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DOI: 10.1515/eces-2018-0028 ECOL CHEM ENG S. 2018;25(3):405-418

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DETECTION OF WASTEWATER TREATMENT PROCESS DISTURBANCES IN BIOREACTORS USING THE E-NOSE TECHNOLOGY

WYKRYWANIE ZAKŁÓCEŃ PROCESU OCZYSZCZANIA ŚCIEKÓW W BIOREAKTORZE Z WYKORZYSTANIEM E-NOSA

Abstract: Wastewater treatment processes are subject to numerous disturbances during biological treatment of wastewater. In order to achieve and sustain suitable conditions of the process, basic wastewater parameters should be frequently monitored. While great improvements have been made in the automatization of treatment process, little is known about automatic measuring systems that can detect unusual process conditions in a bioreactor. Tracking these parameters can be difficult and the time required for the determination might vary from several minutes to few days. The objective of this study is to evaluate the use of an electronic nose in-house device (based on a non-selective gas sensor array) for the detection of process disturbances in a lab-scale sequencing batch reactor (SBR) during biological treatment of wastewater with activated sludge. Measurements were performed during a 12-hours working cycle. Continuous analyses of the headspace were performed using a sensor array based on the resistive Metal Oxide Semiconductor type (MOS) gas sensor. Based on the data obtained and the PCA analysis, this study showed that the e-nose technology can be used to predict or retrieve information about potential disruptions during wastewater processes using the e-nose technology.

Keywords: e-nose, gas sensors array, MOS, SBR, wastewater treatment disruptions

Introduction

The evaluation of wastewater treatment process in bioreactors with activated sludge mainly relies on specific physicochemical parameters such as: Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), pH, Oxygen Uptake Rate (OUR), Total Suspended Solids (TSS), Total Organic Carbon (TOC), as well as the phosphorus and nitrogen content [1]. These methods are well-known and widely employed, allowing a relatively precise control over the treatment process and with the final goal of meeting the standard requirements including processes efficiency [2-4]. However, due to their complexity and time-consuming nature, these techniques might be expensive and

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operationally difficult for a constant monitoring of treatment. Some of the experimental procedures may take several days to complete and obtaining consistent results might be hard to achieve due to potential inconveniences (e.g. BOD_5). Generally, on-line measurement methods are still scarcely used due to their short lifespan and high failure rate of measurement devices or their high cost, which translates into extensive investments

Monitoring wastewater quality based on the analysis of air collected from the headspace may be conducted with multi-sensory systems [5]. These devices, coupled with a signal processing and interpreting computer system, are called electronic noses. An electronic nose is designed to mimic the olfactory sense of a human. While it does not constitute an objective substance detector, the device is constituted of a gas sensors array [6] that sends signals defining each analyzed gas sample. Combinations of signals are largely unique for individual gas samples, and they are commonly known as gas fingerprints [7]. Due to their way of operating, it is virtually impossible for electronic noses to determine individual components of a gas sample. Rather, the device is used to determine general characteristics of gases. The signals, obtained via the array, correspond with some degree of certainty to multiple physicochemical properties of the gas samples. For example, these signals allow the determination of total volatile organic compounds [8], some chemical substances [9, 10], odour concentrations, as well as the other gas sample parameters [11]. Signals can also be used for measurements of a liquid concentration in equilibrium with the gas phase. Due to their different applications and low cost, electronic noses are widely employed in numerous fields of science and branches of industry. The e-nose was also successfully implemented in the medical field [12, 13]. In addition, the e-nose has been practically used in the pharmaceutical [14], cosmetology [15], and food industry [16] together with other fields [17-19].

The sensor array of an electronic nose includes a set of low-selective gas sensors which produces a complex, multi-dimensional set of signals. Each of the sensors forming an array is sensitive to different groups of chemical compounds. Hence, every gas mixture yields a distinct signal profile [20]. Gas sensors utilized in electronic noses can be divided into four different groups: thermal, optical, gravimetric, and electrochemical. The sensors that are most commonly employed in electronic noses include metal oxide semiconductor (MOS) resistance sensors, conducting polymers (CP), quartz crystal microbalance (QCM) or surface acoustic wave (SAW) sensors [21]. Recently biosensors and bioelectronic noses have been increasingly applied for environmental measurements [22].

Prior to being used in a sensor array, a gas sensor must meet a number of requirements [23]. Monitored parameters include: selectivity, reaction time, sensitivity to a given gas, signal recovery, lifespan, as well as power consumption. Taking into account the arrangement of sensors in relation to the direction of gas stream flow, one can distinguish between parallel and serial arrays. In the former, the influent gas reaches all sensors (that are usually arranged in a circular fashion) simultaneously, whereas in the latter, the stream of gas flowing through the chamber reaches the sensors in a consecutive manner, possibly causing signal distortions [24].

