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FORECASTING METHODS FOR ASSESSMENT OF THE BIODEGRADABILITY OF WASTEWATER FROM ORGANIC SEPARATORS

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The objective of this study is to evaluate the performance of the organic matter separation process based on the BOD_5/COD ratio by monitoring of biodegradability parameters using forecasting methods. The main pollutants in wastewater are organic compounds (defined as BOD_5 and COD) that occur in abundance, nutrients and suspended solids. Biodegradability can be estimated based on the ratio between BOD_5 and COD. Low rates may indicate a reduced susceptibility of wastewater to biodegradation. The descriptive statistics used to identify the characteristics of the measured parameters BOD_5 and COD and BOD_5/COD ratio for samples of three station with separators of organic matter, IS, SV1, SV2 GPS located in the northeastern part of Romania. Time series analysis showed that the performance of the separation process is not affected by seasonal factors. The trend of the time series with the seasonality index follows a linear model of a stationary process. The single exponential smoothing was used for the forecasting model of the variation of the degree of biodegradability of wastewater discharged following the process of compared to the limit value of 0.4 of the BOD_5/COD ratio.

Keywords: biodegradability, BOD_5/COD ratio, separators, forecast, time series analysis

1. Introduction

An organic matter/oil separator is a pressure vessel used to separate a stream of water into gaseous and liquid components. To meet the requirements of the process, oil separators are normally designed in stages, in which the first stage separator is used to separate the preliminary phase, while the separators for the second and third stage are applied for the additional treatment of each phase. individual (oil and water) [1].

The separators are usually dimensioned according to the settling theory or the retention time for the liquid phase [2].

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The liquid capacity of most separators is dimensioned to provide sufficient retention time to allow the formation and separation of gas bubbles. More retention time is required for separators that are designed to separate oil from water as well as liquid gas mixtures.

Several types and sources of water flows are used in the separation operations: wastewater from oil tanks mixed with rainwater, fresh sources (river or lake), and storm water [3]. Contaminated flows generally generate from two primary sources – intermittent flows from normal hose down or industrial process operations and meteoric water runoff. Meteoric waters runoff flows usually greatly exceed all other flows.

Water sources are treated for disposal. The water produced must be cleaned of oils and solids dispersed and dissolved at a level appropriate to the following purposes: environmental, discharge into tanks or directly in the treatment wastewater plants.

Separation performance may be affected by factors such as flow rates, fluid properties, configuration, internal structures, control system, etc. [4]. The separator is correctly dimensioned and functional if the removal of organic substances is carried out within the estimated retention time. This requires a careful study of the biodegradability of organic substances, to correlate the rate of biological degradation with the hydrodynamic flow regime and the mixing of the polyphasic medium, which leads to the loss of harmfulness of organic matter to the extent established conventionally. In this way, it will be possible for the organic substance to be degraded to the extent accepted within a correctly estimated useful time period but not for a too long period of time. The residence time of wastewater from the separator is proportional to the aspect ratio, which leads to increased contact time and increased coalescence between fat globules, resulting in increased efficiency of biodegraded organic matter separation as the aspect ratio increases.

Biodegradability is a very complex notion, because it tries to correlate the organic substance with the activity of biomass and the values of the environmental parameters in which the microorganisms grow. The quantitative relationship between the chemical structure and the biochemical activity of the cellular material, important in the assessment of biodegradability, is not yet fully defined. For this reason, the quantitative expression of biodegradability is done indirectly. The environmental conditions in which the process takes place are of particular importance in the assessment of biodegradability, because a slightly biodegradable substance will not be effectively degraded unless the values of physical-chemical parameters allow the activity. The biodegradability index, B.I. (BOD_5/COD ratio), is a parameter for evaluate the biodegradation capacity of wastewater. A ratio of less than 0.2 indicates an effluent that is not biodegradable. A range of 0.2 ÷ 0.4 indicates slow biodegradability. When the ratio is 0.4 ÷ 0.5, the wastewater presents a medium biodegradability, greater than 0.5 are easily biodegradable [5].

If an organic substance is difficult to biodegrade, it degrades at a slow rate and cannot be removed from the water to be discharged into the emissary, where the process will continue over time, with a consumption of oxygen reserves in the water mass [6]. Separators are used to separate vapor-liquid-solid mixtures. Their performance is determined by the characteristics of the separate fluid, the size of the vessel and the type of internal systems installed (filters), the important parameters in the sizing and selection of the filter separator. The influent wastewater of separator may contain a large amount of non-biodegradable organic matter. Organic matter in wastewater can be estimated as an equivalent amount of chemical oxygen demand (COD) or biological oxygen demand (BOD). Increasing the low BOD_5/COD ratio can be achieved by adding organic chemicals that have a high BOD_5/COD ratio, such as glucose, methanol and acetic acid.

