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Rapid on-line method of wastewater parameters estimation by electronic nose for control and operating wastewater treatment plants toward Green Deal implementation

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ABSTRACT

In order to comply with legal regulations related to wastewater quality, the operational mode of facilities at wastewater treatment plant (WWTP) should be properly adjusted according to parameters of influents, however it is very difficult without frequently performed measurements. Currently there are known many techniques and devices for assesment of wastewater parameters such as chemical oxygen demand, biochemical oxygen demand, total organic carbon, as well as phosphorus and nitrogen compounds. In spite of the far reaching improvements of treatment process automatisation, there still isn't developed a automatic and fast measuring system of wastewater parameters. Rapid on-line method of wastewater parameters estimation by electronic nose and computer simulations could be recomended as an alternative solution in many WWTPs in comparation with traditional approch. Within this paper the analysis of real-time data obtained from laboratory bioreactor were used to estimate wastewater parameters in order to develop the inexpensive and fast-responding measuring for the WWTPs. The elaborated method enables continuous and relatively low cost monitoring of the wastewater quality even in many key points of operating and control WWTP. In this context, computer simulation support with on-line e-nose measurments could be cheap and useful tool to improve the WWTP efficiency.

Keywords: On-line measurement; Wastewater parameters estimation; Electronic nose; Modelling strategies; Operating and control of WWTPs

1. Introduction

After the treatment process is finished at a wastewater treatment plant (WWTP), the produced effluents are subsequently released to rivers or other water bodies, possibly having a negative impact on the environment. Numerous legal regulations and directives, determining the acceptable pollutant levels in an effluent stream, have been

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issued. The operation of facilities in a wastewater treatment plant should match the parameters of the wastewater influent, in order to meet the strict requirements laid down in the regulations and maintain adequate level of the wastewater quality indicators. However, this may not be possible without conducting measurements on a regular basis. At present, numerous methods and devices exist for the purpose of evaluating such wastewater parameters as total organic carbon (TOC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), oxygen uptake rate (OUR), as well as the level of nitrogen and phosphorus compounds. Even though the automatization of treatment process has been greatly improved over the years, there is still no system for automatic measuring of relevant wastewater parameters. Determining the above-mentioned parameters by means of proper methodology may take between 1 h (in the case of COD) and 5 d (for BOD_5). Measuring other parameters with immersed sensors presents the problem of lack of repeatability caused by the biological film coating the sensors or other kind of block measurement areas of the sensor [1]. Additionally, the high cost of professional measuring equipment constitutes a severe hurdle. Thus, measurements in numerous local wastewater treatment plants are conducted rarely, while the treatment process is carried out drawing on the observations made by experienced staff. As an alternative, an on-line estimation of wastewater parameters performed by means of an electronic nose and computer simulations can be proposed for numerous wastewater treatment plants.

At present, electronic noses (e-noses) are utilized to measure odorous compounds. An e-nose is a device which mimics the human olfactory sense, and comprises an array of several non-specific gas sensors [2]. Individual sensors are partially sensitive to various groups of chemical compounds. Every gas mixture creates a unique signal profile, which may be compared to fingerprints in dactyloscopy, as an identical combination is extremely unlikely to form in two different gas samples. Hence, the term "gas fingerprint" is commonly used in relation to signal combinations [3,4]. The obtained multidimensional set of signals is subsequently analyzed. For this purpose appropriate statistical analyses of multidimensional data are used, such as principal component analysis (PCA) [5], support vectors machines (SVM) [6], decision trees (DT) and random forests (RF) [7] or artificial neural networks (ANN) [8,9].

Some authors have attempted to compare the standard parameters of sewage to an e-nose response [3,10]. Most frequently, it consisted in the evaluation of the e-nose system to recognition and classification of sewage odours concerning their location in a WWTP as well as the odour concentration assessment. In some earlier studies, attempts were made to employ the e-nose for the assessment of standard physical-chemical parameters of sewage such as COD, TSS, volatile suspended solids (VSS), and turbidity, but the correlation coefficient was quite weak ($r = 0.52 \div 0.67$) [3].

The gas sensors utilized in analyses are non-selective to single chemical compounds and – contrary to chromatography – do not allow for an accurate qualitative and quantitative analysis. Single sensors do not yield satisfactory results, because a given signal may be generated by many different gas samples. An array of multiple sensors produces a virtually unique set of signals, enabling a precise differentiation between the investigated samples. The sensors used for this purpose should be sensitive to various groups of pollutants. 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 [11].

The VOC profile of wastewater is diverse in relation to its content and concentration. As many as 450 compounds can be identified in the gases produced in the course of wastewater treatment; roughly 100 of them are considered strong odorants [12], distinguished by a broad range of odours. These substances can be divided into four main groups [13]:

- Sulfur compounds: hydrogen sulfide, dimethyl sulfide, diethyl sulfide, diallyl sulfide, carbon sulfides, sulfur dioxide, methyl mercaptan, ethyl mercaptan, propyl mercaptan, butyl mercaptan, tert-butyl mercaptan, allyl mercaptan, crotyl mercaptan, benzyl mercaptan, thiocresol, and thiophenol;
- Nitrogen compounds: ammonia, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, cadaverine, pyridine, indole, and skatole;
- Acids: acetic, butanoic, and valeric;
- Aldehydes and ketones: formaldehyde, acetaldehyde, butyralde-hyde, isobutyraldehyde, isovaleraldehyde, acetone, and butanone.

The presence sulfur and its derivatives is somewhat problematic, as sulfur compounds lead to the poisoning of sensors, subsequently causing signal drift and, eventually, decalibration of the device. However, this problem is relatively insignificant in the biological part of the wastewater treatment plant. Apart from hydrogen sulfide, many other substances can be enumerated, including dimethyl sulfide, methanetiol, as well as mercaptans [14].

The VOC concentration above the water surface strictly depends on micropollutants concentration in wastewater. The change of pollutants concentration is caused by three different methods, that is, volatilization, sorption on solid compartments and biodegradation [15]. Volatilization mostly pertains to volatile organic compounds [16], polycyclic aromatic hydrocarbons [17], surfactants [18], and such micropollutants as, for instance, acetone, hydrogen sulphide, and phenol [19]. The intensity of this process is highly dependent on the operating conditions, including temperature, pressure, aeration and mixing. Volatilisation by stripping takes place in the aeration tank. This is due to air, which raises the mass transfer of pollutants between phases. In primary and secondary settlement tanks, where the surface of wastewater is still, surface volatilisation predominates. Gas pollutants generated in the course of wastewater treatment processes may be identified by means of an electronic nose. Apart from volatilization, biodegradation also yields (bio)gases – either nitrogen or carbon compounds – depending of what the oxygen conditions in wastewater are. Therefore, the measurements performed by means of an electronic nose display both the concentrations of pollutants dissolved in wastewater, and their degradation degree.

