

Use of Mathematical Modelling in Water and Wastewater Area

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Nowadays, there are many problems related to water pollution, which is a result of intermittent or continuous release of pollutants in the environment. Novelty of this paper is to identify an alternative able to overcome the limitations and drawbacks of the traditional methods in the wastewater field. In this line, a commercial bioactivator, namely, Micropan complex was used for wastewater treatment. The influence of contact time, initial pH and bioactivator amount was studied. The optimal parameters determination was achieved through an experimental model created using MATHCAD 14 programme. The correlation coefficient value indicates the precision with which the set of experimental values was characterized by the determined function. The value obtained was 0.889. When coefficient is the closer to 1 the better description is achieved.

Keywords: mathematical modelling, water, wastewater, Micropan complex

It is absolutely undeniable that environmental problems get worse day by day in a very fast rhythm, people being directly affected by this situation [1].

The world is more crowded, polluted, urbanized and more unbalanced compared to the last century [2]. This situation is maintained by a lack of balance between man and nature, an eco friendly lifestyle in terms of ecosystems values and prevalence of unhealthy consumption habits [3].

Pharmaceuticals are a large and diverse group of compounds designed to prevent, cure, treat diseases and improve health [4]. The use and consumption are increasing consistently due to the discoveries of new drugs, the expanding population, and the inverting age structure in the general population [5]. The presence of the pharmaceutical products in the wastewater represents a major concern for the environmental protection engineers [6, 31].

Every year, thousands of tons of pharmaceutical products are produced, which are used both in human and veterinary medicine [7]. Wastewaters discharged from the pharmaceutical factories are hazardous and toxic, characterized by high organic matter content, toxicity, persistent colour and high salt contents [8, 32]. Although the exact fate of pharmaceutical compounds in the wastewater treatment plants is not well understood, there are a lot of studies showing that many compounds are only partially removed and some are not removed at all [9-11].

There are different reasons of poor removal of pharmaceuticals in wastewater treatment plants. One of them is that some of the compounds are highly persistent and can not be removed by degradation processes. Another reason states that the hydrophilic character of most compounds allows them to be easily swept away from the system [12].

Bioactivators are natural bioremediation product that quickly stimulates microbial activity which results in faster

organic matter degradation. Those products do not contain any chemicals or additives. They are non-toxic, non-hazardous and harmless to humans, animals, plant-life and the environment in general [13].

In this context, the paper aimed to identify a treatment method that could efficiently remove pollutants giving high content of organic matter and enable the wastewater to be discharged into receiving water or be reused for industrial purposes.

Experimental part

Synthetic wastewater characterization

Analytical grade hydrogen potassium phthalate was purchased from Sigma – Aldrich, Germany. The main chemical properties of this compound are revealed in table 1.

Table 1
MAIN CHEMICAL PROPERTIES OF HYDROGEN POTASSIUM
PHTHALATE [14]

Chemical formula	C ₈ H ₆ O ₄ K
Molecular weight (g/mol)	204.22
Solubility (g/L) at 20°C	80
Physical state	crystals
LD50/LC50	dermal, guinea pig >1g/Kg; oral, rat > 3200 mg/Kg

The experiments were done on synthetic aqueous solutions with initial COD (chemical oxygen demand) = 1500 mgO₂/L in a batch system.

Reagents

In order to adjust the initial pH of the synthetic wastewater sample to an acidic pH, a 0.1 N sulphuric acid (H₂SO₄) solution was prepared using sulphuric acid (95-97% p.a. Merck, Germany). In order to adjust the initial pH of the sample to an alkaline value, a 0.1N sodium hydroxide

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(NaOH) solution was prepared using sodium hydroxide (p.a. Merck, Germany).