The efficiency of the organic matter used for wastewater treatment was studied and is here presented.

2. Materials and Methods

2.1. The samples location

The samples were collected from the northeastern area of Romania, from three stations with pre-treatment systems with separator of rainwater and wastewater from car washes. Monthly samples were taken between January 2016 and June 2020. The coordinates of the sample locations are indicated in Table 1.

Table 1

Sample coordinates

Cod station	GPS reading
IS	Longitude N23°39’20.74”, Latitude E121°24’32.90”
SV1	Longitude N47°38’21.84”, Latitude E26°15’13.18”
SV2	Longitude N47°31’44.18”, Latitude E25°33’39.96”

The effluent samples were collected at the liquid and hydrocarbons separator discharge pipe in plastic bottles and stored at approximately 4^oC to minimize biodegradation while being transported to the laboratory.

2.2. Data analysis

BOD_5 was determined by measuring the dissolved oxygen concentrations in the sample under analysis at the beginning and end of the incubation period. Incubation of water samples as such, oxygen-saturated or samples diluted in convenient proportions with oxygen-saturated dilution water and seeded, was performed at a temperature of 20°C and in the dark for a period of 5 days ± 6 hours. The BOD_5 indicates the amount of dissolved oxygen consumed by bacteria and other microorganisms under specified conditions by the biochemical oxidation of organic matter in water during the incubation period of 5 days. The

BOD_5 indicates how much dissolved oxygen (mg/L) is needed in a given time for the biological degradation of the organic wastewater constituents [7, 8]. COD was analyzed using the volumetric method with potassium dichromate and represents the amount of oxygen needed to completely transform organic matter into final products. The mass concentration of oxygen equivalent to the amount of potassium dichromate consumed for oxidation in acidic medium of dissolved and suspended organic matter in wastewater was measured using a reflux system and volumetric titration.

The value of B.I. is a measure of the biodegradability of organic matter and will vary depending on the characteristics of the wastewater. According to national legislative regulations, Government Decision 352/2005 – Regulation NTPA-002/2002 [9], the BOD_5/COD ratio equal or greater than 0.4 is established as loading limit with pollutants from industrial and urban wastewater for discharge into the sewerage system of the localities and/or directly in the wastewater treatment plants (WWTPs).

2.3. Descriptive analysis

The descriptive data analysis process describes what happened in a set of quantitative data collected, cleaned, processed to ensure that all information is formatted correctly and that there are no extreme values that should be removed and significant conclusions will be drawn by manually reviewing the data set or by using statistical methods. The Z score indicates whether a data value is higher or lower than mean and how far it is from mean.

$$Z\ score = (x - mean) / standard\ deviation \qquad (1)$$

where x is real value.

Mean and median are indicators of the central trend that locate the distribution of data at certain points. Mean is the indicator that shows the central trend of the series of values and usually shows where the data tends to be grouped. Median is an indicator of the central trend, the mean values of the data set and is not affected by the influence of extreme values. The standard error is used to refer to the standard deviation of various sample statistics, such as the mean or median. The standard deviation is expressed with the same unit of measurement as the values of the analyzed data and is an indicator of their spread. The coefficient of variation is the ratio between the standard deviation and the mean, when the mean is non-zero and is expressed as a percentage. The range indicates the presence of high or low values. Standard deviation indicates the spread of measured data from the mean. Kurtosis is the standard measure of a distribution of the values of a data set, derived from Karl Pearson, the high values indicating the presence of aberrant values.

Skewness is a measure of the asymmetry of the distribution of a random variable with real value in a data set. Pearson median skewness, subtracts the median from the mean, multiplies the difference by three, and divides the product by the standard deviation [10].

The coefficient of variation (CV) is a standardized measure of the dispersion of a probability distribution used to express the accuracy and repeatability of the values of a data set. In the predictive analytics process, data analytics techniques are used to make predictions about what will happen in the future taking into account the results of the descriptive analysis. Excel and Number Cruncher Statistical System (NCSS) were used for statistical calculations [7,11].

2.3.1. Time series analysis and forecast

A time series is defined as a certain amount that is measured sequentially over time over a given interval and aims to deduce what happened to a series of data points in the past and try to predict what will happen to the future.