From a sensor array operation standpoint dividing a gas sample into individual chemical compounds can be irrelevant. Given the partial selectivity of sensor arrays, a broad spectrum of polluted air profiles emitted during wastewater treatment can be revealed, recorded and distinguished [25]. The analysis of results obtained during the laboratory research conducted with a sequencing batch reactor (SBR) indicates that, by employing the multi-dimensional signals analysis methods, each profile, understood

as a combination of sensor signals, may be assigned to a given class, representing individual phases of reactor operation. SBRs are often used for scientific research and implementation of new solutions or exploitation strategies [2, 26-28].

Based on literature, multi-sensory arrays allow the identification of wastewater in respect to the level of pollution. Usually, it involves assessing the possibility of using the e-nose to identify and classify odors, depending on where they originate in a wastewater treatment plant [29, 30] and evaluate the concentration of odor in the relevant air samples [31-33]. This is as important issue since WWTPs are one of the main nuisance source of odorous air emissions, in particular stages of the wastewater treatment [34] as well as bioaerosol source [35, 36]. Moreover, attempts were made to correlate the data obtained from sensors arrays with basic physicochemical parameters determining the wastewater quality, including BOD_5 [29, 37], hydrogen sulfide [38], COD and TSS [39] or volatile organic compounds [30]. Satisfactory results were also obtained in relation to the odour concentration value [25]. It was assumed that highly polluted wastewater should differ noticeably from the wastewater polluted to a lesser degree. Some studies indicate that electronic noses may serve as an early detection system, revealing compounds that could potentially be hazardous to microorganisms involved in biological treatment of wastewater [40]. Sensor array systems were also utilized to detect non-specific waste accidentally discharged into the sewage network [41, 42]. These include, among others, hardly-biodegradable crude oil derivatives which may hinder the operation of the activated sludge, as well as any correlated process in a plant. This research shows that the electronic nose technology can be employed as an early warning system, notifying about the presence of compounds that could negatively affect the biological treatment process. The following step includes a potential implementation of the electronic nose system for monitoring wastewater treatment processes in an actual plant setup. Specifically, this study evaluated disruptions in wastewater treatment processes in an SBR with activated sludge by means of an array of resistive MOS-type gas sensors. The carried out measurements and the data obtained were validated by means of Principal Component Analysis (PCA).

Materials and methods

A schematic of the test stand including the SBR used for the treatment of wastewater is shown in Figure 1. The bioreactor allowed the reduction of organic compounds and nutrients (carbon, nitrogen, and phosphorus) during the reactive phase that consisted of mixing and aeration. The equipment included three independent 10 dm^3 SBRs. The reactors comprised an aeration system with a membrane diffuser, luminescent/optical dissolved oxygen (LDO) probes, a mechanical stirrer, as well as a monitoring control station - which maintained an adequate dissolved oxygen level - and a temperature stabilization system consisting of a water bath coupled with a thermostat [43]. An average dissolved oxygen concentration of 2 mg O_2 dm^{-3} was measured and kept constant throughout the experiments, while the temperature of the sewage was maintained stable at 20 °C.

The wastewater used in this study was sampled from the primary settling tank of the municipal wastewater treatment plant in Lublin (South-eastern Poland), where the daily volume of wastewater Q_d averages 60 000 m^3 d^{-1}. This mechanical-biological plant operates in a continuous flow arrangement, where the chambers of the bioreactor utilize a Bardenpho technology with no need for additional chemical reagents [26, 44]. The activated sludge, used for the inoculation during the bioreactor start-up, was also collected at described above plant.

The sludge parameters were as follows: mixed liquor volatile suspended solids (MLVSS) = 4.15 g dm^{-3}, mixed liquor suspended solids (MLSS) = 5.45 g dm^{-3}, sludge volume index (SVI) = 179 cm^3 dm^{-3}, and a sludge retention time (SRT) of 15 days.

