to detect fires in chemical storage facilities, to identify environmental pollutants in diesel and gasoline exhaust [23], to monitor odors in and around livestock farms [24], to assess odor nuisance from landfills [25], to characterize odors emitted from various stages of a wastewater treatment plant [26], to survey industrial odors and gaseous emissions [27], and to analyze odors from poultry farms [28]. The main application of E-tongues in the environmental field is the detection of physicochemical parameters in wastewater [29]. However, the ability of E-noses to predict the concentrations of physicochemical parameters in wastewater has never been investigated.

In this study, the capability of an E-nose based on six semiconductor gas sensors, and an E-tongue configured as five working electrodes for qualitative analysis of wastewater is verified. The highlight and novelty of this work is to verify for the first time the capability of a

fabricated E-nose and E-tongue to study the physicochemical parameters of wastewater and to compare the results obtained by each measurement system. The wastewater measurement data are processed qualitatively by chemometric techniques, such as Principal Component Analysis (PCA), Discriminant Function Analysis (DFA), Hierarchical Cluster Analysis (HCA), and Support Vector Machines (SVMs). In the case of quantitative analysis, Partial Least Squares Regression (PLSR) was performed to predict the concentration of physicochemical parameters of the wastewater using the data collected from the E-nose and E-tongue against their actual concentrations.

2. Materials and methods

2.1. Wastewater sampling and analytical methods

To study the composition of wastewater, 30 samples were collected from a WWTP in the city of Meknes in Morocco at different treatment points (**Fig. 1**). The collected samples are P₁: wastewater samples collected at a location where solids and grit are removed, P₂: wastewater samples collected at a location where oil and grease are removed, P₃: wastewater samples collected in the bioreactor, and P₄: distilled water. All collected samples were kept in the dark and brought refrigerated (4°C) to the laboratory for electronic sensing analysis.

Parallel analytical tests were carried out to determine the pH, the conductivity, the contents of total organic carbon (TOC), calcium (Ca), magnesium (Mg), Iron (Fe), manganese (Mn), potassium (K), sodium (Na), silicon (Si), phosphate (PO₄), sulfate (SO₄), nitrate (NO₃), chloride (Cl), fluoride (F), and bromide (Br).

2.2. Techniques used for physicochemical parameters analysis

The wastewater was sampled with 20 mL amber glass bottles. After sampling, no stabilization with inhibitors took place. The samples were diluted 1:10 with distilled water for further analysis. The cations were determined by inductively coupled plasma optical emission

spectrometry (ICP-OES) (iCAP 6000, Thermo-Fisher). The anions were analyzed by ion chromatography (883 Basic IC plus, Metrohm) with a Metrosep A Supp 5 - 100/4.0 column (Metrohm). In addition to the analysis of the anions and cations, the pH value and the conductivity were determined with a portable pH meter (HQ Series Portable Meters, Hach) and the total organic carbon (TOC) with a TOC cuvette test (Hach).

2.3. Electronic setups and signals acquiring

2.3.1. E-nose setup and signal acquisition

The electronic nose used in this work was equipped with an array of six metal oxide semiconductor (MOS) gas sensors. An overview of the system is presented in the supplementary information ([Fig. S1](#)). The sampling section consisted of a 2 L Tedlar® bag connected to a micro air pump with a flow rate of 250 mL/min. Gas sensors model MQ were chosen based on their sensitivity to most VOCs that can be found in the environment. These gas sensors and their target gases are MQ-3 (alcohols, benzene, CH₄, hexane, LPG, Co), MQ-4 (CH₄, LPG, H₂, alcohol), MQ-5 (LPG, CH₄, H₂, alcohol), MQ-8 (H₂, alcohol, LPG, CH₄, CO), MQ-9 (CO, LPG, CH₄), and MQ-135 (NH₃, NO_x, Alcohol, Benzene, smoke, CO₂). It also contains a relative humidity sensor and a temperature sensor to monitor the environmental conditions during each measurement. All sensors were installed in a 270 cm³ Teflon chamber. A data acquisition unit, consisting of a hardware data acquisition card, namely NI-USB 6212 from National Instruments, and a software application in the form of a graphical user interface (GUI) running in a computer, was used.

The Normalized conductance ratio ($G-G_0/G_0$) was chosen as the sensor response signal for the E-nose. In this expression, G represents the conductance of the sensor when exposed to the gas sample and G₀ represents the conductance when the sensor is exposed to synthetic air. Before and after each E-nose measurement, synthetic air is injected into the sensor chamber for 5 minutes to clean the sensors' surface so that the signal is at baseline. During the E-nose

analysis, the headspace of the wastewater sample was pumped for 5 minutes into the sensor chamber at a flow rate of 250 mL/min. A total of 40 water and wastewater samples were used in this study. For each sample, 60 ml aliquots were measured to assess reproducibility. Four features were extracted from the E-nose responses, which are:

- The conductance difference $\Delta G = (G_s - G_0)$. Here, G_s is the average conductance value during the last sixty seconds of the measurement and G_0 is the average conductance value during the first sixty seconds of the measurement.
- The area under the curve (AUC) calculated between the first sixty and the last sixty seconds of the measurement. It was estimated based on the trapezoidal rule.

2.3.2. E-tongue setup and data acquisition

The E-tongue system consists of five working electrodes, a counter electrode (platinum), and a reference electrode (Ag/ AgCl, diameter 2 mm, saturated in 3 M KCl). The five working electrodes are made of gold (Au), glassy carbon (GC), platinum (Pt) from CH Instruments, Texas, USA (diameter of 2 mm and length of 5 mm), copper (Cu), and palladium (Pd) from BAS Inc, Tokyo, Japan (diameter of 1.6 mm and length of 6 mm). These working electrodes respond in the form of voltammograms related to the electrochemical properties of the samples. Detailed information on the E-tongue system are provided in the additional information ([Fig. S2](#)). For E-tongue measurements, a potential is first applied to the working electrodes. Then, electro-active species in solution are reduced or oxidized at the electrodes' surfaces and the resulting current is measured.

For analysis with the E-tongue, the electrodes were immersed in a beaker of wastewater samples and interfaced with a portable potentiostat (PalmSens BV, the Netherlands) using a relay box. In effect, a constant potential is applied to the reference electrodes and a variable potential is measured on the working electrode. In addition, the current between the counter electrode and the working electrode is measured. The cyclic voltammetry technique was applied

for electrochemical measurements over a potential range of -0.2 to 0.6 V and a scan rate of 50 mV/s. Forty water and wastewater samples were used in this study. For each sample, ten aliquots of 60 mL were measured to assess reproducibility. Two features were extracted from the E-tongue responses, which are:

- The change in current $\Delta I = (I_{\max} - I_{\min})$ calculated as the difference between the maximum and minimum current values.
- The area (A) between the oxidation and reduction phases in the voltammograms. This area is estimated by the trapezoidal method.

2.4. Multivariate analysis techniques

Data processing is carried out using multivariate analysis techniques, such as unsupervised (PCA, HCA) and supervised (DFA, SVMs) methods.