A time series is a collection of observations of well-defined data items obtained through repeated measurements over time. Time series descriptions separate time components in terms of trends (long-term direction) and seasonal variation (systematic, calendar-related movements) and irregular cycles (unsystematic, short-term fluctuations) [12 -14]. Time series analysis can identify the nature of the phenomenon represented by the sequence of observations and the prediction of future values of the time series variable. This requires the identification of a data model from the time series observed and described more or less formally.

2.3.2. Stationarity process

Stationarity means that the statistical properties of a process that generates a series of time do not change over time, only the way they change does not change over time. A stationary time series is one whose properties do not depend on the time at which the series is observed. Time series with trends or seasonality are not stationary - trend and seasonality will affect time series at different times. Time series can be stationary or non-stationary. Stationary series are characterized by the statistical equilibrium around a constant mean value, as well as a constant dispersion around that mean value. There are several types of stationary. A series is stationary in the broad sense, weak sense or second order if it has a fixed mean and a constant variance. A series is strictly stationary if it has, in addition to a fixed mean value and a constant variance. Time series can be presented in graphs or plots. Statistical Package for the Social Sciences (SPSS), NCSS or other applications can be used to produce a time sequence graph [15].

2.3.3. Trend stationarity and index seasonality

A stochastic process is trend stationary if an underlying trend be removed, leaving a stationary process. Meaning, the process can be expressed as:

$$y_i = f(i) + \varepsilon_i, \tag{1}$$

where f(i) is any function $f : \mathbb{R} \rightarrow \mathbb{R}$ and ε_i is a stationary stochastic process with a mean of zero [16]. Seasonal indices are a measure of the degree of seasonality, used to smooth the data to allow forecasting trends. Updating the seasonal index uses exponential smoothing. A difficulty in updating a seasonal index with exponential smoothing is that an additional parameter must be estimated [17]. Forecast software packages can automatically perform a parameter search that ensures the best match of the data.

2.3.4. Forecast analysis

Forecasting is a technique to establish relationships and trends, which can be projected into the future, based on historical data and certain assumptions [18]. The purpose of building a time series model is to predict the series at one or more steps in the future and a statement about the accuracy of the forecasts. Of course, the forecast error increases as the forecast expands from a step forward to larger steps in the future. When making predictions we assume that the model is known exactly and that the parameter values do not change. A predictive model of time series can have as processing mode, automatic regression (AR), exponential weighted moving average (EWMA), exponential smoothing, forecast, forecast error, moving average (MA), random walk or variation. Selecting the right forecasting method depends on many factors such as large data sets, forecast accuracy and computational cost [19].

2.3.5. Single Exponential Smoothing Model

Exponential Smoothing is a technique for smoothing time series data using the exponential function. The raw data sequence is often represented by X_t la t=0, and the output of the exponential smoothing algorithm is commonly written as S_t, which may be regarded as a best estimate of what the next value of X will be. When the sequence of observations begins at time t=0, the exponential smoothing algorithm is given by the formulas 2 and 3:

$$S_0 = X_0 \tag{2}$$

$$S_t = \alpha X_t + (1 - \alpha) S_{t-1},\ t > 0 \tag{3}$$

were α is the smoothing factor, the value being in the range: $0 < \alpha < 1$.

Single exponential smoothing is a time series analysis technique that uses a history of values with associated weights that predict future value. When there are no seasonal trends and variations, the data model is approximately horizontal, which means that the data fluctuates around a constant media. Value weights are allocated exponentially as more data is added. An exponential smoothing of the time series is obtained by exponentially attributing the value of the weight associated with the previous values between 0 and 1, called the exponential smoothing constant (alpha), predicting the next value. It is calculated as follows:

$$F_t = \alpha Y_t + (1 - \alpha) F_{t-1} \text{ (for } t \geq 2) \tag{4}$$

where:
F_t is exponentially smoothed forecasted value; Y_t is observed value of the time series at time t; F_{t-1} is exponentially smoothed forecasted value at time t-1; α is the smoothing constant [20].

$$F_1 = Y_1 \; ; F_2 = \alpha Y_2 + (1-\alpha) F_1; F_3 = \alpha Y_3 + (1-\alpha) F_2, \ldots F_t = \alpha Y_t + (1-\alpha) F_{t-1} \quad (5)$$

Mean absolute percentage error (MAPE) was used as a measure of the accuracy of the predictive model and works best if there are no extremes to the data (and no zeros). Typical MAPE values for the interpretation of industrial and business data are: <10 - Highly accurate forecasting; 10÷20 - Good forecasting; 20÷50 - Reasonable forecasting; >50 - Inaccurate forecasting [21].

$$MAPE = \frac{1}{T} \sum_{t=1}^{T} \left| \frac{x_t - f_t}{x_t} \right| \times 100 \quad (6)$$

where:

x_t = observed value of data at time *t*; f_t = forecasted value at time *t*; *T* = total number of observations.