Using electronic noses at wastewater treatment plants has been discussed in scientific literature. Usually, it involves assessing the possibility of an e-nose application in identifying and classifying odours, depending on where they originate in a wastewater treatment plant [20,21] and evaluating the concentration of odour in the relevant air samples [22–24]. In some studies, an electronic nose was used to estimate the standard wastewater pollution parameters, including BOD [25,26], COD, VSS, TSS, and turbidity [3]. The afore-mentioned studies assumed that highly polluted wastewater should be discernible from the wastewater characterized by low level of pollutants. What follows is that e-noses can be used also for an early detection of hazardous chemical compounds capable of disrupting the operation of organisms in the biological part of a WWTP. For instance, this includes the hardly-biodegradable derivatives of crude oil, which are detrimental to the activated sludge and its operation, hampering the course of the treatment process [10]. A gas sensor array, which is capable of identifying multiple types of pollutants, can be successfully used for this purpose.

An electronic nose was also used for odour classification in light industrial treatment plants, as well as municipal wastewater treatment plants [27]. As part of the study, a total of 144 air samples were collected from various treatment processes, including initial treatment, sedimentation tanks, biological treatment, and discharge of treated wastewater. The gas sensor array signals were analyzed with neuron networks, comprising 12 input neurons, as well as two hidden layers with 12 neurons each. Individual odour types yielded high correlation of up to 0.99.

Computer modelling can be supplemented with wastewater parameters estimated in real-time. The modelling of wastewater treatment processes can be carried out by means of, for instance, TOXCHEM+, BASTE, WATER8/WATER9, GPS-X, and WEST software [28].

In Europe, models are mainly used by scientists for research purposes in terms of process optimisation and energy efficiency; in turn, the majority of their users overseas, mainly in North America (U.S.A. or Canada), are designers in private companies. Simultaneously, there are clear global trends in the use of increasingly sophisticated computer tools for optimising biochemical processes based on the activated sludge method [29].

Average conditions are reflected by the results of general fate models, which are mostly created as steady-state models. On the other hand, dynamic models allow for an evaluation of wastewater in actual, dynamically changing conditions. GPS-X is software which may be applied for dynamic simulation of biological treatment of wastewater. It utilizes the activated sludge model (ASM) with 13 constituent components (in its first version) to describe the transformation and removal of both carbon and nitrogen. The activated sludge model and its updated versions, that is, ASM2, ASM2D and ASM3, can be used in the case of COD, BOD, TSS and nitrogen compounds. On the other hand, TOXCHEM+ software may be employed to simulate other compounds.

ASM is a complex physical-chemical-biological system, characterized by plethora of interactions between the local conditions, state variables, as well as the dynamic input variables. The previously conducted simulation studies [29–32] proved that both the software architecture and simulation platform (including, for instance, GPS-X, SIMBA, and BIOWIN), were adequate for this purpose. At present, they are used on a regular basis in many developed countries, such as European Union member states, Japan, Australia, the USA, and Canada. This process was facilitated by the advent of more powerful computers, as well as the greater knowledge of the metabolism of the concerned bacteria or their specific groups [32]. Computer simulations and mathematical models of wastewater treatment plants, coupled with electronic noses supplying data about estimated wastewater parameters, can be used for an on-line control of WWTP processes. Owing to such a solution, the overall efficiency of the systems may be improved. As evident from the mapping of energy consumption carried out at a wastewater treatment plant, approximately 20%–30% of total plant operation costs can be reduced by adjusting the aeration of the biological treatment process. The widely-described [21,30] problems of inefficient aeration of the aerobic zones of bioreactor and the excessive capacity of the aerated volume both stem from varying influent load, as well as discharge limits for low concentrations of ammonium in the effluent. These phenomena are known to generate additional, unnecessary costs in numerous wastewater treatment plants. Mathematical modelling/computer simulation with an electronic nose may be utilized for an on-line monitoring and control of the wastewater (its content of carbon, and nitrogen, compounds), as well as the prediction of the dynamic behaviour of input/output variables and local conditions in a given part of a wastewater treatment plant system.

2. Materials and methods

The study aimed to assess the viability of real-time control biological treatment processes at a wastewater treatment plant by conducting on-line measurements with an electronic nose and performing computer simulations. The first stage involved a laboratory research conducted by means of a sequencing batch reactor (SBR). The laboratory set utilized in the study is presented in Fig. 1.

The concentration of organic compounds and nutrient (N, P, and S in particular) during the active phase of treatment involving mixing and aeration can be reduced by means of an SBR. Under aerobic conditions, pollutants undergo transformation to CO_2, H_2O as well as oxidized inorganic P, S and N compounds; then, removal of organic compounds and oxygen bound in nitrates follows. Methane is produced under anaerobic conditions by a specific group of microorganisms. Each treatment process is performed in one volume in a proper sequence; therefore, monitoring can be carried out by means of only a single measurement device. In the classical WWTP operating in the flow mode, comparable data should be ensured by conducting measurements in several locations [33].

The semi-automatic SBR which utilized the activated sludge method and operated in 12-h cycles. At the beginning of the cycle continuous mixing was activated lasting 9 h. Simultaneously, together with mixing, continuous aeration was activated for a period of 2.5 h, and then intermittently in order to sustain oxygen concentration at the level of

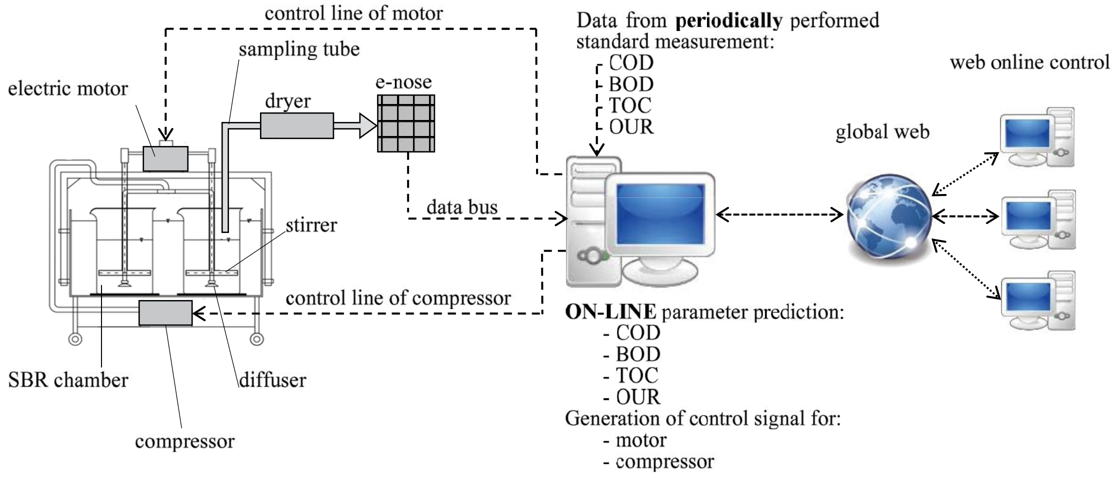

Fig. 1. Scheme of the proposed control system.