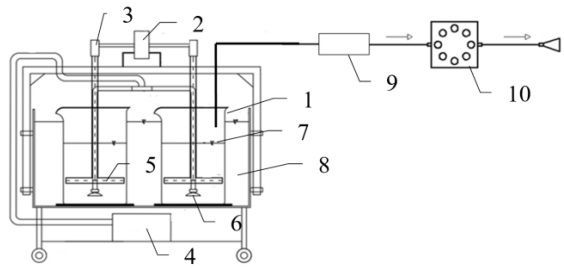

Fig. 1. Schematic of the laboratory SBR and headspace sampling method used in this study (1 - SBR chamber; 2 - electric motor; 3 - transmission; 4 - membrane blower; 5 - stirrer; 6 - diffuser; 7 - level of sewage; 8 - temperature stabilization system; 9 - desiccant-membrane dryer; 10 - gas sensors array)

During the experiment, the SBR (Fig. 1) operated at a 12-hours cycle (Fig. 2) and it was connected to a multi-sensory measurement system. Continuous mixing of wastewater lasted for 9 hours, starting from the second hour of the cycle. After 2 hours, the continuous aeration mode was switched on for 2.5 hours, followed by sequential aeration in several minutes' intervals. This step was required to maintain a desired concentration of dissolved oxygen in the bioreactor. In the final phase of the cycle, a 2-hour long sedimentation and decantation occurred while the treated wastewater was discharged. The reactor chamber was then filled with untreated wastewater.

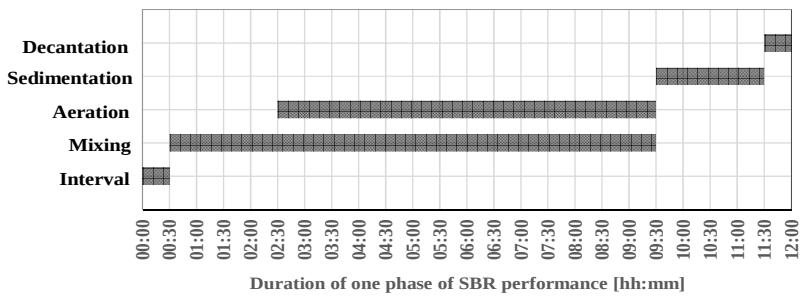

Fig. 2. Timing major phases of the SBR operation cycle

A sensor array was utilized to control the stability of the wastewater treatment process. The selection of gas sensors was based on the following criteria: (i) low number of sensors, (simpler system and lower construction costs with the possibility of repeated measurements), (ii) low selectivity of sensors, (iii) universal type (available in most of the countries and proven effective in similar applications), (iv) relatively low power consumption (allowing to use these sensors in mobile devices), (v) uniformity of sensor types within an array.

Measurements of the gas phase collected from the reactor headspace was carried out by means of an array comprising eight MOS-type Figaro TGS 2600 series sensors, a temperature

sensor (Maxim-Dallas DS18B20), and a relative humidity sensor (Honeywell HIH-4000). All of sensors were characterized by a small size and power consumption up to 300 mW [45, 46]. Their low cost, universal availability and reliability allowed utilizing them in multiple experiments. This allows for a partial comparison of results, because any commercially available sensor has precisely identical characteristics. A complete comparison could be performed only for e-noses with identical gas sensors, calibrated in the exact same way. The placement of sensors is depicted in Figure 3, whereas their physicochemical parameters are presented in Table 1.

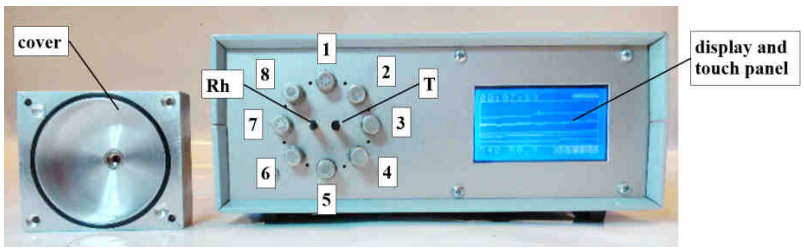

Fig. 3. Front view of the sensors array: 1 - TGS2600-B00, 2 - TGS2610-C00, 3 - TGS2611-C00, 4 - TGS2612-D00, 5 - TGS2611-E00, 6 - TGS2620-C00, 7 - TGS2602-B00, 8 - TGS2610-D00, T - DS18B20, Rh - HIH-4000

Carrying out measurements with MOS-type sensors involves recording changes in the resistance of the sensing element. According to the manufacturer's application schemes, the output voltage has to be measured in the resistive divider comprising sensing element R_S and the load resistor R_L connected to the ground circuit. Afterwards, the resistance of sensing element is determined according to the formula $R_S = R_L \cdot (V_C - V_{OUT}) \cdot (V_{OUT})^{-1}$, where: R_S - resistance of the sensing element [kΩ], R_L - resistance of the load resistor [kΩ], V_C - input voltage of the divider [V], V_{OUT} - output voltage of the divider [V].