Materials

The bioactivator *Micropan complex* used in this study was purchased from Eurovix USA. *Micropan complex* is a natural biological promoter ideal to optimize the biological degradation processes of the organic substratum present in the wastewater entering in wastewater treatment plant. The microorganisms and the enzymes contained are highly effective in the metabolization of organic components and improving the quality of the outflow which will meet law requirements more easily [13, 15]. In table 2 are presented the main characteristic of the bioactivator.

Table 2
MICROPAN COMPLEX MAIN CHARACTERISTICS [15]

Composition	Physical characteristics
Fucus-laminariae active principles	Powder
AGAR broth medium	Humidity 4%
Liothamnium and calcereum seaweed	pH in solution 6-7
Mineral salts mordenite and dolomite	No Flammability
Mineral biocatalysts rich in trace elements	Color light brown

Equipment

The stirring was maintained using a HSC – Velp magnetic stirrer (Italy). The pH measurement was done using a Consort C380 pH-meter (0.01 pH resolution, Pt1000 sensor, United Kindom). In the COD sample analysis in order to maintain the temperature constant at 150° C for 2h a Velp DK6 (Italy) digester was used. The temperature was maintained constant at 25± 2°C using a FOC 225E –Velp Scientifica incubator (Italy).

Analytical method description

Chemical oxygen demand represents the equivalent amount of oxygen required for the oxidation of organic substances in sulphuric acid medium and excess of 0.25N potassium dichromate ($K_2Cr_2O_7$) solution in the presence of silver sulphate (Ag_2SO_4) which complexes chlorides and also acts as a catalyst.

The potassium dichromate excess is titrated with a 0.25 N of double iron (II) and ammonium sulphate solution ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) using as indicator the ferrous orthophenanthroline (1/40 mol/L solution). The reactant ratio was: sample: $K_2Cr_2O_7:H_2SO_4 = 2:1:3$. the COD value in the sample was calculated as follows [16]:

$$COD = \frac{(V_1 - V_2) \cdot f \cdot 2 \cdot 1000}{V_2} \left[\frac{mgO_2}{L} \right] \quad (1)$$

where:

V_1 = the volume of 0.25N double iron (II) and ammonium sulphate solution, used for titration of blank sample in mL;

V_2 = the volume of 0.25N double iron (II) and ammonium sulphate solution, used for titration of the wastewater sample in mL;

f = the factor of 0.25N double iron (II) and ammonium sulphate solution.

The factor determination of 0.25N double iron (II) and ammonium sulphate solution was done with the 0.25N potassium dichromate solution. The procedure was: 10 mL of 0.25N potassium dichromate solution, 90 mL of distilled water, 30 mL concentrated sulphuric acid were placed in an Erlenmayer vessel and the mix was carefully cooled. The solution was titrated with 0.25N double iron (II) and ammonium sulphate solution using as indicator the ferrous orthophenanthroline, until the color turned to reddish-brown.

The factor of 0.25N double iron (II) and ammonium sulphate solution was calculated using the following formula [17]:

$$f = \frac{V_{K_2Cr_2O_7}}{V_{Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}} \quad (2)$$

where:

$V_{K_2Cr_2O_7}$ = the volume (10 mL) of 0.25N potassium dichromate solution;

$V_{Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ = the volume of 0.25N double iron (II) and ammonium sulphate solution used for titration.

Working procedure

All the experiments were made in duplicate and the mean result was given.

The synthetic stock solutions with an initial COD = 1500 mgO₂/L were prepared by dissolving a required quantity of hydrogen potassium phthalate in deionised water.

In order to determine the optimal parameters that ensure higher organic matter removal efficiencies from wastewater, an experimental model created using Mathcad 14 programme was used. According to the experimental model, 17 samples of wastewater were prepared.

At the beginning of each experiment, from stock solution, aliquots of 200 mL were taken and contacted with different *Micropan complex* amounts: 1, 3 and 5 g.