3. Results and Discussions

Descriptive analysis used to identify the characteristics of the measured parameters for each station are presented in Table 2 for BOD_5, COD and Table 3 for the BOD_5/COD ratio. The Z score analysis for the BOD_5/COD ratio showed that there were no outliers.

The reported variability is due exclusively to the uncertainty in the process parameters that characterize the performance of the installation. The mean value of each parameter is relatively small, which indicates a good elimination of organic matter. The distributions of the variables are asymmetric, this resulting from the values of the Kurtosis and Skewness coefficients, characterized by numerous extremely high values, which decrease the degree of biodegradability. The values of the coefficient of variation show a moderate variability of the data set for the BOD_5 and COD concentrations and a reduced variability of the BOD_5/COD ratio data analysis.

For all analyzed samples, the results obtained show that the final wastewater resulting from the separation process has values of BOD_5 in the range 2.07 to 190 mgO_2/L (IS), 2.11÷231 mgO_2/L (SV1) and 1.95÷211 mgO_2/L (SV2). All values are below the limit value imposed by Government Decision 352/2005 – Regulation NTPA 002/2002 (300 mgO_2/L), Fig. 1.

Table 2

Descriptive analysis for BOD and COD parameter for three station – IS, SV1, SV2 (2016 ÷ 2020)

Statistical	**IS**		**SV1**		**SV2**	
	BOD$_5$ (mgO$_2$/L)	COD (mgO$_2$/L)	BOD$_5$ (mgO$_2$/L)	COD (mgO$_2$/L)	BOD$_5$ (mgO$_2$/L)	COD (mgO$_2$/L)
Mean value	33.58	94.67	16.84	41.31	23.22	62.81
Standard Error	6.97	19.84	4.64	9.45	5.25	13.75
Median value	9.43	22.58	6.27	15.39	9.93	26.33
Standard Deviation	51.25	145.82	34.06	69.45	38.60	101
Coefficient of Variation	1.53 ± 0.14	1.54 ± 0.15	2.02 ± 0.33	1.68 ± 0.23	1.66 ± 0.18	1.60 ± 0.17
Minimum value	2.07	4.80	2.11	5.22	1.95	4.83
Maximum value	190	495	231	417	211	528
Range	188	490	229	412	209	523
Kurtosis	2.62	2.25	30.19	16.21	11.69	9.39
Skewness	1.96	1.89	5.06	3.65	3.26	2.96
Sample no.	54	54	54	54	54	54
Confidence level of mean (95%)	13.99	39.80	9.30	18.96	10.53	27.57

Table 3

Descriptive analysis for BOD$_5$/COD ratio for three station – IS, SV1, SV2 (2016 ÷ 2020)

Statistical	**IS**	**SV1**	**SV2**
	BOD$_5$/COD	BOD$_5$/COD	BOD$_5$/COD
Mean value	0.388	0.395	0.385
Standard Error	0.005	0.005	0.005
Median value	0.401	0.403	0.400
Standard Deviation	0.039	0.035	0.037
Coefficient of Variation	1.000 ± 0.009	0.088 ± 0.017	0.095 ± 0.024
Range	0.146	0.233	0.222
Kurtosis	2.35	9.57	13.4
Skewness	-0.628	1.063	-2.783
Minimum	0.298	0.321	0.200
Maximum	0.444	0.554	0.422
Sample no.	54	54	54
Confidence level of mean (95%)	0.011	0.010	0.010

The COD concentration was 4.80 ÷ 495 mgO$_2$/L, 5.22 ÷ 417 mgO$_2$/L and 4.28 ÷ 528 mgO$_2$/L, for IS, SV1 and SV2 station with maximum values exceeded at COD = 528 mgO$_2$/L for SV2 station in June 2018 (maximum allowable concentration of COD is 500 mgO$_2$/L), Fig. 1.