2 gO_2/m^3. In the final part of the cycle, a 2 h sedimentation phase was initiated and finished with decantation, during which the treated wastewater was discharged and after which the reactor was loaded with raw wastewater. The SBR reactor enabled reduction of organic compounds and nutrient concentration (compounds of carbon, nitrogen and phosphorus) during an active phase of treatment mixing and aeration. The laboratory equipment consisted of three independent SBR reactors, each with a 10 dm^3 chamber. All reactors were equipped with a mechanical stirrer, aeration system with membrane diffuser, and temperature stabilization system. During the experiment, the temperature of sewage was kept at 20°C ± 0.1°C. The measurements were conducted during the whole cycle, but the results from the final part of the sedimentation phase were taken for subsequent analysis of treated wastewater quality. Wastewater treated in the bioreactor during the study was collected from a primary settlement tank of a municipal wastewater treatment plant) in Lublin (Poland), characterized by the daily flow rate of Q_d = 65 000 m^3/d.

Activated sludge used during the experiment was was characterized by the following parameters: mixed liquor suspended solids (MLSS = 3.2 g/dm^3), mixed liquor volatile suspended solids (MLVSS = 2.4 g/dm^3), the food to microorganism ratio (F/M ratio = 0.10 g BOD_5/gMLVSS·d), sludge volume index (SVI = 235 mL/dm^3) and a sludge retention time (SRT) of 15 d.

The gas samples were taken from the wastewater headspace in a bioreactor chamber; the volume of samples equalled 200 cm^3/min. The samples were dehumidified by means of DM-110-24 Perma Pure dryer with nafion tubing and silica gel. The measurement was performed with an array comprising eight MOS-type TGS Figaro sensors, that is, TGS2600-B00, TGS2602-B00, TGS2610-C00, TGS2610-D00, TGS2611-C00, TGS2611-E00, TGS2612-D00, and TGS2620-C00. Additionally Maxim-Dallas DS18B20 temperature sensor and Honeywell HIH-4000 relative humidity sensor were both used to measure and evaluate stability of environmental conditions. The measurements were conducted continuously over 60 d, with the readout frequency of 1 s.

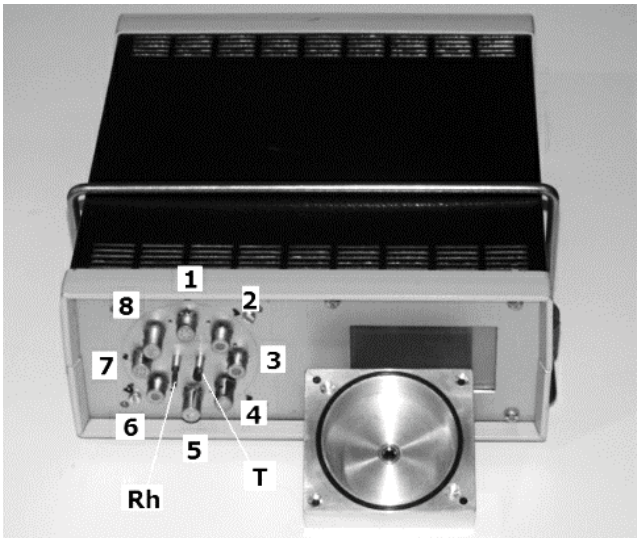

Fig. 2. An electronic nose with MOS gas sensors – prototype prepared by authors.

The measurement performed with MOS sensors involved registering changes in the resistance of the sensing element in the sensors utilized in the study is presented in Fig. 2. In line with the application scheme recommended by the manufacturer, the input voltage was measured in the resistive divider comprising a sensing element R_S and a load resistor R_L connected to the circuit ground. The resistance of a sensing element was subsequently determined with the formula $R_S = R_L\ (V_C - V_{\mathrm{OUT}})(V_{\mathrm{OUT}})^{-1}$, where R_S – resistance of a sensing element (kΩ), R_L – resistance of a load resistor (kΩ), V_C – input voltage of the divider [V], V_{OUT} – output voltage of the divider (V).

To calibrate readouts from electronic nose system the liquid phase of treated sewage was subjected to standard measurements involving: $N–NO_2$, $N–NO_3$, $N–NH_3$, COD, TSS, VOC, as well as pH and turbidity. A HACH DR2800 spectrophotometer was used for measuring the $N–NO_2$, $N–NO_3$, $N–NH_3$, COD, and TSS. The analysis was conducted

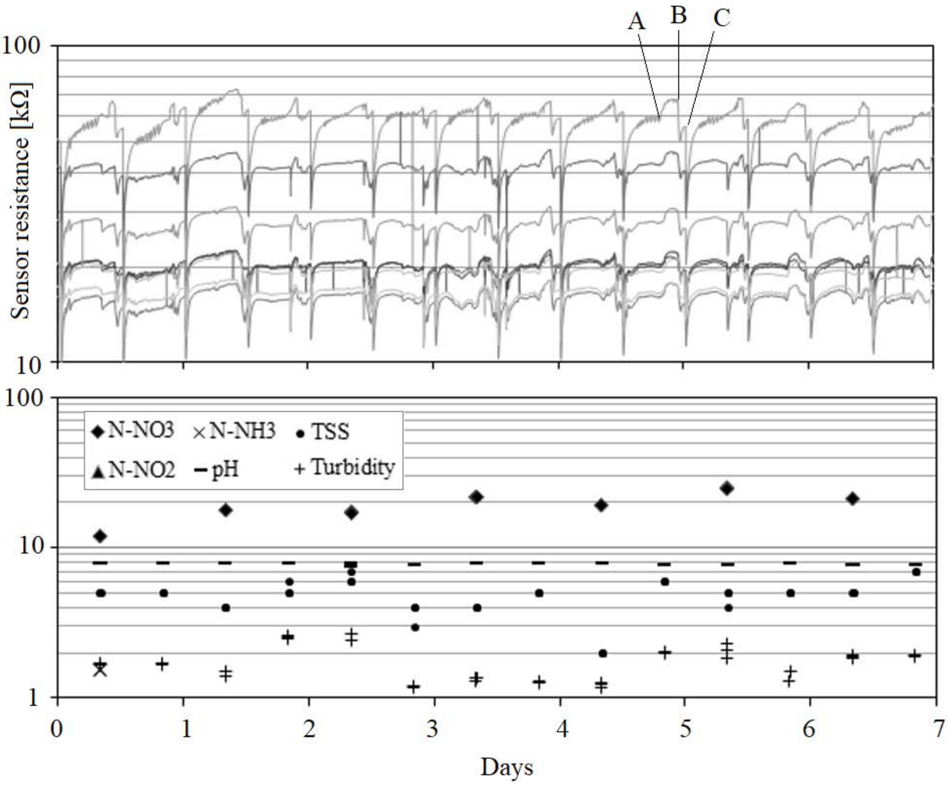

Fig. 3. Results of measurements conducted over the period of one week, from both the standard measurement (lower part) and a gas sensor array (upper plot), (A) beginning of sedimentation, (B) raw sewage load and (C) start of aeration.

according to the HACH-Lange methodology with cuvette tests. Apart from that, HACH HQ40D digital pH meter was utilized to measure the pH, while turbidity was evaluated with Eutech Instrument TN-100 turbidimeter. Pollution level was measured after the SBR sedimentation phase concluded. Due to the odour nuisance commonly attributed to the emission of volatile organic compounds at a wastewater treatment plant, the VOC levels were measured as well by means of a Photovac Voyager portable gas chromatograph, which operated in VOC mode on column V and was equipped with a PID detector. The air sample was collected with a long probe; the sampling time equalled 30 s. The studies proved that after calibrate the electronic nose to the prediction of chemical oxygen demand, highly accurate (r = 0.98) COD estimation is feasible. This method of indirect COD value estimation may serve both as a preliminary measurement device for estimating wastewater parameters on-line, and as an early detection system that identifies excessive biological loads or non-typical pollutants.