PCA is an unsupervised linear method often used to analyze data obtained from multisensory systems. It is used for dimension reduction and allows a clear visualization of the dataset and simplifies its interpretation. The mechanism of PCA is based on the representation of the data in a new orthogonal coordinate system. Indeed, the axes are organized according to the variance of the data, keeping as much information as possible in the first axes [30].

DFA is a statistical method that determines Discriminant Functions (DF) using one or overall independent variables that maximize distance between groups and minimize distance within groups. The DFA is performed to check whether the variables used are enough to obtain a clear discrimination between the studied clusters [31].

HCA is a statistical procedure, providing a better alternative of accurate representation and classification of high-dimensional data, and it used the full dimensionality of the data to create a classification dendrogram. The aim of performing HCA is to separate data into specific groups based on similarity or distances between different observations. HCA results can be

presented as a dendrogram, in which distances between observations are determined in different observations [32].

Multi-class SVMs is a non-linear supervised learning technique. It can be built using two strategies. The first one is by using "one-vs.-one" or "one-vs.-all" approaches. In the second, all the data are considered. In this study, the "one-vs.-one" method is applied to differentiate between water and wastewater samples [33].

3. Results and discussion

3.1. Physicochemical parameters determination of water and wastewater samples

The concentrations determination of pollution parameters of some influent wastewater samples were illustrated in **Table 1**. It can be seen from this table that the measured parameters do not exceed the concentration limit mentioned by the World Health Organization (WHO), which confirms that the Meknes wastewater treatment plant respects the standard concentration for the different components [34-39].

The pH refers to the measurement of hydrogen ion activity in the solution. Determination of pH plays an important role in the wastewater treatment process. Acidic (low pH) or basic (high pH) conditions alter the rate of microbial growth, the function of metabolic enzymes, and can stop the growth of most microorganisms that require a pH between 6.5 and 8.5. As seen in the table, the pH values measured for all the studied samples are acceptable except for P₃.

Conductivity is the ability of water to carry an electric current. The increase in conductivity of water samples is due to the increased mobility of ions. In fact, a higher conductivity value indicates that there are more chemicals dissolved in the water. From the table, it is noticed that the water samples have a low conductivity value compared to the wastewater samples. This is due to the low concentration of physicochemical parameters found in the water samples compared to the wastewater samples.

Total Organic Carbon (TOC) refers to the amount of carbon present in any organic compound. TOC measurement is a mandatory requirement for wastewater treatment companies in many countries around the world. The TOC concentration of water is a basic indication of the extent of organic contamination and the purity of the water. High organic content means increased growth of microorganisms, which contribute to the depletion of oxygen reserves. In this study, the TOC of the wastewater is over 300 mg/l but the water is only 10.2 mg/l.

To clearly see the differences in the physicochemical parameters of the analyzed samples, **Fig. 2** shows a plot of the data as a histogram graph. It can be seen from this figure that the wastewater samples have high concentration for all physicochemical parameters compared to water sample (control). As remarked, the compound, which is present at highest concentration in the three wastewater samples is chloride. Indeed, it is also remarked that there are different concentrations of each physicochemical parameter from site to site.

3.2. E-nose and E-tongue responses

Figure 3 shows the normalized conductance of the sensor array of the E-nose exposed to the headspace of water and wastewater samples. Indeed, **Figures 3(a, b, c)** show the plot of conductance change of sensor responses of wastewater influent collected from P₁, P₂, and P₃, respectively. However, **Fig. 3(d)** shows typical responses of the six-sensor array of distilled water collected from P₄. According to **Fig. 3**, the normalized conductance increases with the exposure time. This can be explained by the presence of reducing chemicals on the sensing surface of n-type semiconductor gas sensors. As seen, distilled water (control) has the lowest response compared to the wastewater samples. In addition, it is noted that the MQ-9 gas sensor has the highest response for all analyzed samples.

Figure 4 shows the electrochemical responses of the E-tongue system towards wastewater samples of P₃. As can be seen, the amplitudes of the oxidation and reduction

currents differ according to the analyzed samples. It should be noted that the intensity of the voltammogram corresponding to copper electrode (Cu) is higher than the others.

3.3. Data analysis results

3.3.1. Qualitative analysis results

PCA was conducted on the E-nose and E-tongue database (**Fig. 5**). **Figure 5(a)** reports, in a two-dimensional plot (PC1-PC2), the electronic nose data coming from the measurements corresponding to the analyzed samples. As one can see, the variances explained by the first and the second principal components were 73.88% and 19.78%, respectively. In this plot, the analysed samples appear to be well separated. As well as electronic nose results, PCA performed on E- tongue data points out the existence of four clusters based on their collection point in the WWTP (**Fig. 5(b)**). The variance explained by the first two principal components were 72.91% and 14.32%, respectively.

DFA is one of the best classification methods, as this procedure maximizes the variance between categories and minimizes the variance within categories to optimize resolution. To confirm the PCA results, DFA was applied to the same database gathered from the E-nose and E-tongue. **Figure 6 (a,b)** shows the DFA plot corresponding to the E-nose and E-tongue database with a score of 98.1%, and 99.9% of the data variance, respectively. The first two discriminant functions (DF₁ and DF₂) show a very satisfactory classification of the wastewater samples, without overlap of the four groups.

HCA is an unsupervised technique and was used in this study to confirm the results obtained by PCA and DFA. **Figure 7** shows the HCA results of the studied samples by using the E-nose and E-tongue database, respectively. From **Fig. 7(a)**, at a distance $d = 7000$, it appears an overlap between all samples except for those of P₂. Indeed, at a distance $d = 4000$, good separation between headspace of samples of P₁, P₃, and P₄ was achieved. Furthermore, from **Fig. 7(b)**, at a distance $d = 190$, the dendrogram illustrates that the samples from P₃ and

P₄ are clearly separated from the other samples. Furthermore, samples corresponding to P₁ and P₂ were overlapped. Moreover, at a distance $d = 87$, the samples from P₁ and P₂ were also separated to each other except of one sample from P₁ which overlapped with P₂. Therefore, by using various grouping hypothesis, it can be concluded that water and wastewater samples are well discriminated using the E-nose and E-tongue systems.

Table 2 shows the SVMs confusion matrixes of the recognition of water and wastewater samples using the E-nose and E-tongue systems. Therefore, the SVMs model provided 100% and 97.5% success rate in the recognition and classification of analyzed samples using E-nose and E-tongue, respectively. It can be noticed that the E-nose system is able to distinguish all samples according to their collection point, without any overlapping. By using the E-tongue, only one error is reported for the recognition of the samples studied. Therefore, the SVMs results confirm the previous results obtained using the PCA, DFA, and HCA methods. Based on these results, it is argued that the E-nose and E-tongue systems are very promising and capable of discriminating water and wastewater samples.