Measurements were carried out in a continuous mode over a period of 60 days, with a measurement frequency of 1 Hz, which adds up to 5.1×10^5 of 8-dimensional data. These measurements included filling, mixing and aeration, as well as sedimentation and decantation. The gas sensors were flushed with clean air during the decantation and filling phases. The flow of sample stream was constant and amounted to 200 cm^3 min^{-1}. Given the detected humidity, the samples were dried with a DM-110-24 Perma Pure membrane dryer composed of a Nafion tube and granular silica gel. During the measurements, the temperature of gases inside the sensor chamber of the electronic nose averaged 35 °C (±2 °C), while the relative humidity reached 20 % (±5 %). High temperature of the considered gases resulted from the operation of heaters built in MOS-type sensors, which could have also mitigated a potential danger of water vapor condensing from gases. The thick walls of the sensor chamber prevented temperature changes in gas samples.

PCA was employed for the analysis of the data obtained from each individual SBR operation phase. PCA involves the selection of new, mutually independent variables (i.e. axes) which describe the variability of the analyzed dataset in a detailed way [47]. The designated variables have no physical significance per se, and no unit. Their contribution in the total dataset covariance (expressed as percentage) is the sole marked value. However, this type of plotting reveals differences and relations between the data, normally within hidden multi-dimensional datasets. PCA also allows decreasing the number of dataset

dimensions, losing only a small portion of information. The measurement data can subsequently be grouped and the results can be depicted graphically. Since as few as two or three new PC variables are enough to describe up to 90 % of dataset variables, the data can be plotted in two- or three-dimensional graphs.

Table 1

Specification of gas sensors applied in array [46]

Type	**Description**	**Detection range [ppm]**	**Heating element** Voltage Resistance Current Power	**Sensing element:** Voltage Load resistance Power Resistance in gas	**Sensitivity (change ratio)**
TGS2600-B00 Figaro	general air contaminants	1-30 (H2)	5.0 ±0.2 V 83 Ω 42 ±4 mA 210 mW	5.0 ±0.2 V > 0.45 kΩ < 15 mW 10-90 kΩ clean air	0.3-0.6 for $\frac{R_S(10\text{ ppm }H_2)}{R_S(\text{air})}$
TGS2602-B00 Figaro	general air contaminants	1-30 (EtOH)	5.0 ±0.2 V 59 Ω 56 ±5 mA 280 mW	5.0 ±0.2 V > 0.45 kΩ < 15 mW 10-100 kΩ clean air	0.15-0.5 for $\frac{R_S(10\text{ ppm EtOH})}{R_S(\text{air})}$
TGS2610-C00 Figaro	butane, liquid petroleum gas	500-10000	5.0 ±0.2 V 59 Ω 56 ±5 mA 280 mW	5.0 ±0.2 V > 0.45 kΩ < 15 mW 0.68-6.8 kΩ iso-butane 1800 ppm	0.56-0.06 for $\frac{R_S\ (3000\text{ ppm})}{R_S\ (1000\text{ ppm})}$
TGS2610-D00 Figaro	butane, liquid petroleum gas (carbon filter)	500-10000	5.0 ±0.2 V 59 Ω 56 ±5 mA 280 mW	5.0 ±0.2 V > 0.45 kΩ < 15 mW 0.68-6.8 kΩ iso-butane 1800 ppm	0.56-0.06 for $\frac{R_S(3000\text{ ppm})}{R_S(1000\text{ ppm})}$
TGS2611-C00 Figaro	methane, natural gas	500-10000	5.0 ±0.2 V 59 Ω 56 5 mA 280 ±25 mW	5.0 ±0.2 V > 0.45 kΩ < 15 mW 0.68-6.8 kΩ methane 5000 ppm	0.6-0.06 for $\frac{R_S(9000\text{ ppm})}{R_S(3000\text{ ppm})}$
TGS2611-E00 Figaro	methane, natural gas (carbon filter)	500-10000	5.0 ±0.2 V 59 Ω 56 ±5 mA 280 ±25 mW	5.0 ±0.2 V > 0.45 kΩ < 15 mW 0.68-6.8 kΩ methane 5000 ppm	0.6-0.06 for $\frac{R_S(9000\text{ ppm})}{R_S(3000\text{ ppm})}$
TGS2612-D00 Figaro	methane, propane, iso-butane	1-25 % LEL	5.0 ±0.2 V 59 Ω 56 ±5 mA 280 mW	5.0 ±0.2 V > 0.45 kΩ < 15 mW 0.68-6.8 kΩ methane 5000 ppm	0.5-0.65 for $\frac{R_S(9000\text{ ppm})}{R_S(3000\text{ ppm})}$
TGS2620-C00 Figaro	alcohol, solvent vapors	50-5000	5.0 ±0.2 V 83 Ω 42 ±4 mA 210 mW	5.0 ±0.2 V > 0.45 kΩ < 15 mW 1-5 kΩ ethanol 300 ppm	0.3-0.5 for $\frac{R_S(300\text{ ppm})}{R_S(50\text{ ppm})}$