The second-stage of the study involved the creation of a suitable SBR model by means of the dynamic simulator, which is based on the ASM. The real-time data obtained in the course of tests including a laboratory sequencing batch reactor were modelled and used for the comparison of computer simulation and the data collected by the electronic nose. This enabled to develop a cheap and responsive measuring system for wastewater treatment plants, which allows for a continuous and relatively inexpensive monitoring of wastewater quality. The operating conditions of the wastewater treatment process can be optimized in accordance with the obtained results. Such a solution could decrease the negative environmental impact of the effluent and cut the operating costs by saving energy consumption, leading to an overall improvement in the efficiency of a treatment plant operation.

3. Results and discussion

The proposed real-time control system for a wastewater treatment plant utilizes continuous measurements performed by means of an electronic nose coupled with computer models of the WWTP. This solution enables predicting the values of wastewater effluent parameters and subsequent adjustment of the treatment process, including, for instance, matching the aeration intensity to the wastewater quality.

3.1. Electronic nose monitoring of SBR process

The typical shape of signals and sensor resistance (8 sensors) values obtained during the measurements is presented in the figure below (upper chart). Additionally, the results of standard measurements (N–NO_2, N–NO_3, N–NH_3, TSS, COD, turbidity) are presented on lower chart in Figs. 3 and 4..

The values of sensors resistance were analysed using ANN and was compared to results of standard measurements. The parameter characterized by best correlation (r = 0.988) and narrow confidence interval reaching approximately 10 mg/dm^3 (i.e., 17% of the measured scale) was chemical

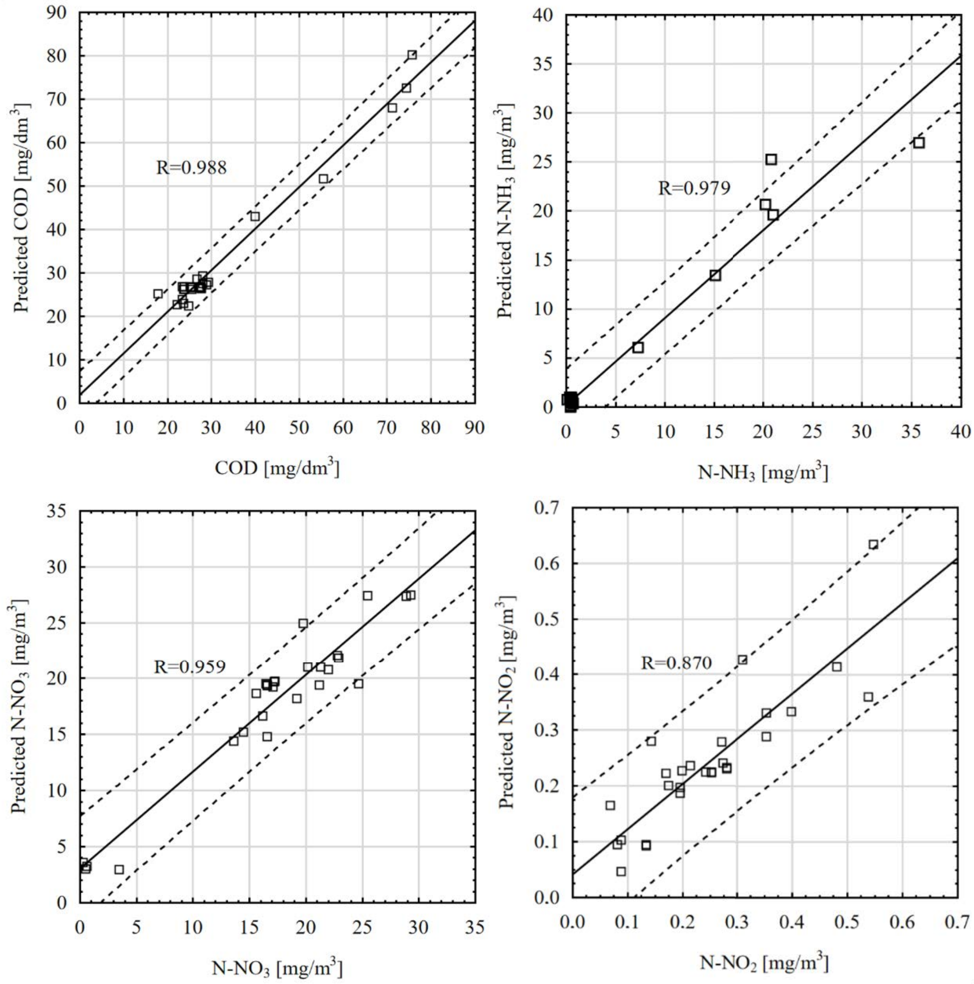

Fig. 4. Dependences between the measured parameters and the parameters predicted by means of an e-nose: COD, N–NO_3, N–NO_2, N–NH_3.

oxygen demand. Similarly high correlation was obtained in the case of turbidity (r = 0.940), total suspended solids (r = 0.938), as well as nitrogen compounds N–NO_2 (r = 0.869), N–NO_3 (r = 0.958), N–NH_3 (r = 0.978). However, because an electronic nose is unable to measure these parameters in a direct way, it should be treated as an additional device for estimating wastewater parameters on-line, and as an early detection system identifying abnormal conditions. This includes diversified concentration of pollutants and the presence of potentially hazardous substances (such as pesticides or petroleum derivatives) which may negatively impact the biological part of wastewater treatment process. Measurements of wastewater quality parameters should be conducted regularly, in order to adjust their prediction algorithm to the current situation [10].

3.2. Utilisation of multiple networks

Nowadays, very efficient computers allow to utilise many artificial neural networks to predict specific parameter and afterwards to count mean values for many networks. In order to determine the application possibility of multiple networks to predict particular wastewater quality parameters (COD, N–NO_3, N–NO_2, N–NH_3) as well as best parameters of artificial neural networks (number of hidden neurons, activation functions of hidden neurons, and output), 10,000 networks with one hidden layer consisting of 1 to 100 hidden neurons were tested. To activate the hidden and output neurons, the linear (lin), logistic sigmoid (log), hyperbolic tangent (tanh), and the exponential (exp) functions were used. Summary table of basic statistics for particular chemical indicators as well as COD was shown in Table 1. The lowest mean value of prediction accuracy was observed for N–NO_2 in range 0.49–0.62, especially for linear function of hidden layer (Fig. 5). The COD has highest average score in all variants of activation function.