3.3.2. Quantitative prediction for the contents of physicochemical parameters

3.3.2.1. *Partial least squares regression based on E-nose and E-tongue data*

The PLSR model was evaluated by comparing the values of Root Mean Squared Error of Calibration (RMSEC) and Root Mean Square Error of Cross-Validation (RMSECV) that represent model and cross-validation errors, respectively [40]. If they are similar, the model could be selected as having good prediction ability [41]. PLS regression was performed to model the relationship between the physicochemical parameters with different concentrations versus the E-nose and E-tongue data, respectively. One latent variable and a leave-one-out cross-validation method were used to build these models. The calibration curve shown in **Fig. 8(a)** represents the concentration of phosphate predicted by the E-nose versus the real concentration of phosphate found in each sample. Besides, the calibration curve shown in **Fig.**

8(b) represents the concentration of phosphate predicted by E-tongue versus the real concentration of phosphate found in each sample. The PLS regression yielded a calibration model with good correlation between experimental and estimated concentrations of phosphate using E-nose and E-tongue with correlation coefficients of about 0.99 for training and testing sets. These results prove that the proposed E-nose and E-tongue systems can predict the concentration of phosphate in water and wastewater samples.

The same behavior was observed for the prediction of the concentration of the other physicochemical parameters with good correlation coefficients R by using both systems. The calculation of correlation coefficient (R), as well as Root Mean Square Error of Calibration (RMSEC), and Root Mean Square Error of Cross Validation (RMSECV) for training and testing sets were described in **Table 3** for E-nose and E-tongue.

The results depicted in this table show that the correlation coefficient R is higher than 0.91 for all parameters, except for iron (Fe) which remains 0.84. Furthermore, the RMSEC and RMSECV values are lower than 9.34 and 11.29, respectively. These results demonstrate that there is a good calibration between the predicted and real concentration of physicochemical parameters using E-nose and E-tongue signals.

In addition, the R -values obtained by the E-tongue are higher compared to those obtained by the E-nose for all parameters (except for calcium (Ca), manganese (Mn) and fluoride (F) in the testing set). Furthermore, the RMSEC values obtained by E-tongue are lower than the ones obtained by E-nose for all parameters with the exception of calcium (Ca) and silicon (Si) in the testing set. Moreover, the RMSECV values obtained by E-tongue are lower compared to those obtained by E-nose for all parameters with the exception of calcium (Ca), Magnesium (Mg), Iron (Fe), Manganese (Mn), Silicon (Si), Phosphate (PO₄) and Fluoride (F) in the testing set. Based on these outcomes, it can be said that the results obtained by E-tongue are better than E-nose for the prediction of physicochemical parameters.

3.3.2.2. HCA results

Figure 9 shows the results of the HCA as a dendrogram obtained by processing the data corresponding to the calibration of the E-nose (**Fig. 9(a)**) and the E-tongue (**Fig. 9(b)**) versus the concentrations of physicochemical parameters. As shown in the dendrogram in **Fig. 9(a)**, at $d = 53$, the headspace of wastewater samples (P_4) is clearly separated from the others. Similarly, at $d = 28$, the P_2 samples are also separated. However, the samples from P_1 overlapped with those from P_3 . In the case of the dendrogram in **Fig 9(b)**, at $d = 25$, the wastewater samples of P_3 and P_4 are clearly separated from each other but the samples of P_1 and P_2 overlapped. Interestingly, at $d = 15$, the P_1 and P_2 samples are well separated from each other. These results reveal that the calibration results obtained by the E-tongue are better than those obtained by the E-nose.

4. Conclusion

Wastewater is known to have many negative impacts on the environment and human health. In general, sensing systems that are easy to handle, on-site, affordable and capable of analyzing wastewater are rare in the literature. In the present study, the use of detection systems, such as an E-nose and an E-tongue that meet these requirements was highlighted. The effectiveness of the developed E-nose, consisting of six tin dioxide (SnO_2) sensors, and an E-tongue, consisting of five working electrodes made of noble and non-noble metals, in distinguishing samples from different stages of wastewater treatment was therefore investigated. Their ability to distinguish between water and wastewater samples was the main objective of this study. The second was to differentiate wastewater at different points in a WWTP. Thus, the prediction of some physicochemical parameters of the studied samples was carried out using both systems. Furthermore, the ability of the proposed E-nose and E-tongue to classify water and wastewater samples was proven by applying multivariate analysis techniques, such as PCA, DFA, HCA, and SVMs. A strong agreement was found between the

satisfactory discrimination obtained by the two systems and the different concentrations of physicochemical parameters found in each sample. Furthermore, using PLS regression, a good calibration between the E-nose and E-tongue as a function of the concentrations of the physicochemical parameters was obtained with a correlation coefficient higher than 0.91 for both systems. The results obtained by HCA when applied to the calibration of the data reveal that the E-tongue is better than the E-nose in predicting the concentrations of the physicochemical parameters. These results indicate that the E-nose and E-tongue systems can be used as inexpensive, portable, easy-to-use tools for wastewater analysis.

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Figures

Fig. 1.

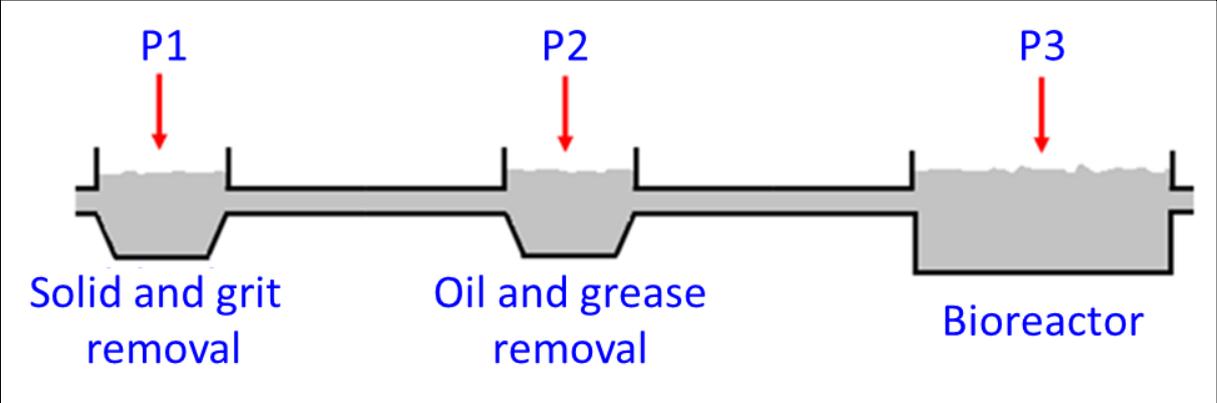


Fig. 2.