The samples placed in Erlenmayer vessels provided with glass stopper were continuously stirred at 200rot/min only after adding the bioactivator. In order to establish the treatment process efficiency, samples were taken after 2, 4, 6, 8, 10 h and analysed. Prior analysis, samples were filtered on blue ribbon filter paper. The COD value was determined according to the method presented in SR ISO 6060/ 1996 [16].

Results and disscutions

Experimental model for optimal parameters setting in high organic matter content wastewater treatment

In order to determine the optimal parameters that ensure higher organic matter removal efficiencies from wastewater an experimental model created using MATHCAD 14 programme was used. The experiments were carried out using an orthogonal factorial experimental programme “centered compound” type.

The optimum region can be considered to be a region “almost stationary” and can be well approximated by means of a second order polynomial mathematical model. The centred compound programme is a 2^k factorial supplemented programme, being formed by a factorial programme at two levels of the factors which contains a 2^k number to which is added an additional 2^{k+1} number [18].

The 2k additional experimental points are along the axes and a point is obtained with the factor's values form the experiment center x = 0, y = 0, z = 0.

The number of the required experiments is calculated:

$$2^k + 2k + 3$$

$$X = \begin{matrix} & x & y & z \\ \begin{matrix} -1 & -1 & -1 \\ -1 & -1 & 1 \\ -1 & 1 & -1 \\ -1 & 1 & 1 \\ 1 & -1 & -1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \\ 1 & 1 & 1 \\ -2 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -2 \\ 0 & 0 & 2 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{matrix} & \end{matrix} \quad (3)$$

For central point (0, 0, 0) two additional experiments were performed. Thus, in the orthogonal "centered compound" type mathematical model, matrix X with the three variables noted: x (initial pH value), y (contact time) and z (bioactivator amount) was be used.

Selected mathematical models chosen to characterize the investigated properties changes according to the three independent parameters (x, y, z) are trivariant second order polynomial response functions with the following form:

$$f(x,y,z) = \text{solf}_0 + \text{solf}_1x + \text{solf}_2y + \text{solf}_3z + \text{solf}_4xy + \text{solf}_5yz + \text{solf}_6xz + \text{solf}_7x^2 + \text{solf}_8y^2 + \text{solf}_9z^2 \quad (4)$$

Where solf coefficients are the solution matrix elements determined by second order multivariant polynomial regression. Mathematical model coefficients estimation for the factorial experiment was done by analytical solving with an original calculation programme realised using MATHCAD 14 which solved the linear system [19, 30]:

$$\begin{pmatrix} n & \sum x & \sum y & \sum z & \sum x^2 & \sum y^2 & \sum z^2 & \sum xy & \sum yz & \sum xz \\ \sum x & \sum x^2 & \sum xy & \sum xz & \sum x^3 & \sum xy^2 & \sum xz^2 & \sum x^2y & \sum x^2z & \sum x^3 \\ \sum y & \sum xy & \sum y^2 & \sum yz & \sum xy^2 & \sum y^3 & \sum yz^2 & \sum xy^2 & \sum y^2z & \sum y^3 \\ \sum z & \sum xz & \sum yz & \sum z^2 & \sum xz^2 & \sum yz^2 & \sum z^3 & \sum xz^2 & \sum yz^2 & \sum z^3 \\ \sum x^2 & \sum x^3 & \sum x^2y & \sum x^2z & \sum x^4 & \sum x^2y^2 & \sum x^2z^2 & \sum x^3y & \sum x^3z & \sum x^4 \\ \sum y^2 & \sum xy^2 & \sum y^3 & \sum y^2z & \sum xy^3 & \sum y^4 & \sum y^2z^2 & \sum xy^3 & \sum y^3z & \sum y^4 \\ \sum xz & \sum x^2z & \sum xy^2 & \sum xz^2 & \sum x^3z & \sum xy^2z & \sum xz^3 & \sum x^2z^2 & \sum xz^3 & \sum x^3z \\ \sum xy & \sum x^2y & \sum xy^2 & \sum xyz & \sum x^3y & \sum xy^3 & \sum xyz^2 & \sum x^2y^2 & \sum xyz^2 & \sum x^3y \\ \sum yz & \sum xy^2 & \sum yz^2 & \sum yz^3 & \sum xy^3 & \sum yz^3 & \sum yz^4 & \sum xy^3 & \sum yz^4 & \sum yz^4 \\ \sum xz & \sum x^2z & \sum xyz & \sum xz^2 & \sum x^3z & \sum xyz^2 & \sum xz^3 & \sum x^2z^2 & \sum xz^4 & \sum x^3z \end{pmatrix} \begin{pmatrix} \text{solf}_0 \\ \text{solf}_1 \\ \text{solf}_2 \\ \text{solf}_3 \\ \text{solf}_4 \\ \text{solf}_5 \\ \text{solf}_6 \\ \text{solf}_7 \\ \text{solf}_8 \\ \text{solf}_9 \end{pmatrix}$$