Fig. 6 shows a example chart for the N–NO_2 prediction accuracy (quality) for each combination of activation f., and different numbers of hidden neurons. To assess the quality of N–NO_2 prediction a validation data subset was taken, which was not used to learn the neural network. It can be discerned that networks with neurons in the range 1–10 have significantly lower values of validation quality. Networks with neurons in the range 10–20 are almost identical to the

Table 1
General statistic of networks validation quality for all activation functions variants

Parameter	Activation of hidden layer	Activation of output layer	% Valid obs.	Mean	Median	Maximum	Lower quartile	Upper quartile	Std. Dev.	Standard error
$N–NH_3$	Tanh	Lin	100	0.968164	0.968639	0.993562	0.962710	0.975611	0.010547	0.000408
	Lin	Tanh	100	0.859990	0.849643	0.911647	0.844732	0.872917	0.021138	0.000850
	Log	Lin	100	0.959442	0.962646	0.988348	0.953022	0.967843	0.013849	0.000548
	Log	Tanh	100	0.944898	0.951583	0.989902	0.937876	0.965420	0.041330	0.001641
	Log	Log	100	0.917179	0.903178	0.995402	0.890342	0.962313	0.042122	0.001697
	Log	Exp	100	0.959470	0.963063	0.994591	0.951850	0.973141	0.027542	0.001139
	Lin	Log	100	0.965936	0.967887	0.971889	0.967428	0.968465	0.005953	0.000245
	Exp	Exp	100	0.943528	0.954353	0.993635	0.941096	0.969684	0.062297	0.002436
	Tanh	Tanh	100	0.965424	0.969483	0.989726	0.960921	0.975488	0.018510	0.000742
	Lin	Exp	100	0.955380	0.957361	0.971276	0.952075	0.959448	0.007108	0.000283
	Exp	Tanh	100	0.914400	0.937818	0.986253	0.920198	0.953215	0.086270	0.003355
	Exp	Lin	100	0.933659	0.935748	0.980084	0.922453	0.951341	0.032925	0.001308
	Exp	Log	100	0.959762	0.965063	0.993893	0.949224	0.976396	0.026470	0.001037
	Lin	Lin	100	0.864429	0.857632	0.920239	0.852599	0.873261	0.017164	0.000693
	Tanh	Exp	100	0.962170	0.973313	0.996663	0.956585	0.981285	0.049552	0.002021
	Tanh	Log	100	0.952593	0.963076	0.993686	0.942718	0.973017	0.031223	0.001296
$N–NO_2$	Log	Tanh	100	0.845738	0.861941	0.901958	0.842573	0.875602	0.063343	0.002592
	Tanh	Tanh	100	0.840501	0.857782	0.919030	0.833922	0.871755	0.062907	0.002481
	Exp	Lin	100	0.846473	0.865485	0.907545	0.836045	0.881111	0.066420	0.002691
	Log	Lin	100	0.833222	0.855306	0.903002	0.824561	0.870410	0.078700	0.003224
	Lin	Lin	100	0.606379	0.618174	0.657439	0.595758	0.629073	0.034294	0.001376
	Tanh	Lin	100	0.842561	0.857573	0.920244	0.830565	0.873980	0.055344	0.002228
	Tanh	Log	100	0.849668	0.858862	0.914105	0.846971	0.868525	0.048394	0.001897
	Log	Exp	100	0.853202	0.867285	0.920008	0.860332	0.872769	0.060655	0.002497
	Tanh	Exp	100	0.853971	0.864836	0.898053	0.859311	0.870319	0.059091	0.002362
	Lin	Exp	100	0.496225	0.485989	0.630407	0.480780	0.494524	0.035562	0.001457
	Log	Log	100	0.850094	0.868881	0.903312	0.854264	0.876403	0.067084	0.002567
	Lin	Log	100	0.564289	0.562415	0.669617	0.511641	0.613662	0.054786	0.002226
	Exp	Exp	100	0.865738	0.872535	0.894689	0.862119	0.878959	0.049784	0.001932
	Exp	Log	100	0.856350	0.863890	0.900486	0.855122	0.871105	0.043989	0.001770
	Lin	Tanh	100	0.623211	0.624035	0.654573	0.618969	0.629969	0.012624	0.000495
	Exp	Tanh	100	0.804333	0.840407	0.899716	0.792704	0.862945	0.099844	0.003968
$N–NO_3$	Exp	Lin	100	0.949616	0.951520	0.964377	0.947512	0.954592	0.010015	0.000386
	Log	Log	100	0.940394	0.954280	0.976767	0.946453	0.958921	0.079053	0.003127
	Lin	Exp	100	0.859854	0.866398	0.884768	0.852268	0.871208	0.015659	0.000635
	Tanh	Log	100	0.955305	0.959284	0.977106	0.954721	0.964144	0.020002	0.000815
	Lin	Tanh	100	0.897713	0.897022	0.913969	0.891755	0.903564	0.006814	0.000267
	Tanh	Tanh	100	0.951512	0.953698	0.971760	0.950504	0.956383	0.013957	0.000570
	Lin	Lin	100	0.896497	0.898059	0.916496	0.886941	0.907017	0.012273	0.000475
	Log	Lin	100	0.950826	0.954010	0.975566	0.950724	0.956472	0.018360	0.000758
	Log	Exp	100	0.944699	0.958444	0.978821	0.954116	0.962618	0.093117	0.003773
	Tanh	Lin	100	0.955256	0.956643	0.975583	0.954162	0.958961	0.012905	0.000519
	Tanh	Exp	100	0.963127	0.966726	0.981460	0.960259	0.972559	0.043674	0.001729
	Log	Tanh	100	0.944643	0.948050	0.965640	0.943978	0.951441	0.015980	0.000638
	Lin	Log	100	0.910076	0.910962	0.920522	0.906219	0.914765	0.005651	0.000225
	Exp	Exp	100	0.938494	0.957520	0.986628	0.953717	0.961124	0.142364	0.005645
	Exp	Tanh	100	0.944838	0.947034	0.973568	0.941496	0.951605	0.012004	0.000479
	Exp	Log	100	0.927764	0.957192	0.976439	0.949941	0.960348	0.074788	0.003079

(Continued)