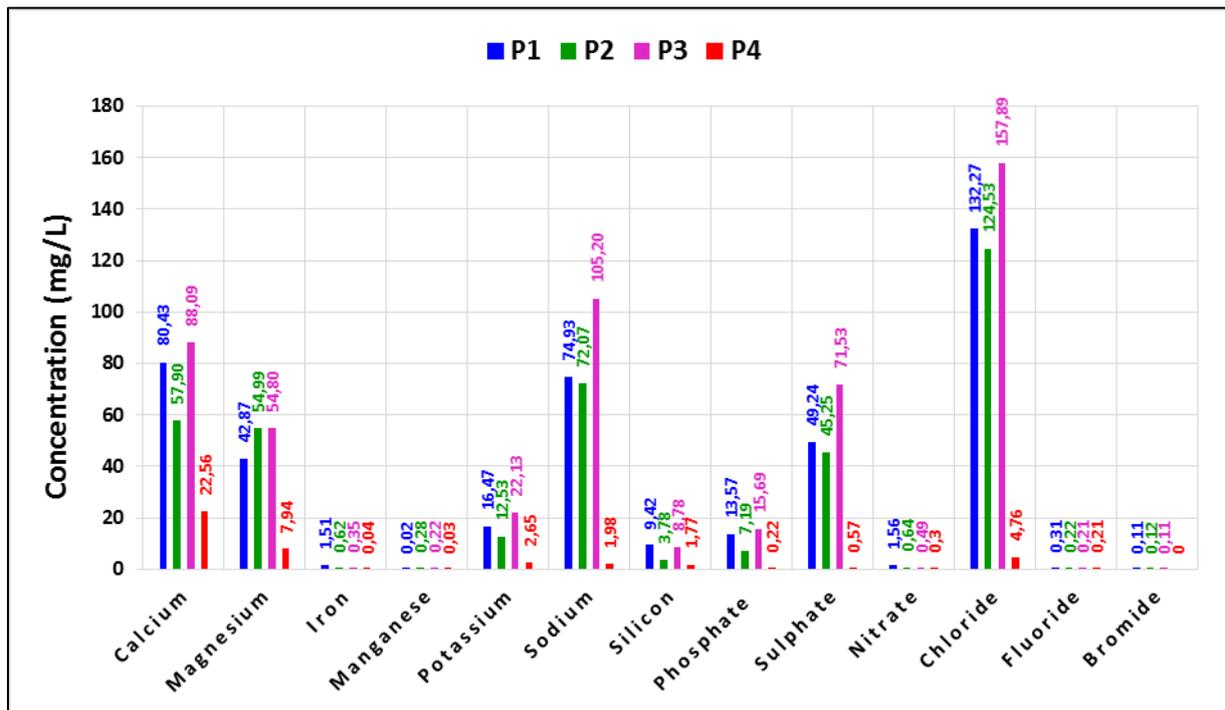


Fig. 3.

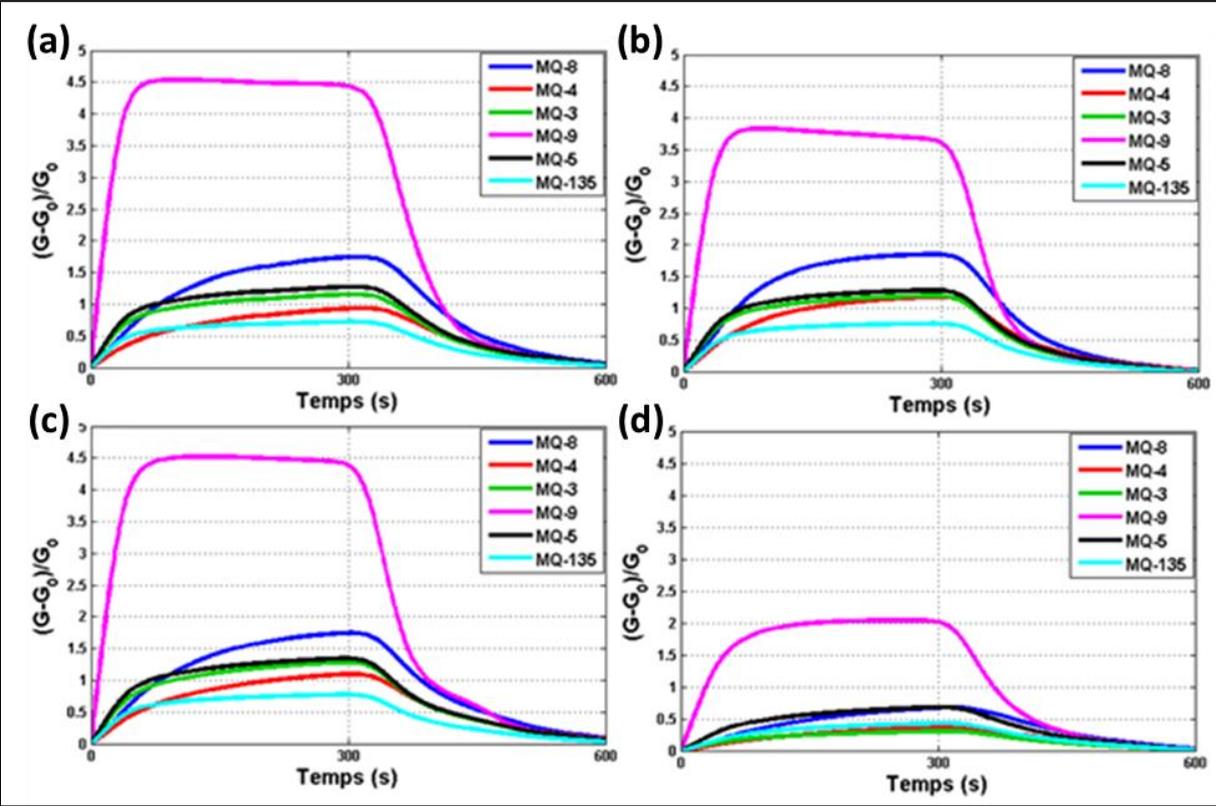


Fig. 4.