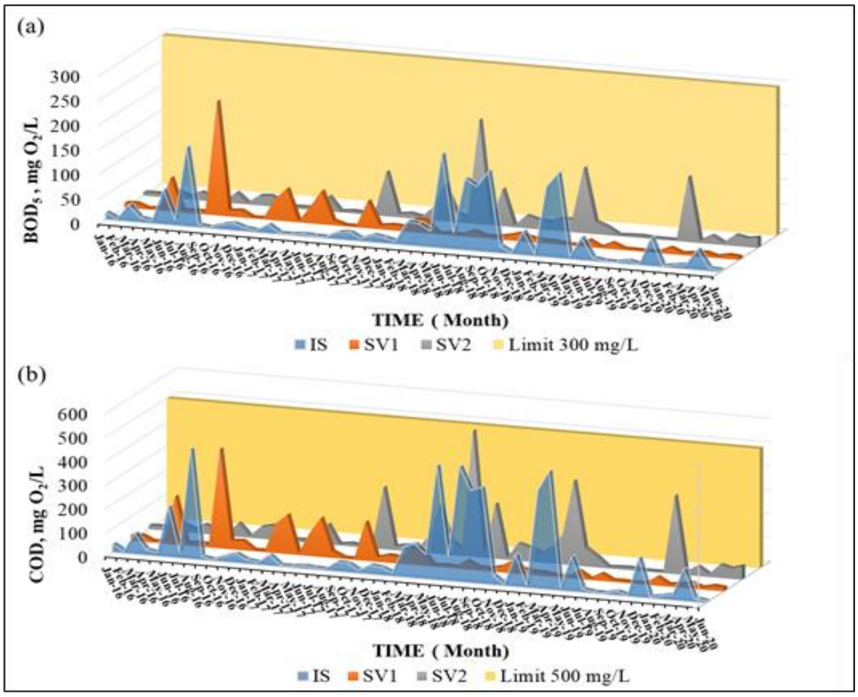

Fig. 1. Variation of concentration BOD_5 (a) and COD (b) for three station – IS, SV1, SV2 (2016 ÷ 2020)

Fig. 2 shows the variation of the mean value of the BOD_5/COD ratio for each month and the monthly mean for the time interval January 2016-June 2020. The degree of biodegradability below the limit of 0.4 shows that the performance of the separation process was affected by certain factors in 2016, 2018 and early 2019 in correlation with the maximum values of the BOD_5 and COD concentration from this period. The evaluation of the variation of the BOD_5/COD ratio shows that in that period the amount of wastewater with a high load of organic matter exceeded the amount of rainwater introduced in the separator without re-evaluating the parameters that influence the separation process (retention time in the separator or liquid flow). The obtained results show that, from the value of the monthly mean of the degree of biodegradability related to the value of minimum 0.4, the performance of the separation process was in the period January 2016 - June 2020 of 25% for IS station, 42% for SV1 station and 33% for SV2 station, effluents requiring biological treatment.