Parameter	Activation of hidden layer	Activation of output layer	% Valid obs.	Mean	Median	Maximum	Lower quartile	Upper quartile	Std. Dev.	Standard error
COD	Lin	Tanh	100	0.927846	0.927754	0.933884	0.927754	0.927772	0.000348	0.000014
	Lin	Exp	100	0.975182	0.975177	0.975296	0.975177	0.975186	0.000024	0.000001
	Exp	Tanh	100	0.983038	0.983448	0.988685	0.981977	0.984758	0.004743	0.000191
	Log	Lin	100	0.985049	0.985303	0.988195	0.984429	0.986029	0.001527	0.000062
	Exp	Log	100	0.984411	0.985117	0.988854	0.984076	0.985955	0.003785	0.000150
	Tanh	Exp	100	0.982738	0.983205	0.986650	0.981545	0.984099	0.001943	0.000079
	Lin	Lin	100	0.957869	0.957756	0.960374	0.957751	0.957819	0.000301	0.000012
	Lin	Log	100	0.964542	0.964658	0.965263	0.964617	0.964712	0.000505	0.000020
	Tanh	Tanh	100	0.983032	0.984997	0.989220	0.983784	0.986061	0.038714	0.001515
	Exp	Exp	100	0.983097	0.983469	0.988042	0.981765	0.984814	0.002557	0.000103
	Log	Exp	100	0.981614	0.981761	0.986774	0.980599	0.982863	0.002490	0.000101
	Tanh	Lin	100	0.985583	0.985916	0.989019	0.985011	0.986593	0.001824	0.000071
	Log	Log	100	0.972542	0.983480	0.987625	0.982186	0.984603	0.095978	0.003791
	Exp	Lin	100	0.985474	0.985822	0.988999	0.984870	0.986541	0.002185	0.000088
	Tanh	Log	100	0.980758	0.983450	0.987317	0.981665	0.984570	0.047969	0.001994
	Log	Tanh	100	0.973881	0.983131	0.988696	0.980113	0.985047	0.083163	0.003280

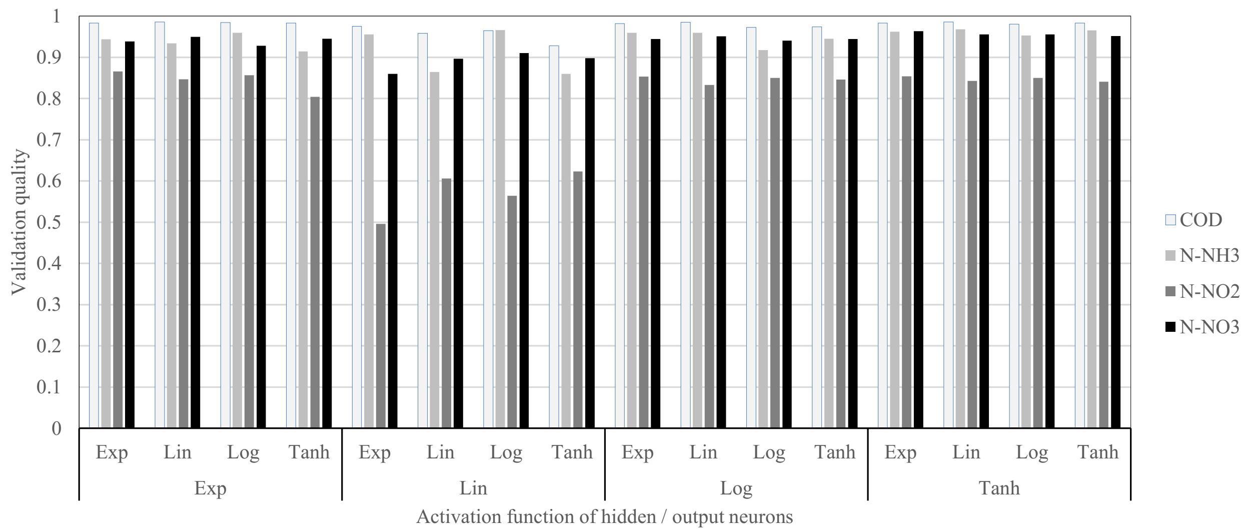

Fig. 5. Averages values of network validation quality for together for COD, N–NO_3, N–NO_2, N–NH_3.

networks with a higher number of hidden neurons. These results indicate that application of a large number of hidden neurons is not reasonable. Therefore for further inquiries one hidden layer with 20 neurons was adopted.

Amount of learning epochs is also important issue, due to due to influence on validation quality (Fig. 7). Network learning was terminated when output error for the testing subset was greater than the error for the learning subset. For most of the applied networks it was enough to use less than 200 learning epochs.

A electronic nose system based on artificial neural networks can be continuously adjusted (ANN learning), which can increases the estimation accuracy of selected parameters. It is possible through cyclical enlargement of measurement data sets [10]. Such system of fast estimation of wastewater parameters should be calibrated individually at each implementation. Estimation of wastewater parameters required approximately 5–15 min.

3.3. Mathematical modelling and computer simulation

Nowadays, comparing optimization performance systems wastewater treatment plant, in major cases focus to improvement operation of the facility in order to improve the quality of life and reduce energy consumption. Definitely so significant computer development technique and modelling, last enlargement in Poland is simple and easily accessible calculation methods (including spreadsheets, databases data, simple computational programs and it depends) on the spot standards as well as designers and WWTP explorers questioning. The effluents from WWTPs are discharged to water bodies or rivers, therefore

