Photo-decolorization of Eriochrome Black T: process optimization with Differential Evolution algorithm

L. Pintilie, M.T. Nechita, G.D. Suditu, V. Dafinescu and E.N. Drăgoi

Abstract**—**In the present study, the process of decolorization of wastewater contaminated with Eriochrome Black T (EBT) was analyzed and optimized. The removal of the dye was performed using a photochemical adsorption/degradation with TiO2 in the presence of hν. The interaction between the concentration of EBT, the amount of photocatalyst and the contact time and their influence on the process yield was analyzed and optimized using the Response Surface Methodology (RSM) and Differential Evolution (DE) algorithm. In the experimental phase, a maximum of 75.35% efficiency was obtained. Through the considered RSM and DE approach, a 98.9% efficiency was reached, proving the capability of the optimizer to improve performance.

Keywords**—** Eriochrome Black T, decolorization, modelling, optimization.

I. Introduction

Numerous studies and various physicochemical methods were proposed and used during the past decades for decolorization of industrial effluents. [1-4]. However, since every single industry from textile to pharmaceuticals, from food to automotive is nowadays a constant consumer of natural and/or artificial dyes and pigments, the interest in decolorization technologies is constantly increasing [5-7]. The azo-dyes are one of the main classes of industrial dyes, generally recognized for their toxicity and stability towards common physicochemical treatments [8].

Eriochrome black T (EBT) is a representative azo-dye with applications in many industries (textile, rubber, paper, pharmaceutical industry, cosmetics) and its elimination from effluents is of outmost importance. Therefore, a large number of procedures were conceived for EBT degradation and/or decolorization in wastewaters [9-17]. A particular attention was devoted to photo-decolorization of EBT, where various compounds with photochemical activity such as ZnO [12, 13], TiO_2 [18, 19], SnO_2 [16] and others [9, 11, 17, 20].

Although the mechanism, the kinetics and influence of various parameters towards photochemical decolorization of EBT were extensively studied, only few attempts to optimize the EBT photo-decolorization process are reported [21, 22] and all of them are based on the classic optimization procedure proposed by Box and Hunter [23]: the response surface methodology (RSM).

In this context, the aim of the current work is to emphasize the role of Artificial Intelligence based approaches in enhancing the optimization of photo-decolorization of Eriochrome Black T. The classic optimization technique RSM was applied for EBT photo-decolorization in presence of commercial TiO_2 and the results were further analyzed and improved using Differential Evolution (DE) algorithm. The experimental results show up to a 25% increase of the process efficiency when DE was used, proving that classic optimization results can be boosted using modern technologies.

II. Materials and methods

A. Materials

EBT powder, supplied by S.C. ChimReactiv S.A., and bi-distilled water were used to prepare the dye solutions. Common commercial TiO_2 powder (M-1319) supplied at FCC purity grade by Mayam [24] was used as such during this study. The TiO_2 powder was characterized by SEM and EDX analysis and successfully applied for photochemical decolorization of methylene blue and black liquor [25, 26].

B. Equipment

The UV light source was a Biocomp UV-lamp with wavelength of 253.7± 0.8 nm. The intensity of incident UV radiation was measured using a GUVA S12SD sensor. The concentration change of EBT, determined by correlation with the solution's absorbance at 535 nm, were recorded with a JASCO V-550 UV-Vis spectrophotometer. To avoid the settling of TiO_2 particles, the UV irradiation of the samples was performed under continuous stirring. After irradiation the TiO_2 powder was separated from the solutions using a BHG Hermle centrifuge. Disposable disc filters 0.45 μm were used for particle separation.

Manuscript received January 19, 2022. This work was supported "Program 4. Fundamental and frontier research. Exploratory research projects" financed by UEFISCDI, project no. PCE 58/2021

L. Pintilie is with the Apavital, str. Mihai Costăchescu No. 6, 700495, Iaşi, România.

M.T. Nechita, G.D. Suditu and E.N. Drăgoi are with the "Gheorghe Asachi" Technical University of Iasi / Department of Chemical Engineering, Bd. Prof. Dimitrie Mangeron, No. 73, 700050, Iaşi, România.