No.	x	y	z	pH	Contact time,h	Micropan complex bioactivator amount, g	COD in solution mgO ₂ /L
1.	-1	-1	-1	6	4	2	525.48
2.	-1	1	-1	6	8	2	300.20
3.	1	-1	-1	8	4	2	522.32
4.	1	1	-1	8	8	2	416.00
5.	-1	-1	1	6	4	4	515.48
6.	-1	1	1	6	8	4	300.20
7.	1	-1	1	8	4	4	631.80
8.	1	1	1	8	8	4	293.88
9.	0	-2	0	7	1	3	703.36
10.	0	2	0	7	10	3	114.35
11.	-2	0	0	5	10	3	301.27
12.	2	0	0	9	10	3	300.20
13.	0	0	0	7	6	3	495.87
14.	0	0	-2	7	6	1	325.48
15.	0	0	0	7	6	3	258.00
16.	0	0	0	7	6	3	258.00
17.	0	0	0	7	6	3	258.00

where:

solf₀ – represents the property value in the central point of the experiment, namely the function value in the coordinates point x=0, y=0, z=0;

solf₁, solf₂, solf₃ – means the direct effect of the ratios characterized by conventional variables x, y or z, on the property;

solf₄, solf₅, solf₆ – means the square effect of the ratios characterized by conventional variables x, y or z, on the property;

solf₇, solf₈, solf₉ – means the interaction effect of the ratios characterized by conventional variables x, y or z, on the property.

In the function expression that characterize the property, as the value of a coefficient is higher than the others (one or two orders of magnitude), the greater is the influence of the term characterized by that coefficient, and therefore the greater is the influence of the corresponding ratio on that property [20]. In table 3 are presented the main operational parameters used in this research.

Table 3
MAIN OPERATION PARAMETERS

Variable	Parameter		
	Wastewater pH	Bioactivator amount, g	Contact time, h
-2			
-1	5	1	2
0	6	2	4
1	7	3	6
2	8	4	8

From the response functions and properties variations graphical representations it is possible to obtain important informations regarding operational parameters influence. In table 4 are revealed the variables used in MATHCAD 14 programme.

In the literature was indicated that the effect of pH is very important parameter because the enzymatic activity depends on the hydrogen ions concentration in solution, optimal reaction temperature varies with enzyme concentration [21]. Also, changes in pH may not only affect the shape of an enzyme but it may change properties of the substrate so that either the substrate can not bind to the active site or it can not under go catalysis [22].