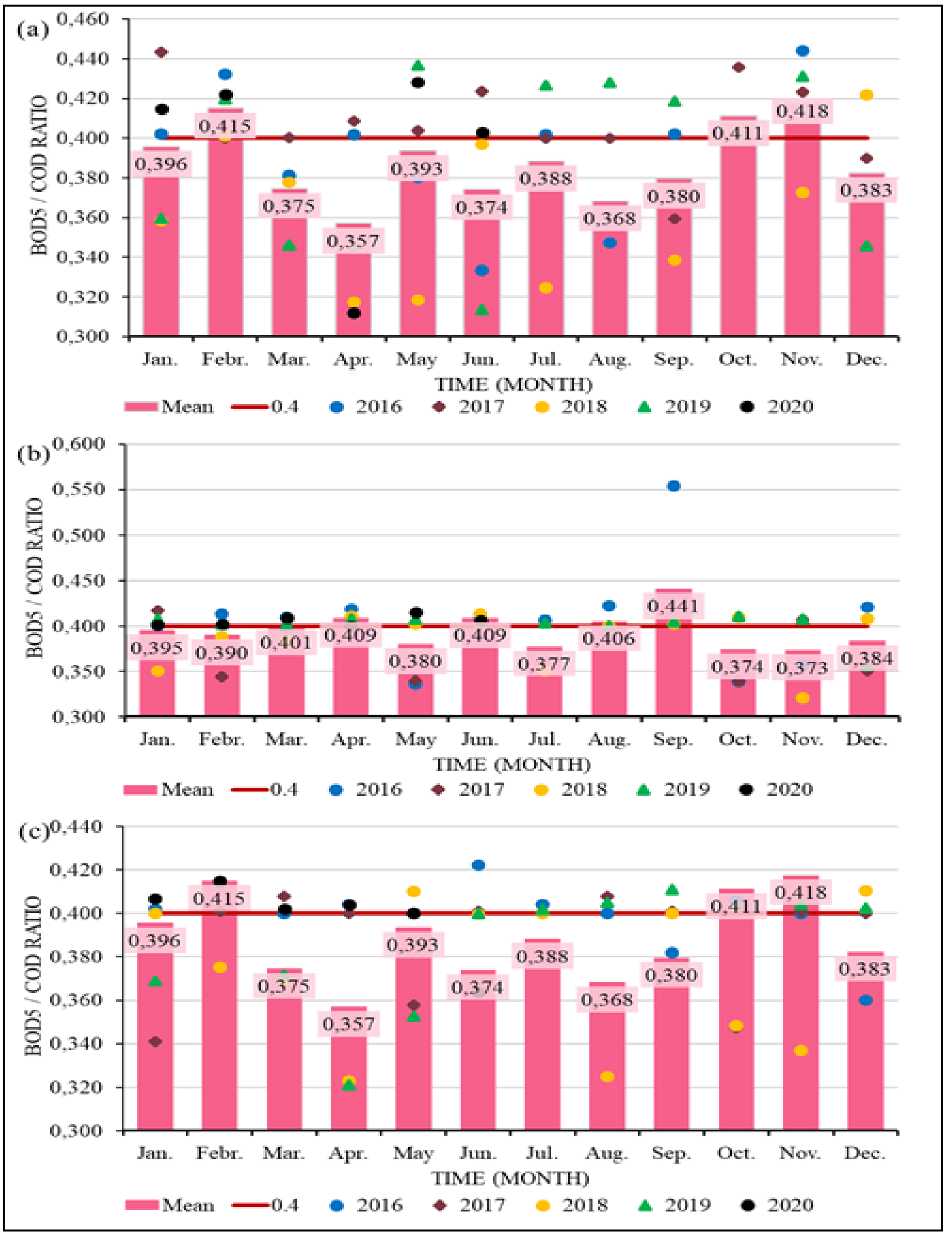

Fig. 2. Variation of the ratio BOD_5/COD monthly for wastewater samples in three station: IS (a), SV1 (b) and SV2 (c), 2016 ÷ 2020

The analysis of the time series of seasonal variation for biodegradability of the analyzed samples (Fig. 3) using the media (n = 6), shows that the performance of the process of separating organic matter from wastewater mixtures (car washes and rainwater) is not affected by seasonal factors. The decreasing variation of biodegradability during Spring 2018 ÷ Winter 2018 for IS station and Spring 2019 ÷ Autumn 2019 for SV2 station were correlated with extreme values of BOD_5 and COD due to the high organic matter loading rate of the influent wastewater.