V. Dafinescu is with the Emergency Hospital "Prof. Dr. N. Oblu", Str. Ateneului No. 2, 700309, Iaşi, România.

C. *Experimental design*

In accordance with the RSM optimization procedure a minimum number of relevant experiments were statistically programmed in order to determine the optimal value of three representative parameters. These parameters and their limits were selected based on the data provided by literature and previous studies [26]. The designated variables were: (Z1) – the amount of TiO_2; (Z2) – the irradiation time and (Z3) – the EBT concentration. The variation range and the actual values of the independent variables used for this study are presented in Table 1.

TABLE I: THE REAL AND CODED VALUES FOR THE INDEPENDENT VARIABLES

Coded factors	X	-1.215	-1	0	1	1.215
Factor on natural scale	Z1	0.0065	0.2	1.1	2	2.1935
	Z2	138.75	300	1050	1800	1961.25
	Z3	0.325	10	55	100	109.675

D. *Experimental procedure*

In accordance with the experimental programming, the samples of EBT solution with required concentration, without any supplementary pH adjustments, were mixed with the adequate amount of TiO_2 and exposed to UV for a well-defined period of time. The decolorization efficacy was checked by measuring the solution absorbance at 535 nm. A calibration curve (Fig. 1) with 99.78 coefficient of determination (R^2) was used for the absorbance – concentration translation. The efficacy of EBT photo-decolorization was calculated using the following equation (1):

$$\eta = \frac{[\mathrm{EBT}]_i - [\mathrm{EBT}]_f}{[\mathrm{EBT}]_i} \cdot 100, \% \qquad (1)$$

where $[\mathrm{EBT}]_i$ and $[\mathrm{EBT}]_f$ are the concentration of EBT g/L before and after the irradiation.

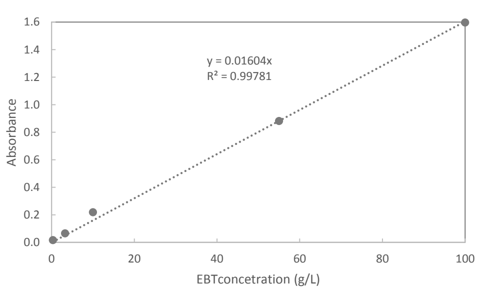

Fig. 1. Absorbance - concentration calibration.

E. *Differential Evolution algorithm*

In order to optimize the process, an alternative to the standard RSM approach was also applied. It is represented by a bio-inspired algorithm based on the Darwinian principle of evolution: Differential Evolution (DE). This approach belongs to the population based meta-heuristic class and it was chosen based on its flexibility and efficiency [27]. DE is among the most popular evolutionary algorithm and has large applicability, being successfully applied for a variety of problems. DE has a simple structure (Fig. 2), the optimization process relying on a series of steps: i) parameter setting and population initialization – where the control parameters are manually set and the population is initialized using a random based approach; ii) mutation – where a new mutated population is created based on the current generation using a strategy called differentiation; iii) crossover – where the characteristics of the individuals from the mutated population are combined with the ones of the individuals from the current one, resulting in a new population called trial; iv) selection – where based on a greedy approach, the next generation population is formed from the current and trial population.

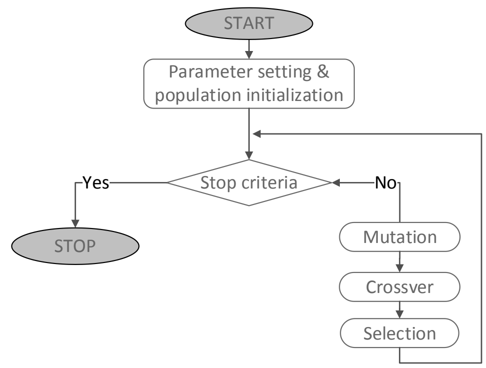

Fig. 2. Schema of the DE algorithm.

The steps mutation, crossover and selection and repeated until a stop criterion is reached. In this work, the stop criterion is represented by the number of generations reaching a pre-set limit. The DE algorithm has a reduced number of parameters: population dimension, number of generations, F (scaling factor) and Cr (crossover rate). In the initial version, F and CR were fixed. However, taking into account the sensibility of the algorithm to these parameters, strategies for their variations were proposed. Therefore, in this work, 3 variants of DE were employed (classical, JADE, and SADE) using the Mealpy framework [28].