In our experiments, PCA was used to reduce the number of data set dimension and find the relations hidden due to the bulk of information. First, a covariance matrix between all the variables was designated. Second, eigenvalues and eigenvectors were designated for the covariance matrix. Eigenvectors were arranged according to the values corresponding to eigenvalues. Then, eigenvectors corresponding to the highest values were selected [5, 47].

The cluster analysis for the reduced data was carried out with the k-means method. A typical k-means algorithm minimizes the squared error function E (1):

$$E = \sum_{i=1}^{k} \sum_{j=1}^{n} \left\| x_j - \mu_i \right\|^2 \quad (1)$$

where i is the ordinal number of cluster, k is the total amount of clusters, j is the ordinal number of data point in i cluster, n is the total amount of data points in i cluster, x_j is the value of data point belonging to the respective i cluster, whereas μ_i is the center of i cluster.

The cluster centers were initially chosen in such way, so as to maximize the cluster distance. Other methods of data discrimination include Linear Calibration Methods (LCM), Linear Discriminant Analysis (LDA), Functional Discriminant Analysis (FDA), Partial Least Squares Discriminant Analysis (PLS-DA), Generalized Linear Models with Regularized Path (GLMNET), Support Vector Machine (SVM) or Artificial Neural Network (ANN) [48-52]. All the statistical calculations and analyses were carried out with the Statistica 10 StatSoft software.

Results and discussion

Sensor array unprocessed outputs obtained during the measurements are presented in Figure 4. Recurring 12-hour long SBR operation cycles can be observed. During the decantation phase and the raw wastewater supply, the sensors were flushed with clean air for 30 minutes. Their resistance was then at peak point. After the addition of wastewater and sealing of bioreactor, a probe was placed again into the SBR chamber and air was collected from the headspace. A drop in sensor resistance occurred, resulting from the greater pollution of air sampled from the headspace when compared with the clean air used for flushing. A 2-hour long mixing constituted the first SBR operation phase. During the initial stage of mixing of the chamber contents (activated sludge, supernatant water and raw wastewater), a sudden increase in the amount of gaseous pollutants occurred in the air and because of this phenomenon the resistance of sensors decreased abruptly. The next phase involved the sequential aeration of the reactor over a period of 7 hours, followed by 2-hours sedimentation. Although the raw wastewater was characterized by a relatively high physicochemical parameters variability, constant monitoring showed numerous recurring cycles, closely resembling an optimal operation of the bioreactor. Any deviation from the typical characteristics denote a change in the bioreactor operation (a potential malfunction of an SBR element) or a drop in the wastewater treatment efficiency caused, for instance, by the influx of substances poisonous to the activated sludge.

At the initial stage of the study (Fig. 4), an experimental SBR failure was simulated and carried out. This step involved turning off aeration and mixing systems; this created suitable conditions for the growth of anaerobic bacteria. A noticeable drop in the resistance of all gas sensors, around 33.4 % compared to the baseline resistance during normal operation, was observed. This step was named as “deepening of anaerobic conditions” (Fig. 4a). Afterwards, the aeration and mixing systems were turned on again. An increased release of malodorous gases (characterized by high olfactory nuisance), resulting from the operation of the activated sludge under anaerobic conditions, was observed. Due to a significant contamination of the air in the headspace of wastewater, the sensor resistance roughly decreased by 77.3 % compared to the baseline conditions. The conditions characterizing the normal operation mode were gradually restored in the following operation cycles.

The two unnatural occurrences are easily discernible from the typical operation of the bioreactor as shown in Figure 4a. This confirms the possibility of employing multi-sensory systems for a continuous monitoring of bioreactors conditions, instantly notifying about any anomalies in its operation. As the sensors are not submerged in an aggressive environment, i.e. wastewater, they are characterized by greater durability in comparison to the ones utilized in other immersive methods.