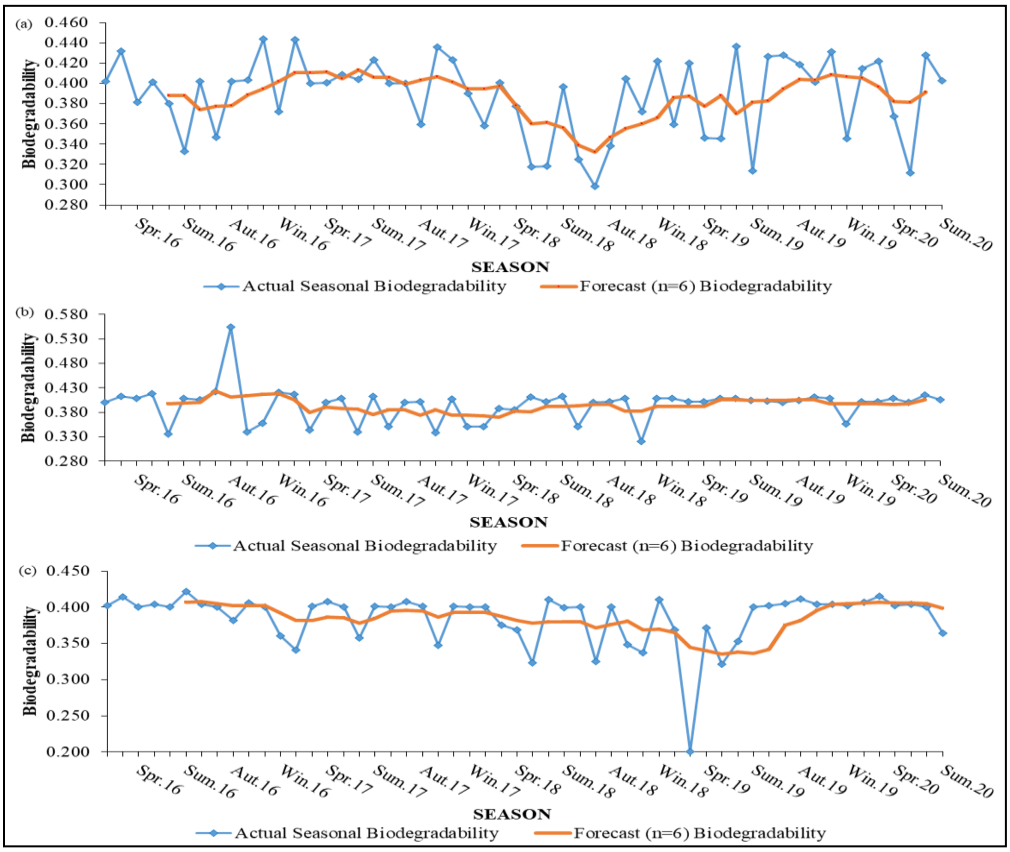

Fig. 3. Time series for seasonal variation of biodegradability of the samples for three station: IS(a), SV1 (b), SV2 (c), January 2016 – June 2020

The analysis of the trend line of the variation of the monthly and annual BOD_5/COD ratio in the period January 2016-June 2020 (Fig. 4) shows that, although the separation process can be processed, it is relatively low and stationary. The regression equations and statistical of the three processes are presented in Table 4.

Table 4

The regression equations and statistical of the three processes in station IS, SV1, SV2

Ratio BOD_5/COD	Intercept	Slope	Std. Err.	P-value	Low. 95%	Upp. 95%
IS	0.3939	0.0002	0.039	7.6E-39	0.372	0.415
SV1	0.3941	3.8E-05	0.035	5.1E-41	0.375	0.414
SV2	0.3935	-0.0003	0.036	3.7E-40	0.373	0.413