Table 4
Variables used in MATHCAD 14 programme

Second order multivariant polynomial function assumed to characterize the change of investigated property has the form of the equation (4). Considering:

$$gz(x,y) = g(x,y,0); gx(y,z) = g(0,y,z); gy(x,z) = g(x,0,z) \quad (5)$$

where $i=0, \dots, n-1$

$$i = \quad x_i = \quad y_i = \quad z_i = \quad v_i = \quad f(x_i, y_i, z_i) = g(x_i, y_i, z_i) = gx(x_i, y_i) = gy(x_i, z_i) = gz(x_i, y_i) =$$

0	-1	-1	-1	525.48	498.702	521.382	498.668	535.163	392.455
1	-1	1	-1	300.2	297.17	263.529	240.815	277.31	392.455
2	1	-1	-1	522.32	527.845	548.944	526.23	535.163	420.018
3	1	1	-1	416	324.472	291.092	268.378	277.31	420.018
4	-1	-1	1	515.48	509.335	475.954	498.668	489.735	347.028
5	-1	1	1	300.2	197.002	218.102	240.815	231.883	347.028
6	1	-1	1	631.8	537.157	503.517	526.23	489.735	374.59
7	1	1	1	293.88	222.985	245.664	268.378	231.883	374.59
8	0	-2	0	703.36	715.544	641.375	641.375	641.375	383.523
9	0	2	0	114.35	199.839	125.67	125.67	125.67	383.523
10	-2	0	0	301.27	322.009	355.96	355.96	383.523	355.96
11	2	0	0	300.2	377.134	411.085	411.085	383.523	411.085
12	0	0	-2	495.87	504.939	428.95	383.523	428.95	428.95
13	0	0	2	325.48	414.084	338.095	383.523	338.095	338.095
14	0	0	0	258	290.558	383.523	383.523	383.523	383.523
15	0	0	0	258	290.558	383.523	383.523	383.523	383.523
16	0	0	0	258	290.558	383.523	383.523	383.523	383.523

In order to verify the characterization accuracy of the property variation by resulting functions f and g , the correlation coefficients **corelf**, respectively **corelg** were defined for each function determined. The correlation coefficient was defined by least squares method. The correlation coefficient value indicates the precision with which the set of experimental values is characterized by the determined function [23].

$$medf := \frac{1}{n} \sum_{i=0}^{n-1} v_i \quad (6)$$

v_i = vector of the free term of the polynomial function used to calculate the matrix

$$medfteo := \sum_{i=0}^{n-1} (f(x_i, y_i, z_i) - medf)^2 \quad (7)$$

$$medfexp := \sum_{i=0}^{n-1} (v_i - medf)^2 \quad (8)$$

$$corelf := \sqrt{\frac{medfteo}{medfexp}} \quad (9)$$

$$corelf = \quad \mathbf{0.889} \quad (10)$$

$$medg := \frac{1}{n} \sum_{i=0}^{n-1} v_i \quad (11)$$

$$medgteo := \sum_{i=0}^{n-1} (g(x_i, y_i, z_i) - medg)^2 \quad (12)$$

$$medgexp := \sum_{i=0}^{n-1} (v_i - medg)^2 \quad (13)$$

$$corelg := \sqrt{\frac{medgteo}{medgexp}} \quad (14)$$

$$corelg: \mathbf{0.779} \quad (15)$$

As a conclusion, it can be stated that, the closer to 1 is the coefficient value the better function describes the characterized process. The value obtained is relatively near 1, leading to the conclusion that this function can be properly used for pharmaceutical wastewater treatment process characterization [24].

Plotting the interpolation surface for $x = 0$ and y, z with values in the range $[-2, 2]$ and level curve for $x = 0$

The data presented in figure 1 were processed according to the following calculation programme. The function value in 20×20 points is calculated as follows:

$$fx(y,z) = f(0,y,z), yr=2, zr=2, \text{ and mesh}=20 \quad (16)$$

```

S(mesh,yr,zr) :=
count ← 0
for i ∈ 0..mesh
  for j ∈ 0..mesh
    y ← -|yr| +  $\frac{2 \cdot |yr| \cdot i}{\text{mesh}}$ 
    z ← -|zr| +  $\frac{2 \cdot |zr| \cdot j}{\text{mesh}}$ 
    c ←  $\begin{pmatrix} y \\ z \\ fx(y,z) \end{pmatrix}$ 
    count ← count + 1
cT
    
```

where: $XYZ=S(\text{mesh},x,y,z)$

$$X=XYZ^{<0>} \quad Y=XYZ^{<1>} \quad Z=XYZ^{<2>}$$

From the spatial diagram presented in figure 1 it is observed that for 1g bioactivator amount, at the end of the treatment process, the COD value obtained is about 316 mgO₂/L corresponding to an organic matter removal degree equal to 78%. This results indicated that the Micropan complex it acts as a catalyst and degradation agent for the organic matter. Similar results are given in literature [25,26].