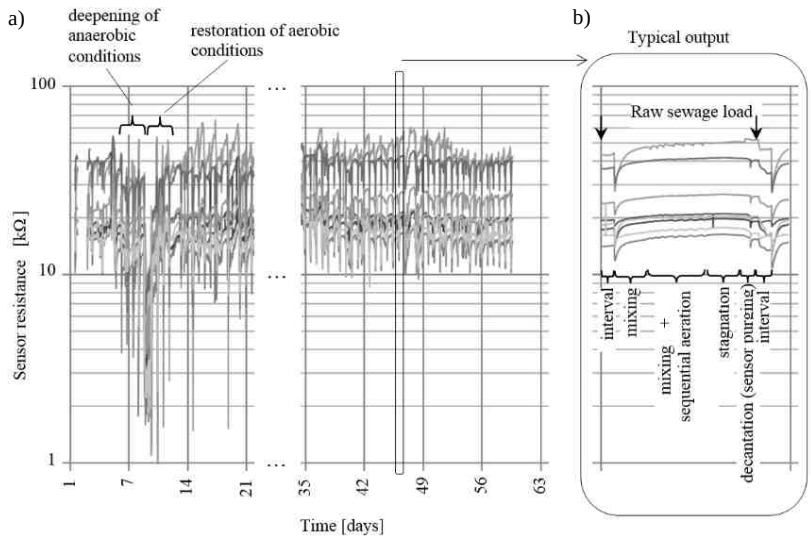

Fig. 4. Unprocessed output from the gas sensor array recorded: a) during continuous monitoring, b) typical repetitive sensor output with process description

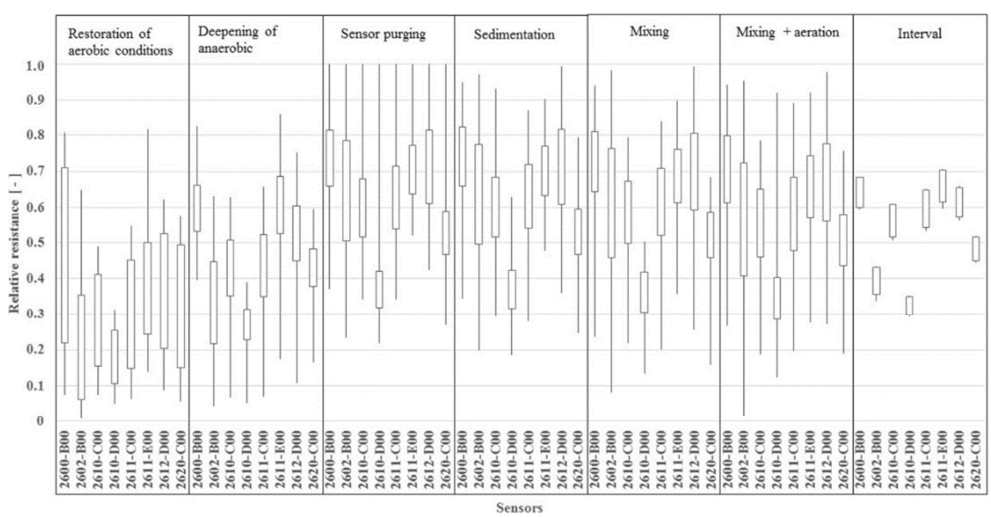

Fig. 5. Statistics analysis of sensor outputs (relative resistance RR) obtained during the measurements. Bars: minimum RR_{min} and maximum RR_{max}, frame: average $\overline{RR}$ ± standard deviation σ

Figure 5 shows the basic statistics pertaining to the individual sensor outputs recorded throughout the entire experiment. For results uniformity, the relative resistance $RR=R_S/R_O$, was determined, where R_S corresponds to the resistance [kΩ] of a sensor during the gas phase measurement, whereas R_O stands for the resistance [kΩ] of a sensor in the clean air environment. The frame presents the range of a standard deviation from the mean value ($\overline{RR} \pm \sigma$), whereas the whiskers correspond to the minimal RR (RR_{min}) and maximal RR (RR_{max}) values. Disturbances characterized by lower mean RR value ($\overline{RR}$) can be clearly distinguished in all the phases of cyclic operation. The first phase of reactor operation is characterized by minimal and maximal readouts close to the range of $\overline{RR} \pm \sigma$. Sedimentation, mixing, and aeration phases seem to be similar to each other; therefore, further complex analysis of multi-dimensional data is required.

PCA allowed to reduce an 8-dimensional set of data (corresponding to the number of sensors) to two new uncorrelated dimensions, which best reflected the variability in the data set. For this purpose, $8.1 \cdot 10^3$ 8-dimensional measurement results, describing individual SBR operation cycles to a most accurate degree (stabilized sensor output), were selected. Multi-dimensional measurement results obtained by means of the afore-mentioned sensor array were projected onto 2-dimensional PCA plane (Fig. 6) with two eigenvectors, designated for the highest eigenvalues of covariance matrix. Eigenvectors are shown Table 2 (5^{th} and 6^{th} column from the left). As a result of mathematical transformations, the new uncorrelated PC1 variable contains 95.67 % of information pertaining to the original data set and may be solely taken into consideration during the interpretation of results. However, in order to improve the chart interpretation, another variable, PC2 (2.67 %) was also accounted for. These two factors added up to 98.34 % of original information from the unprocessed output.