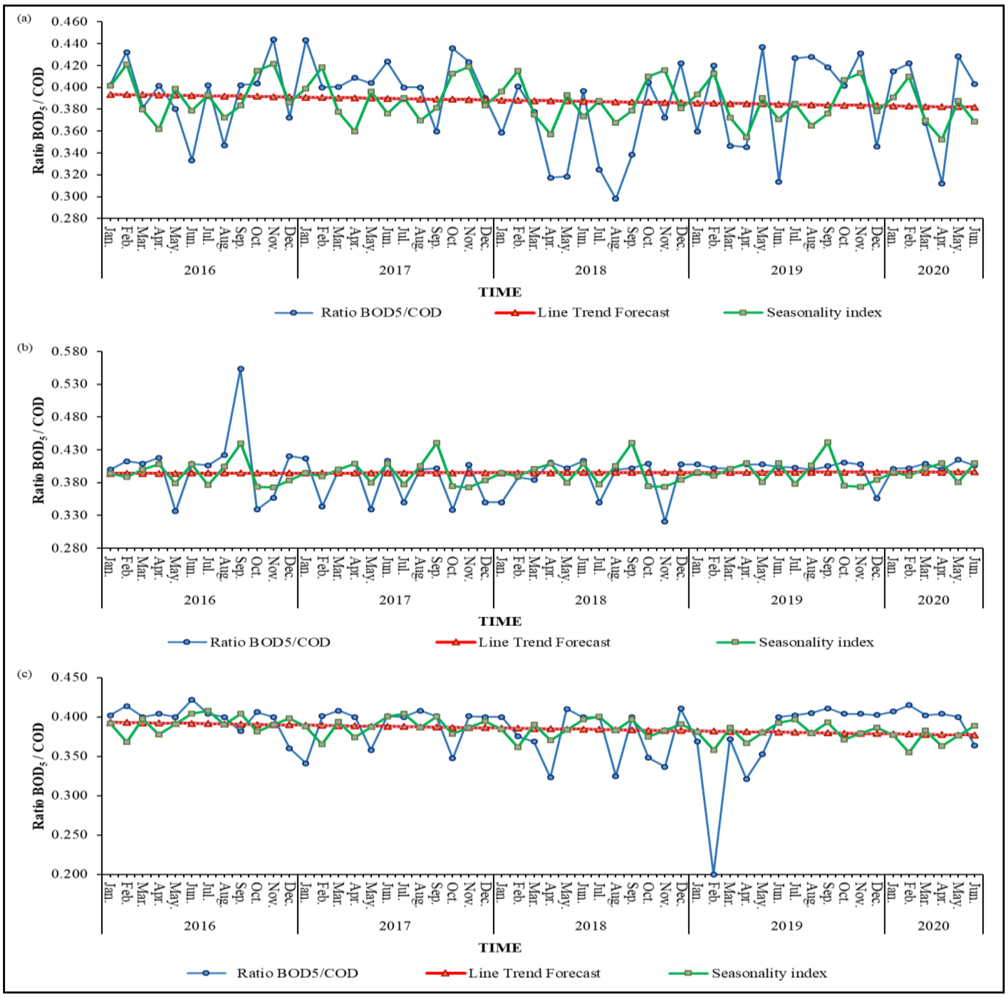

Fig. 4. Linear trend forecast and seasonality index of the BOD$_5$/COD ratio, monthly for IS (a), SV1 (b), SV2 (c), 2016 ÷ 2020

The use of the simple smoothing technique for a predictive model in the data analysis sets is confirmed by the linear regression. Fig. 5 shows the forecast by 2022 of the performance of the organic matter separation process in the effluents of the three stations, IS, SV1 and SV2. Seasonal indices for the BOD$_5$/COD ratio were calculated for each month of the year and a slight variation in their values was observed, which confirms that the performance of the separation processes at the three separators is not affected by seasonal variations.

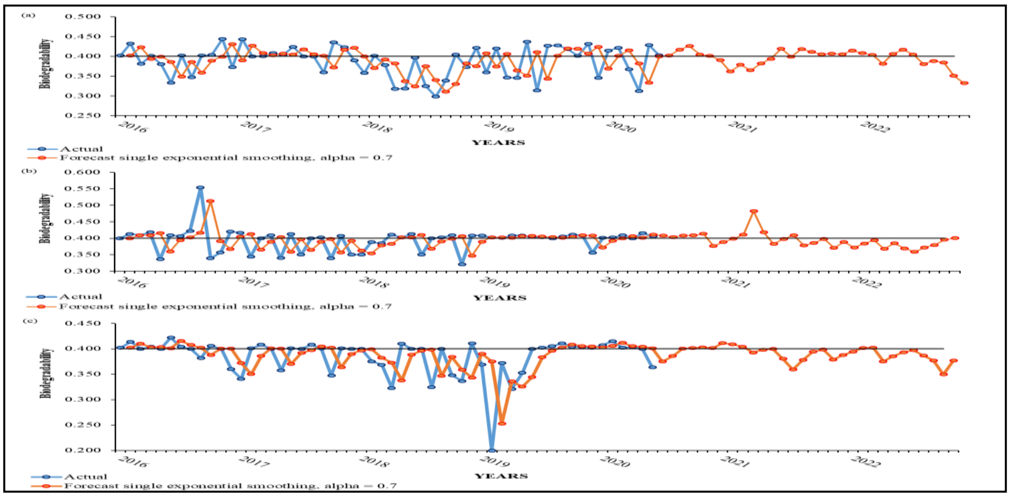

Fig. 5. Forecasting model from biodegradability wastewater in three station with separators of organic matter IS (a), SV1 (b), SV2 (c), 2016 ÷ 2022

According to the forecast model, stations SV1 and SV2 will continue to operate with low performance, unless measures will be taken to change the flow of influences or change the retention time of the liquid in the separators. The IS station have satisfactory performance. The accuracy of the forecast model results from the values of the media percentage of MAPE was 1.08 (IS), 1.41 (SV1) and 1.32 (SV2). MAPE indicates how much error in predicting compared with the real value.

4. Conclusions

A forecasting method to evaluate the performance of the separation processes of organic matter from wastewater mixed with rainwater to be discharged into sewers or treatment plants is proposed in this study. Fifty-four samples from three stations located in the northeastern part of Romania were analyzed and the BOD_5/COD ratio was calculated. The BOD_5/COD ratio values fall in the range 0.298 - 0.444, 0.321-0.554 and 0.200-0.422 for stations IS, SV1, respectively SV2 and indicate a low biodegradability degree of the effluents. Time series analysis shows that the processes are not affected by seasonal variations, but affected by the extreme maximum values of the BOD_5 and COD. The mean absolute values of the percentage errors indicated that the single exponential smoothing forecast model was well chosen in correlation with the presented graphs. The results obtained from physical-chemical and statistical analyzes showed that the effluents discharged from separation processes require biological treatment or improvement of the functional design of the separators.

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