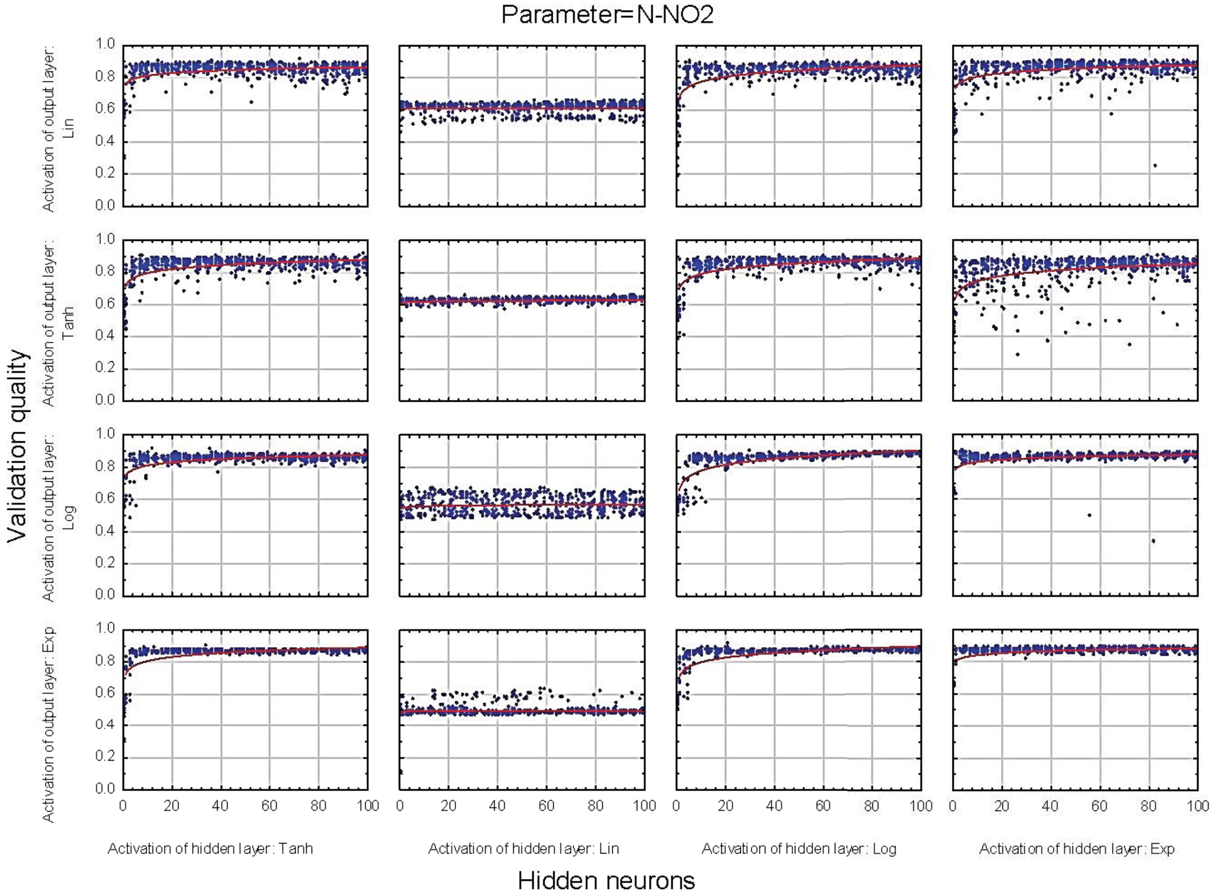

Fig. 6. Quality value of network validation considering number of neurons in hidden layer $n \in$ <1–100> and different transfer function of hidden and output layer for $N–NO_2$ prediction.

can be detrimental for environment toward Green Deal implementation in operation and control of the WWTPs. EGD is a set of policy initiatives by the European Commission with the overarching aim of making the European Union (EU) climate neutral in 2050.

To normalize issues pertaining to wastewater discharging many directives and regulations have been released, which determine permissible levels of pollutants in effluent stream. In order to comply with these regulations and not exceed level of particular indicators of wastewater quality, the operational mode of facilities at WWTP should be properly adjusted according to wastewater parameters of influents. These is very difficult without frequently performed measurements. Currently there are known many techniques and devices for assessment of wastewater parameters such as COD, BOD, TOC, TSS, OUR, level of phosphorus and nitrogen compounds. In spite of the far reaching improvements in automatisation of treatment process, there still isn't developed a automatic measuring system of basic wastewater parameters.

The computer simulation used for comparison with the data obtained by means of an electronic nose provides the description of the actual conditions found in a wastewater treatment plant, enabling to carry out dynamic processes in an efficient way. Real-time control of biological treatment processes conducted on-line with an electronic nose and mathematical modelling/computer simulations that utilize a supervisory system and another treatment device (including dissolved oxygen control and its profile in bioreactor and effluent ammonium) could enable considerable energy savings at a wastewater treatment plant, without exerting a negative impact on the quality of the treated wastewater.

Due to the development of artificial intelligence and machine learning, the computer vision technology is constantly improving and achieving better and better results, often capable of even surpassing human abilities. One of the many applications in artificial intelligence is an automatic image analysis, which is currently a strongly developed branch of information technology that has a number of applications. One of the possible fields of application for automatic image analysis is the recognition and classification of objects observed using microscopic techniques. Such objects can be an activated sludge organisms, mainly protozoa, metazoan as well as bacteria. The rapid on-line method of wastewater parameters estimation by electronic nose supported by microscopic images carried out in this way can provide the information used in analyses of the work of bioreactors with activated sludge, biofilm or hybrid systems. The aforementioned automatic analyses can be used in the future control of the stability of the purification

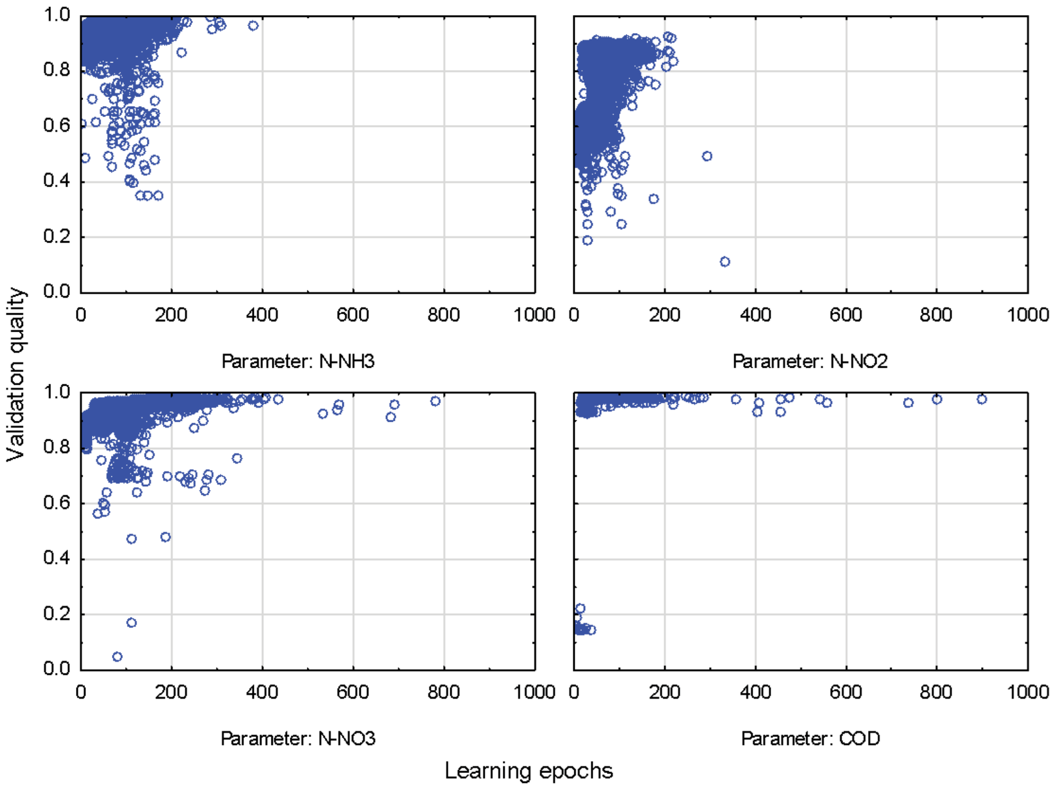

Fig. 7. Dependences between the measured parameters and the parameters predicted by means of an e-nose: COD, $N–NO_3$, $N–NO_2$, $N–NH_3$.

processes carried out, the evaluation of the quality of the treated wastewater, and in the detection of early symptoms of treating process failure. Such analyses can also be used to assess the level and scope of the impact of treated wastewater discharge on the receiving waters.

Required time for determine some parameters according to proper methodology vary from 1–2 h COD for even 5 d BOD_5. For the other parameters obtained by means immersed sensors, there could be problems with lack of repeatability due coating of sensors with biological film. Considerable limitation could be also a cost of professional measuring equipment. Therefore, in many local WWTP the measurement are performed very seldom and treatment process is based mainly on observations of experienced personnel. Rapid on-line method of wastewater parameters estimation by electronic nose and computer simulations could be recommended as an alternative solution in many WWTPs in comparation with traditional approach. However, the algorithms used need adequate and rapid knowledge of WWTP operation parameters to correctly recognize WWTP recommendation as is proposed in Fig. 8.