Table 2

Parameters of eigenvalues (in rows) and two maximal eigenvectors (in columns) of PCA transformation matrix covariance and basic characteristics of variables (sensors)

No.	Eigen-value	Covariance [%]	Cumulative covariance [%]	Feature vector of PC1	Feature vector of PC2	Variables	Variable averaged	*SD**
1	556.77	95.67	95.67	–0.26	0.43	2600-B00	7.46	6.34
2	15.55	2.67	98.34	–0.63	–0.72	2602-B00	15.51	15.11
3	5.54	0.95	99.29	–0.50	0.23	2610-C00	14.92	11.85
4	2.24	0.38	99.67	–0.26	0.05	2610-D00	7.46	6.44
5	1.16	0.20	99.87	–0.19	0.17	2611-C00	5.39	4.61
6	0.45	0.08	99.95	–0.19	0.01	2610-E00	8.95	4.72
7	0.23	0.04	99.99	–0.31	0.30	2612-D00	9.76	7.46
8	0.06	0.01	100.00	–0.23	0.36	2620-C00	6.13	5.70

**SD* - standard deviation

The results obtained from the analysis are shown in Figure 6. The SBR operation phases, as well, as abnormal states can be divided into 5 classes: (i) restoration of aerobic conditions, (ii) deepening of anaerobic conditions, (iii) untreated wastewater - after the addition of raw wastewater, (iv) treated wastewater - after treating process, and (v) clean air. A change in physicochemical properties of the air in the SBR chamber is proportional to the x-axis of PC1. On the left portion of the plot in Figure 6 points representing clean air can be noted. As the pollution level of wastewater increases (greater concentration of volatile substances in the air), there is a shift to the right side of the plot. This shows the

change first from treated wastewater to untreated wastewater and finally to the deepening of anaerobic conditions. Restoration of aerobic conditions is reflected in the graph by a shift to the left. During the restoration of aerobic conditions initial pollutants emission was very intense but then it gradually decreased.

Identifying the state corresponding to aeration is extremely difficult, as the relevant points overlap with the cluster of points reflecting the treated wastewater. On the other hand, the points corresponding to mixing partially overlap with the states following the addition of untreated and treated wastewater.

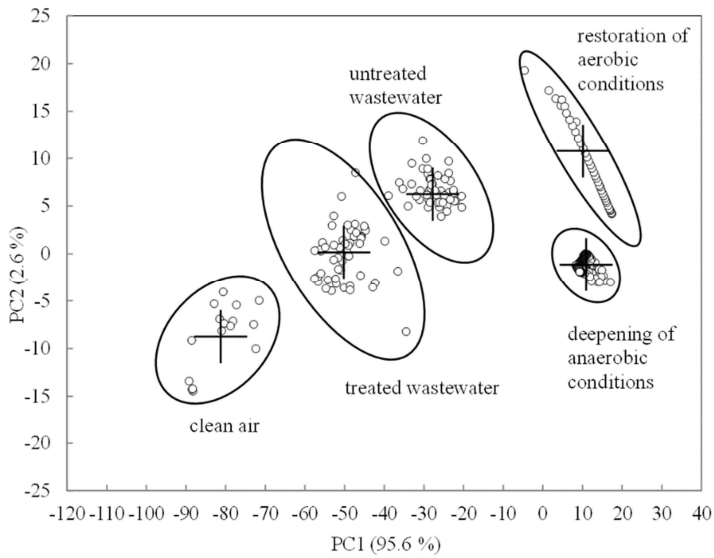

Fig. 6. PCA analysis of different stages in an SBR

Grouping of reduced data was carried out with k-means method. The algorithm found the following clusters in the plane of first two uncorrelated principal components PC1 and PC2: –81.25, –8.75 (clean air); –50.21, 0.14 (treated wastewater); –27.76, 6.25 (after the addition of raw wastewater); 10.12, 10.78 (deepening of anaerobic conditions); 10.91, –1.15 (restoration of aerobic conditions). The centers of the clusters were marked with crosses in Figure 6. Clustering is characterized by high inter-group variance (σ^2_{PC1} = 327896.2, σ^2_{PC2} = 7432.4) and low intra-group variance (σ^2_{PC1} = 4494.9, σ^2_{PC2} = 1848.2).