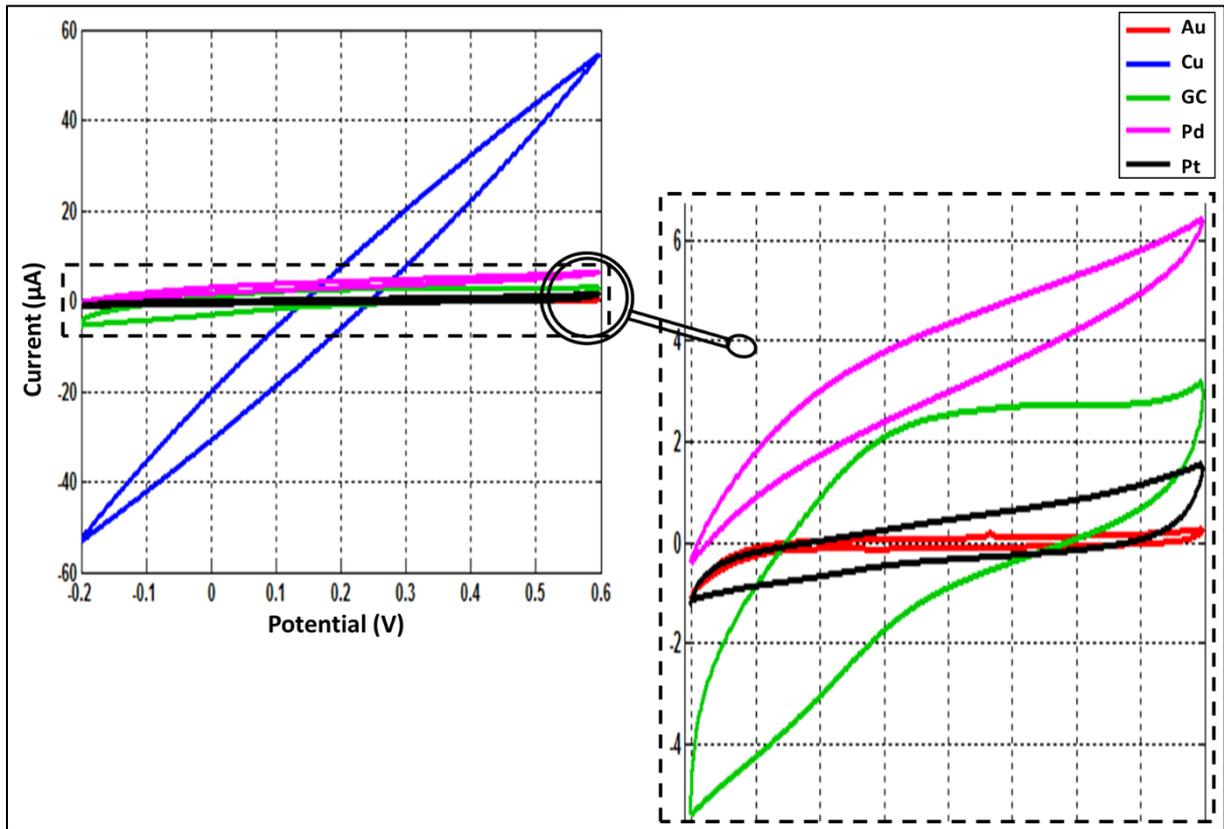


Fig. 6.