Proposed concept of real-time control system besides arguments driven from experiments conducted by authors, looks promising also because also other scientist suggest application electronic nose in analysis and control of WWTP. Various publications report that the odor nuisance of treatment devices can be determined based on e-nose readouts [20,23,24,34–37]. The e-nose usage for odor intensity detection in a WWTP as well as the odor analysis in six object locations was described by Blanco-Rodríguez et al. [38]. The prospective use of a gas sensor array for monitoring the wastewater treatment results in SBRs operating under laboratory conditions has been discussed as well [10,35]. Research indicated that the e-nose can be employed for classifying wastewater as well as odors to their respective location in a WWTP [3,27,36] reported that gas fingerprints can be processed with PCA enabling to interpret and differentiate wastewater samples in relation to origin and quality, relative to their reference (i.e., deionized water). In other WWTPs it was shown that the samples taken from the inlet works, settling tank, and final effluent proved that a nonspecific sensor array allows distinguishing between various types of sewage samples and originating from different treatment works [26,36,39].

The in-situ studies performed in full-scale in WWTPs using an e-nose have already been conducted by the team Łagód et al. [36] and the obtained results are already promising, proving the validity and applicability of the employed methods. The obtained research results confirm that the gas sensor arrays in various configurations can be used for analyzing different mixtures of gases from wastewater headspace. Rapid, relatively cheap, and repeatable operation (provided that the sensors are appropriately flushed before use) are the advantages of the above-mentioned devices. This method can be employed for so-called screening tests (i.e., showing any deviations from the norm). The on-line measurements allow also conducting a constant monitoring of the wastewater table headspace, and hence acquiring

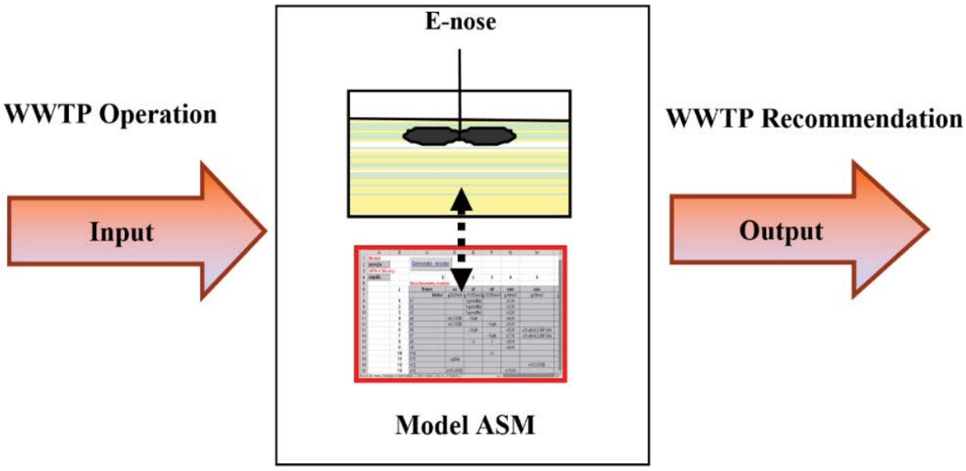

Fig. 8. Concept of real-time control of biological treatment processes conducted on-line with an electronic nose and mathematical modelling/computer simulations.

the information on the conducted processes. Moreover, the operation of multisensor arrays as well as the results obtained from the performed studies can serve as a basis for developing models of wastewater treatment processes and early warning systems. Łagód et al., [36] reported that the intensity of signals from sensors changed along with drops in the level of wastewater pollution; therefore, it was possible to classify the samples regarding their similarity and the analyzed gas-fingerprint corresponded to the pollution level expressed by physical and biochemical indicators. These findings are coherent with other research described in literature of subject which reveal that the treatment stage are also related to the intensity of odor emission [13,33,40,41]. Moreover previous work [36] reported that on the basis of the PCA and the distribution analysed points on the graph, it was possible to notice certain tendencies and correlations between the pollution indicators; what has already been mentioned in the literature [3,10,24,42–45]. In addition, the previous research of authors carried out in a laboratory bioreactor [35], showed a shift in the characteristics of the studied samples towards the values on the x-axis of PCA plot, as the wastewater pollution level increased. Furthermore, the accuracy for training and testing data obtained by decision tree in case of samples taken in full-scale WWTP was very good (reaching 98% and 97%, respectively). There were only two observations of outflow from the bioreactor which were erroneously classified in the secondary settling tank in the test sample; however, this is understandable since both stages are adjacent to each other in the wastewater treatment process. Therefore, a relatively simple predictive model characterized by sufficient accuracy was obtained [36], which suggest that method can be developed and applied in future for standard procedure of processes control in WWTP devices.

4. Conclusion

Improving the efficiency of the wastewater treatment process could be done through real-time measurement of wastewater parameters performed in a continuous manner. Thus far, no commercial devices for on-line measurement and control of standard wastewater parameters were available. The authors' previous studies showed that an electronic nose can be successfully employed for estimation of wastewater parameters in bioreactors with activated sludge [10,36].

Accuracy of ANNs with 10÷20 hidden neurons are almost identical to the networks with a higher number of hidden neurons. Correlation between estimated parameters and measured parameters with standard techniques are very high: chemical oxygen demand COD r = 0.988, turbidity r = 0.940, total suspended solids r = 0.938, as well as nitrogen compounds r = 0.870 for N–NO_2 in range to 0.55 mg/m^3, r = 0.959 N–NO_3 in range to 29 mg/m^3 and r = 0.979 for N–NH_3 in range to 36 mg/m^3. Estimation results characterise quite wide 95% confidence band, reaching approximately 10 mg/dm^3 for COD, 7.5 mg/m^3 for N–NH_3, 9 mg/m^3 for N–NO_3 and 0.3 mg/m^3 for N–NO_2.

The obtained values of wastewater parameters could serve as an early warning system quickly indicating non-standard wastewater parameters. Additionally such system provides continuous relevant information which can be used for data supply for dynamic modelling of processes at a WWTP. Additionally, software based on biokinetic activated sludge model enabled to perform simulations modelling different conditions and dynamic behaviour of input/output variables, as well as local conditions in a selected part of a treatment plant.

Abbreviations

ADC	—	Analog-to-digital converter
ANN	—	Artificial neural networks
ASM	—	Activated sludge model
BOD	—	Biochemical oxygen demand
COD	—	Chemical oxygen demand
CP	—	Conducting polymers
MLSS	—	Mixed liquor suspended solids
MOS	—	Metal oxide semiconductor
OUR	—	Oxygen uptake rate

PCA	—	Principal component analysis
QCM	—	Quartz crystal microbalance
SAW	—	Surface acoustic wave
SBR	—	Sequencing batch reactor
SVI	—	Sludge volume index
SVM	—	Support vectors machines
TOC	—	Total organic carbon
TSS	—	Total suspended solids
VSS	—	Volatile suspended solids
WWTP	—	Wastewater treatment plant

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