In order to evaluate the usefulness of employing sensor array for on-line SBR measurements, the transformation used for Table 2 was extended on all the results obtained from measurements conducted over several days. Afterwards, the distances of each measurement in relation to the 5 defined cluster centers - representing individual SBR operation cycles - was assessed, with the shortest Euclidean distance between the point and center of a cluster determining the group. The detection accuracy of individual states amounted to 78.04 %. In this case a variable content of wastewater collected from the WWTP was probably the reason for a relatively low precision of detection.

Our research suggests that it is possible to discriminate signal fluctuations during a 12 hour operation cycle (Fig. 4). Any deviation from the normal functioning is clearly visible from the plot shown in Figure 4 (e.g. deepening of the anaerobic conditions or restoration of aerobic conditions). A similar behavior with regards to signal fluctuations has been shown previously in literature [41]. Moreover, a consistent response in profiles for the eight sensors was observed during a 5 day period confirming the reproducibility of the signals. These results demonstrate that a chemical sensor array can rapidly detect the presence of organic compounds, such as diesel, in a wastewater [41].

Although the on-line monitoring of the sewage system was performed, there is not available information about a quantization the treatment stages yet. The percentage of accuracy for the classification of these signals reached 78.04 %. Research has shown that the e-nose can be a suitable device for a classification of wastewater. Onkal-Engin et al. [37] performed odors classification respectively to their location in WWTP. Samples were collected at different locations: influent, settling tank, activated sludge and final effluent. A clear classification was obtained with a correlation of 0.99631, corresponding to an RMS error of 0.022407. A percentage of 93.06 % of the outputs were classified successfully with an error below 10 % [53]. Although, no significant odor problems were recorded within the mentioned plant, Onkal-Engin et al. [37] observed that in certain days the nose output was higher when compared to the daily average. This behavior could be linked to the seasonal variations or the nature of the sewage. These variations were also recorded in our research, and are shown in Figure 5. The operation stages as ‘mixing’ and ‘mixing + aeration’ are characterized by a wide band of standard deviation.

This type of wastewater classification has been also shown in other studies. Dewwetinck et al. [39] showed that processing the fingerprints with PCA allowed for the interpretation and differentiation of the wastewater samples in terms of origin and quality, relative to their reference (i.e. deionized water). In other WWTPs, samples collected from the inlet works, settling tank, and final effluent, over a 8 month period showed that nonspecific sensor array can distinguish between different types of sewage samples and from different treatment works [54]. The research conducted by Nake et al. [30] showed that conducting-polymer (CP) sensors appear to be not suited for this application while MOS sensors were a better fit. MOS sensors were able to discriminate between the different odors from outdoor sludge/bark mixer, outdoor deodorization tower, outdoor sludge dewatering and clarifier [30]. All of these studies show that the indirect discrimination of wastewater quality using MOS sensors is possible. Based on the previous studies, we can precisely separate and differentiate between the clusters show in the PCA plot in Figure 6. When the results fell towards the right side of the plot (untreated wastewater), this could mean a potential disturbance during the treatment process. A similar analysis, using PCA, was presented by Bourgeois et al. [42]; every disturbance in the wastewater quality (caused by e.g. heavy rain or chemical pollution) was clearly identifiable in the PCA plot.

Conclusions

The conducted research indicates that a gas sensor array can be successfully employed to monitor wastewater treatment processes in a SBR. The described method allows the identification of individual bioreactor operation phases by accurately recognizing characteristic states and phases of the operation. The sensor array was able to distinguish the following phases: (i) restoration of aerobic conditions, (ii) deepening of anaerobic

conditions, (iii) period after addition of untreated wastewater, (iv) period during discharge of treated wastewater, and (v) introduction of clean air used for flushing the e-nose system.

Multi-sensory systems can be utilized for continuous monitoring of SBRs, instantly notifying about any anomalies during its operation. The detection accuracy of individual states amounted to 78.04 %. These sensors, used in a less aggressive matrix are characterized by greater durability in comparison to the ones utilized in other immersive methods.

In the future, these types of sensors can be applied for an initial assessment of different wastewater quality parameters (e.g. COD). Moreover, using numerical modelling, various simulations can be carried out and used to test different conditions and dynamic behaviour of input/output variables together with the local conditions in a selected part of the process in a WWTP. Finally, the relatively low cost, compared to other techniques, allow the implementation of this device for a broad range of application. However, further research will be required to investigate, for instance, parameters such as long term stability of readings and the influence of both temperature and humidity on the sensors.

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