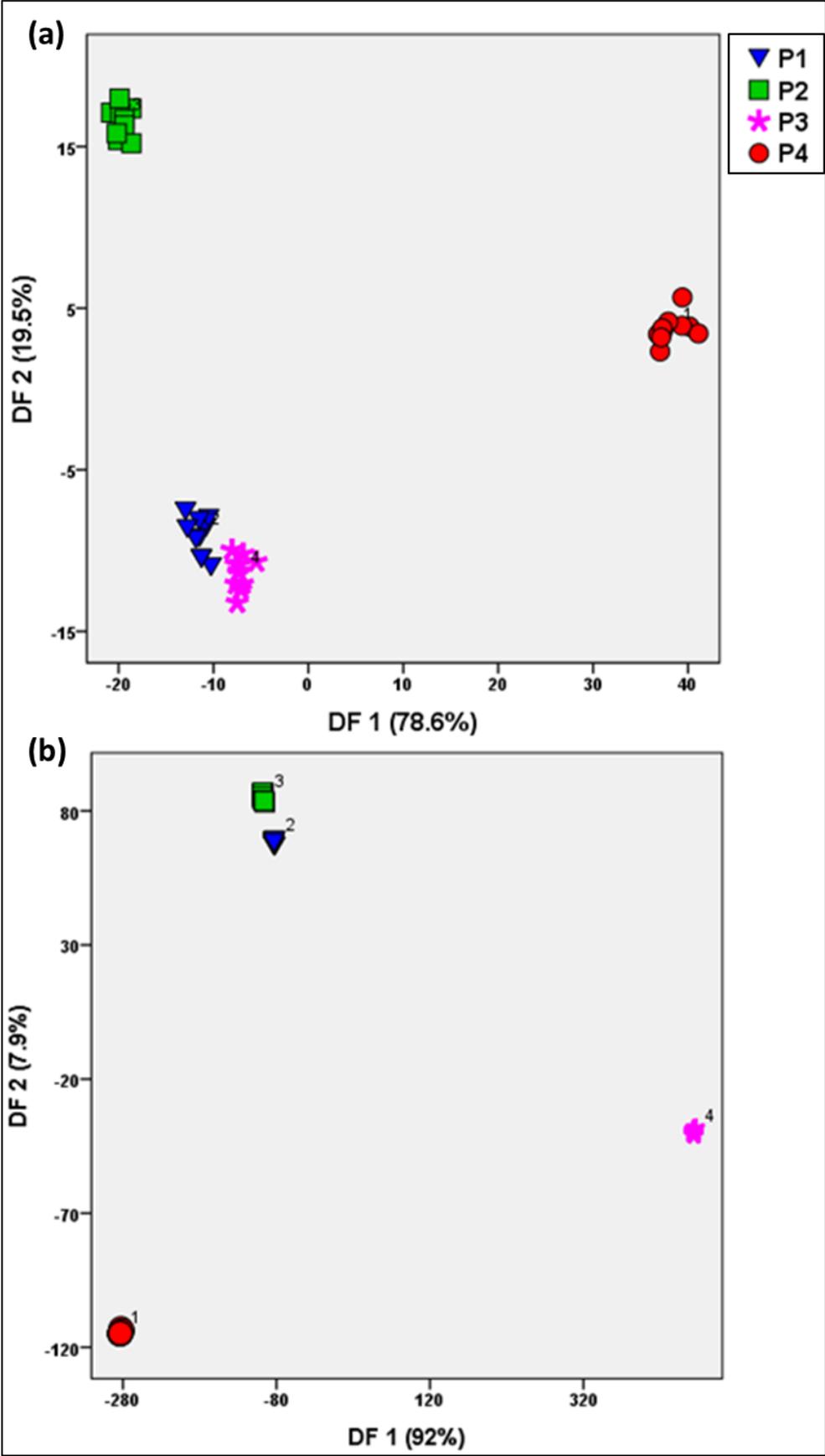


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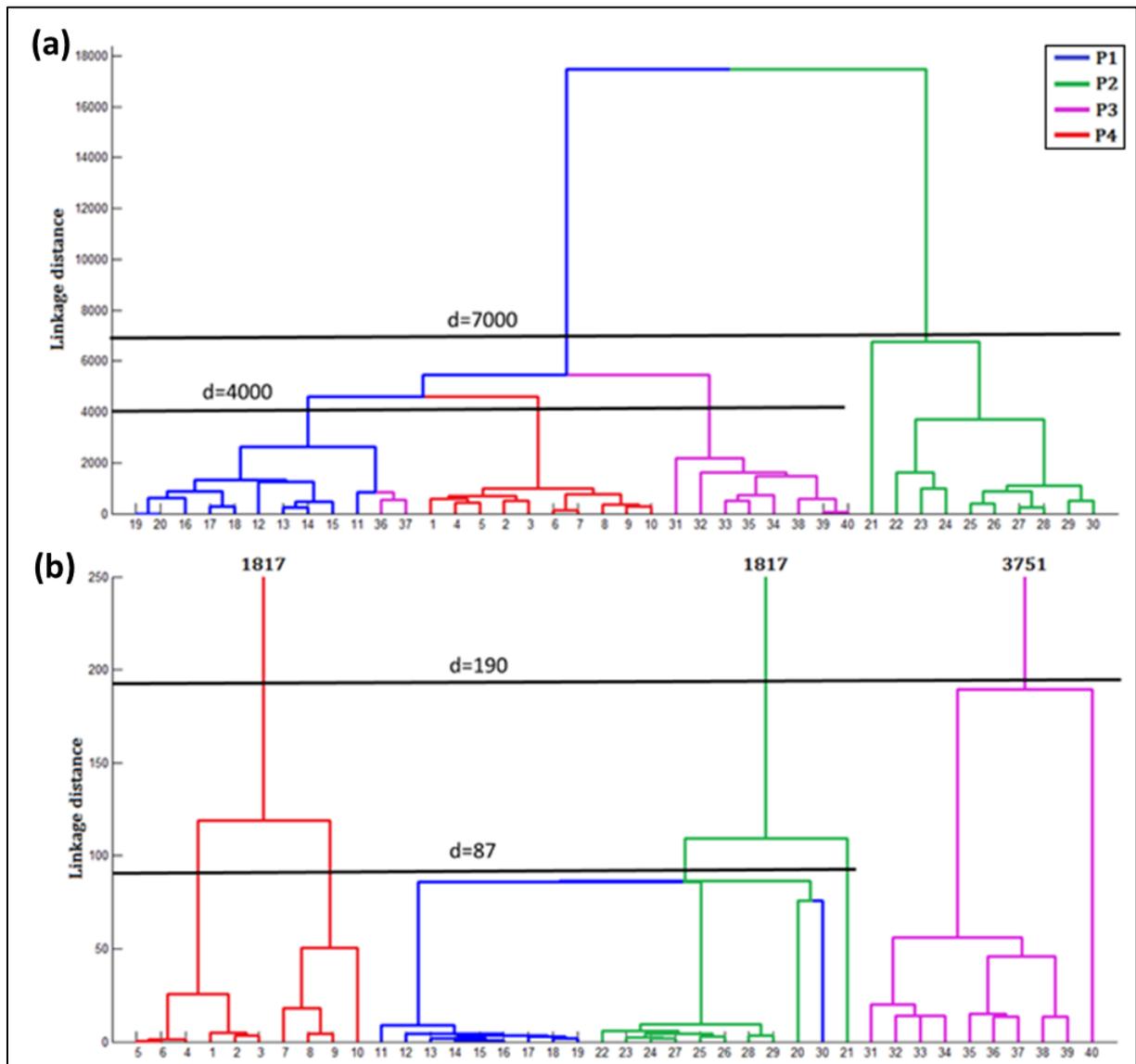


Fig. 8.

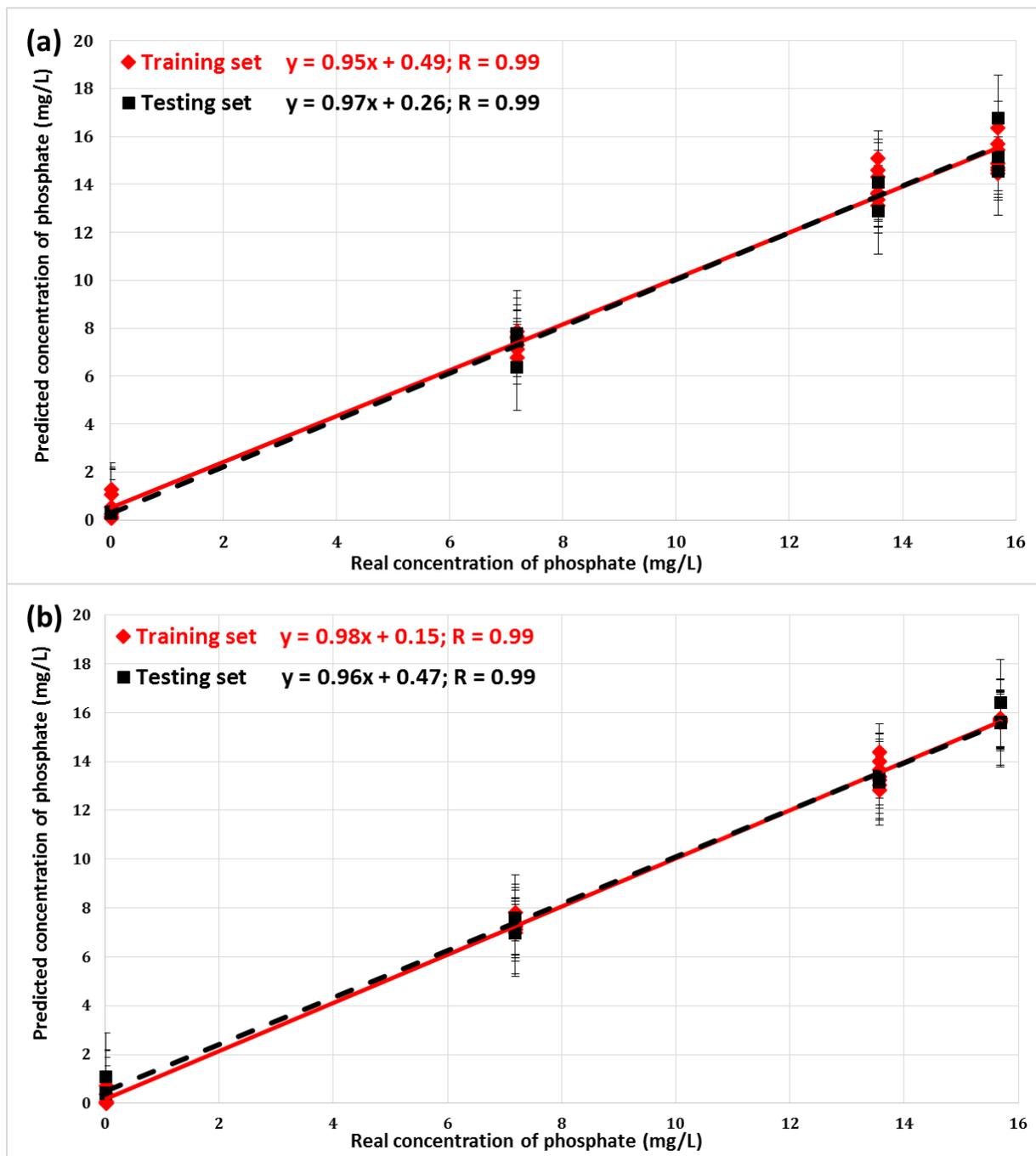
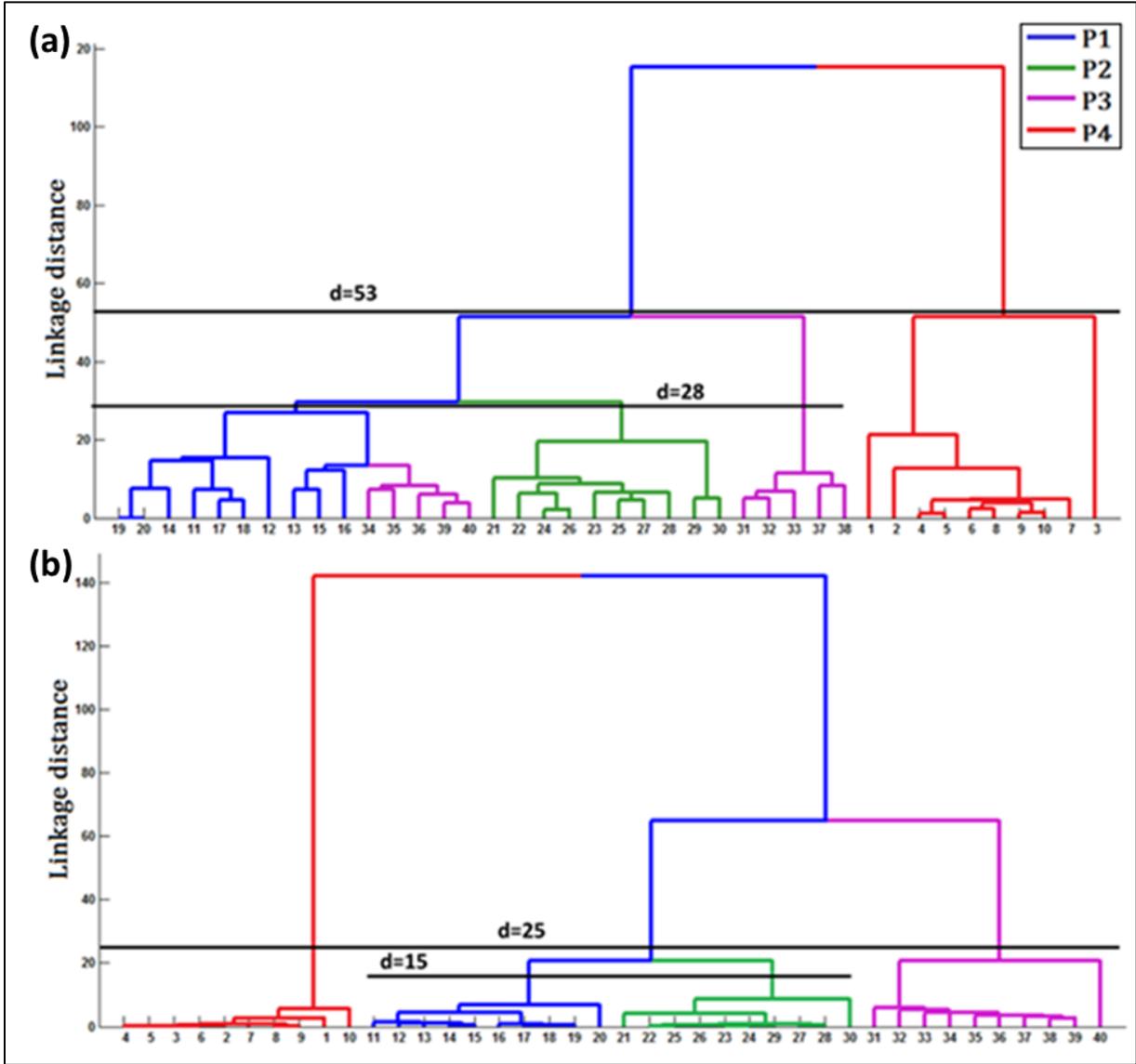