Also, the results highlight that for 3g of bioactivator, the final COD concentration in solution is 175 mgO₂/L leading to an organic matter removal degree equal to 88%, while for 5g of bioactivator, the organic matter removal degree is 86%, corresponding to a final COD concentration of about 196 mgO₂/L. The results obtained showed that increasing the bioactivator concentration above 5g lead to a decrease of the process efficiency. In this case, a *screening effect* to the cell wall appears, protecting the binding sites, and thus causing lower treatment efficiencies. Similar result was reported for other systems [25, 27, 28-30].

In order to obtain level curve for $x = 0$, the following information were used: extreme points for variable z : $z_{low}=-2$ $z_{high}=2$; the number of divisions for the interval on the direction z : $z_n=20$; extreme points for variable y : $y_{low}=-2$ $y_{high}=2$; the number of divisions for the interval on the direction y : $y_n=20$. From figure 2 which represents the spatial diagram projection on the basis of the contact time-bioactivator amount coordinates, results that the best results (in terms of COD concentration decrease, corresponding to a 88% removal degree) were obtained at high contact times situated in the range 8-10 h, for 3g of bioactivator. Also, the final COD concentration in the solution has a value situated under the maximum allowable concentration required by legislation.

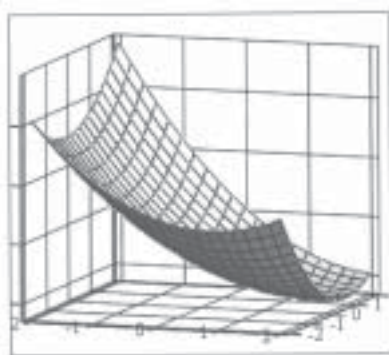


Fig. 1. Surface variation of COD in solution at $x=0$ $y, z=[-2,2]$ in the presence of *Micropan complex* bioactivator

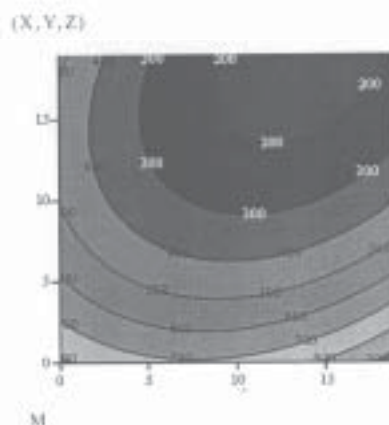


Fig. 2. Surface variation of COD concentration in solution compared to contact time and bioactivator amount

Plotting the interpolation surface for $y = 0$ and x, z with values in the range $[-2, 2]$ and the level curve for $y=0$

In figure 3 is presented the organic matter (COD) variation surface with initial solution pH and bioactivator

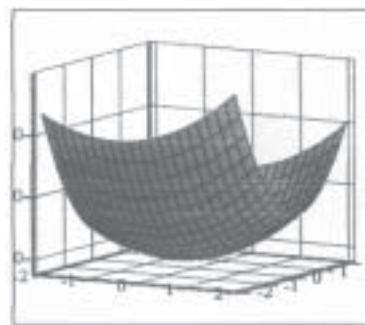


Fig. 3. Surface variation of COD in solution at $y=0$ $x,z=[-2,2]$ in the presence of *Micropan complex* bioactivator