Fig. 9.



Supplementary information

Fig. S1: Electronic nose developed for headspace analysis of water and wastewater samples.

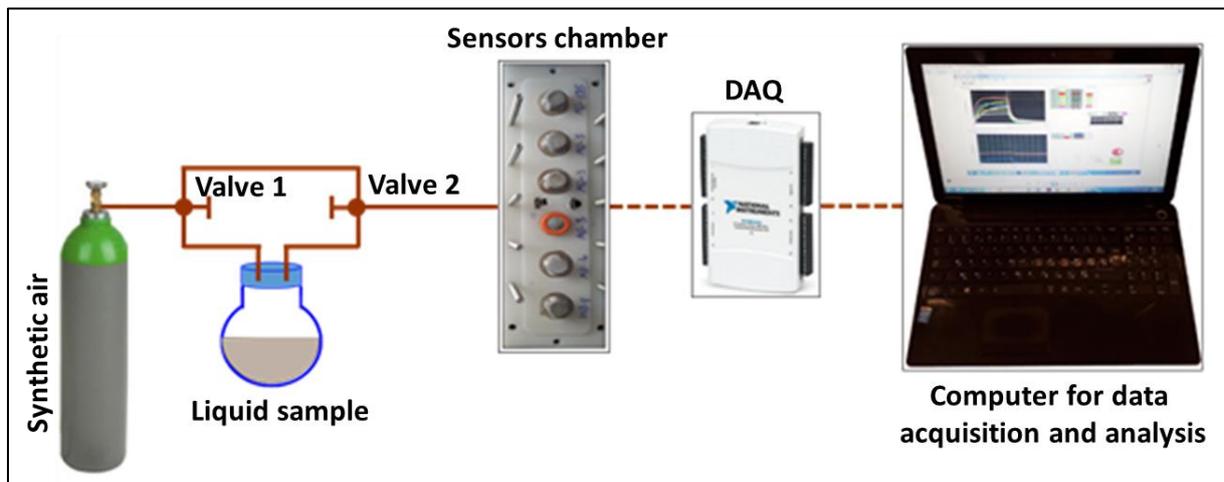
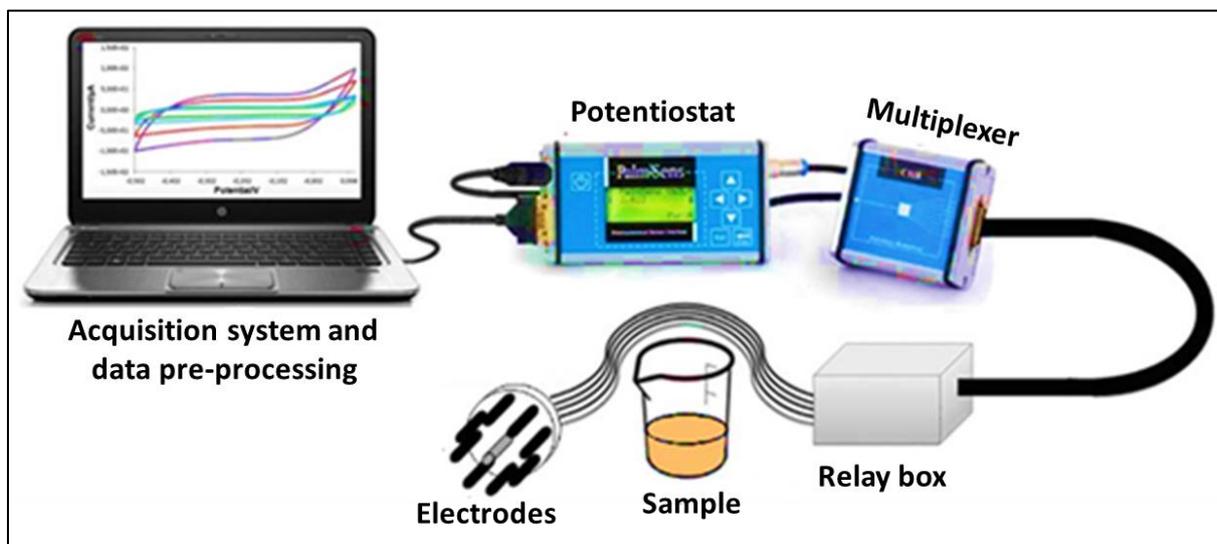


Fig. S2: Voltammetric electronic tongue set-up used for the analysis of water and wastewater samples.



Tables

Table 1: Results of physicochemical parameters determination of water and wastewater samples.

Component (mg/L)	P₁	P₂	P₃	P₄	Maximum limit for potable water (WHO)
pH	8.29	8.48	8.68	8.08	6.5-9.5 [34]
Conductivity (µS/cm)	1390	1169	1497	120.1	500 [35]
Total organic carbon (TOC) (mg/L)	> 300	> 300	> 300	10.2	2 to 200 [36]
Calcium (Ca) (mg/L)	80.43	57.90	88.09	22.56	75 [37]
Magnesium (Mg) (mg/L)	42.87	54.99	54.80	7.94	50 [37]
Iron (Fe) (mg/L)	1.51	0.62	0.35	0.04	0.1 [37]
Manganese (Mn) (mg/L)	0.02	0.28	0.22	0.03	0.1 [34]
Potassium (K) (mg/L)	16.47	12.53	22.13	2.65	Not available
Sodium (Na) (mg/L)	74.93	72.07	105.20	1.98	200 [38]
Silicon (Si) (mg/L)	9.42	3.78	8.78	1.77	Not available
Phosphate (PO₄) (mg/L)	13.57	7.19	15.69	0.22	Not available
Sulfate (SO₄) (mg/L)	49.24	45.25	71.53	0.57	200 [34]
Nitrate (NO₃) (mg/L)	1.56	0.64	0.49	0.3	50 [37]
Chloride (Cl) (mg/L)	132.27	124.53	157.89	4.76	200 [37]
Fluoride (F) (mg/L)	0.31	0.22	0.21	0.21	1.5 [37]
Bromide (Br) (mg/L)	0.11	0.12	0.11	0	0.025 [39]

Table 2: SVMs classification results of water and wastewater samples carried out using E-nose and E-tongue signals with a success rate of 100% and 97.5%, respectively.

	E-nose signals				E-tongue signals			
	P ₁	P ₂	P ₃	P ₄	P ₁	P ₂	P ₃	P ₄
P ₁	10				10			
P ₂		10			1	9		
P ₃			10				10	
P ₄				10				10

Table 3: Correlation coefficient (R), as well as Root Mean Square Error of Calibration (RMSEC) and Root Mean Square Error of Cross Validation (RMSECV) for training and testing sets using the data from both systems.

Components	E-nose signals						E-tongue signals					
	Training set			Testing set			Training set			Testing set		
	R	RMSEC	RMSECV	R	RMSEC	RMSECV	R	RMSEC	RMSECV	R	RMSEC	RMSECV
Ca	0.95	3.84	4.81	0.99	1.78	2.70	0.99	1.15	1.75	0.97	2.81	8.64
Mg	0.95	2.45	3.05	0.98	1.44	2.29	0.98	1.42	1.56	0.98	1.14	5.99
Fe	0.84	0.23	0.27	0.96	0.11	0.16	0.96	0.11	0.11	0.96	0.11	0.37
Mn	0.93	0.03	0.05	0.98	0.02	0.03	0.97	0.02	0.03	0.97	0.02	0.09
K	0.97	1.45	1.98	0.99	1.01	1,60	0.99	0.4	0.41	0.99	0.45	1.38
Na	0.98	6.21	9.23	0.99	5.08	8,07	0.99	0.59	0.66	0.99	0.75	1.27
Si	0.98	0.65	0.88	0.99	0.16	0,35	0.99	0.34	0.5	0.99	0.46	1.94
PO₄	0.99	0.68	1.07	0.99	0.65	1,02	0.99	0.32	0.48	0.99	0.45	2.12
SO₄	0.96	5.49	7.07	0.98	3.47	5,47	0.99	0.64	0.74	0.99	0.7	1.09
NO₃	0.99	0.51	0.63	0.99	0.35	0,55	0.99	0.14	0.16	0.99	0.21	0.42
Cl	0.98	9.34	11.29	0.99	5.76	9,35	0.99	1.75	2.06	0.99	0.84	3.08
F	0.91	0.02	0.02	0.99	0.01	0.01	0.98	0.01	0.01	0.97	0.01	0.04

Figure captions

Fig. 1: Sampling points in a wastewater treatment plant of Meknes city.

Fig. 2: Histogram of the physicochemical parameters determined in the water and wastewater samples.

Fig. 3: Normalized conductance evolution of sensors array exposed to headspace of water and wastewater samples from: (a) P₁ (wastewater samples collected at a location where solids and grit are removed), (b) P₂ (wastewater samples collected at a location where oil and grease are removed), (c) P₃ (wastewater samples collected in the bioreactor), and (d) P₄ (distilled water).

Fig. 4: Cyclic voltammograms corresponding to wastewater samples collected from bioreactor (P₄).

Fig. 5: PCA plot performed for visualization of water and wastewater samples distribution based on: (a) E-nose signals, and (b) E-tongue signals.

Fig. 6: DFA plot displaying patterns of water and wastewater samples based on: (a) E-nose signals, and (b) E-tongue signals.

Fig. 7: HCA dendrogram results of water and wastewater samples measured using: (a) E-nose signals, and (b) E-tongue signals.

Fig. 8: PLS prediction models of phosphate from the water and wastewater samples performed by means of real concentration versus database from: (a) E-nose signals, and (b) E-tongue signals.

Fig. 9: Dendrogram obtained by HCA of water and wastewater samples performed by the correlation of the concentrations of physicochemical parameters versus database from: (a) E-nose signals, and (b) E-tongue signals.

Highlights

- E-nose and E-tongue were used for qualitative analysis of water and wastewater.
- ICP-OES and ion chromatography were used for quantitative analysis of the samples
- Good discrimination of wastewater samples was obtained using chemometric techniques.
- PLSR was used to determine the relationships between parameters and systems responses.
- E-nose and E-tongue were able to predict the levels of wastewater parameters.

Graphical abstract