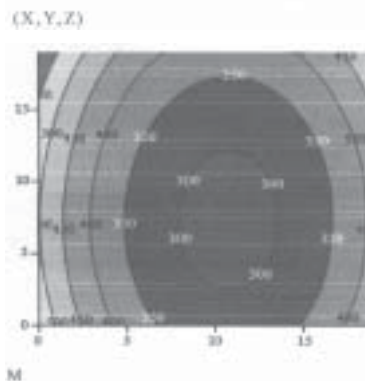


Fig. 4. Surface variation of COD concentration in solution compared to pH and bioactivator amount

amount. In this case, contact time had a constant value, namely, 10 h.

Through the projection of this surface on initial pH - bioactivator amount plane the diagram shown in figure 4 was obtained. From data analysis it is observed that the best results were obtained at acidic pH values, situated between 5 and 7. In this case, for bioactivator amounts ranging from 3 to 5 g, the organic matter concentration (COD) in solution decreased below 200 mgO₂ / L (corresponding to a removal degree of approximately 90%).

Plotting the interpolation surface for $z = 0$ and x, y with values in the range $[-2, 2]$ and the level curve for $z=0$

The spatial diagram from figure 5 presents the COD variation in solution at a constant bioactivator amount, 3g. By plotting this surface on initial pH - contact time plane, the diagram presented in figure 6 was obtained.

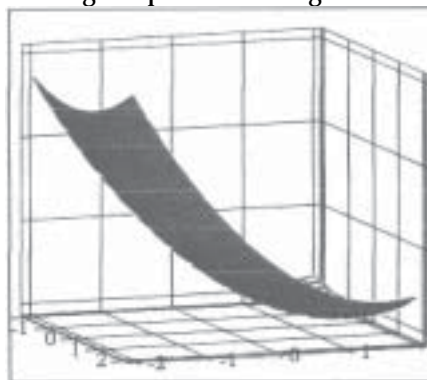


Fig. 5. Surface variation of COD in solution at $z=0$; $x,y=[-2,2]$ in the presence of *Micropan complex* bioactivator

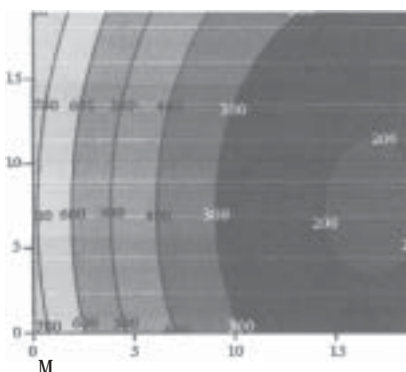


Fig. 6. Surface variation of COD concentration in solution compared to contact time and bioactivator amount

The results highlight that increasing initial pH from 5 to 7 resulted in an organic matter concentration (COD) decrease with 300 mgO₂/L, corresponding to an increase with about 10% of organic matter removal degree. Increasing the pH to 9 did not result in an improvement of the process efficiency, the behavior of the system being relatively similar.

Regarding the influence of contact time, it was observed that there is a significant decrease in the amount of COD with increasing contact time, the best results were obtained after 10 h of contacting the bioactivator with the wastewater.

Conclusions

In this paper was aimed to identify an alternative able to overcome the limitations and drawbacks of the traditional methods in the wastewater field.

The treatment process was conducted in the presence of a commercial bioactivator namely, *Micropan complex*.

Influence of contact time, bioactivator amount and initial pH was investigated and the results showed that: pH = 7, 3g bioactivator and 8-10 h of contact could be considered the optimal conditions because allowed a COD reduction of about 88% in the waste water.

For the polynomial function characterizing the treatment process and operational parameters chosen the correlation coefficient was calculated. Its value was 0.889. The results are considered acceptable.

The mathematical model obtained can be used for interpretation of results characterizing the treatment process.

For an accuracy as high as possible, the experimental research should be conducted on operational parameters variation areas more restricted.

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