III. RESULTS AND DISCUSSION

It is obvious that the efficacy of the photo-decolorization is directly dependent upon each one of the designated variables: the EBT concentration, the amount of TiO_2 and the irradiation time. The combined effect of these key factors was experimentally studied by changing their values in a carefully chosen ranges (Table 1), following the design of experiments (DOE) approach. The MINITAB software (Minitab Institute, USA) was used to process the experimental results. A full second order polynomial model was obtained by multiple regression technique. The regression equation in terms of actual factors (uncoded units) is presented bellow (Eq. 2):

$$\eta = 6.41 + 17.92 \cdot Z1 + 0.0314 \cdot Z2 - 0.763 \cdot Z3 - \\ -7.41 \cdot Z1 \cdot Z1 + 0.000003 \cdot Z2 \cdot Z2 + \\ +0.00661 \cdot Z3 \cdot Z3 + 0.00325 \cdot Z1 \cdot Z2 + \\ +0.0029 \cdot Z1 \cdot Z3 - 0.000338 \cdot Z2 \cdot Z3 \quad (2)$$

By setting one variable at constant value (equal with the median value of the variation range) three dimensional plots were drawn, that display the decolorization efficacy evolution as function of the two remaining variables as in Fig. 3 a, b, c.

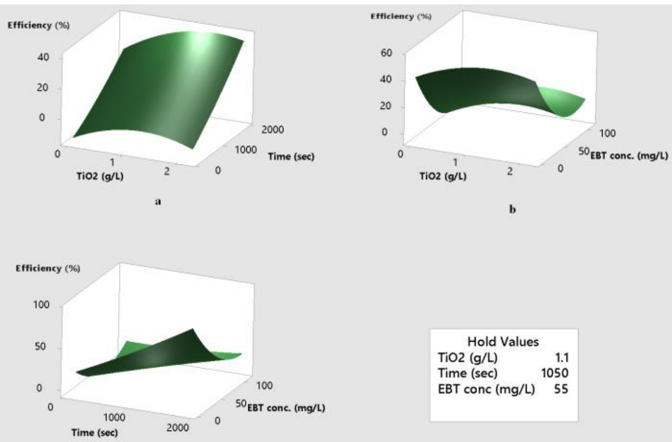

Fig. 3. Surface plot efficiency vs: a – amount of TiO_2 and irradiation time at EBC concentration of 0.055 g/L, b - amount of TiO_2 and EBT concentration at irradiation time t = 1050 s, c – EBT concentration and irradiation time at TiO_2 amount of 1.1 g/L.

The analysis of the 3-D plots and contour plots allows the visualization of maximum and/or minimum points, which leads to accurate identification of the optimal values and shows the impact of the selected parameters over the decolorization efficiency.

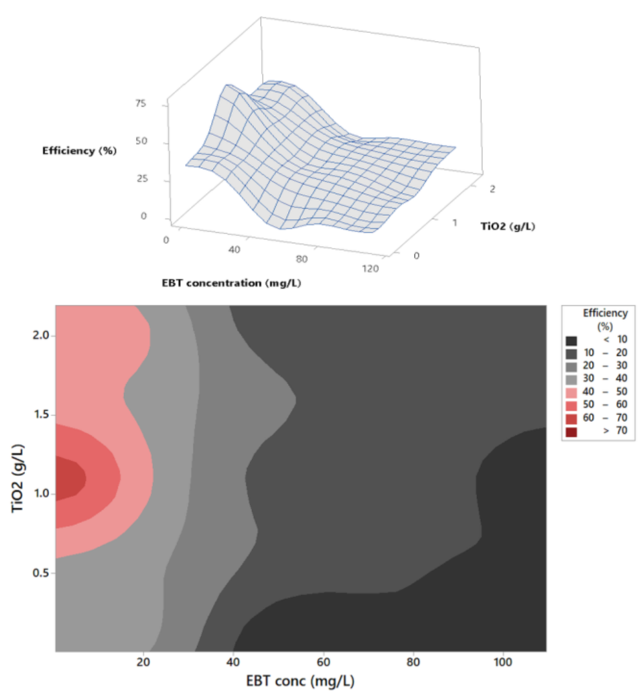

Fig. 4. The effects of EBT concentration and amount of catalyst on the process efficiency: a – 3D response surface, b – 2D contour plot.

The simultaneous effect of the EBT concentration and of the amount of TiO_2 on the decolorization efficacy is presented in Figs 4A and 4B.

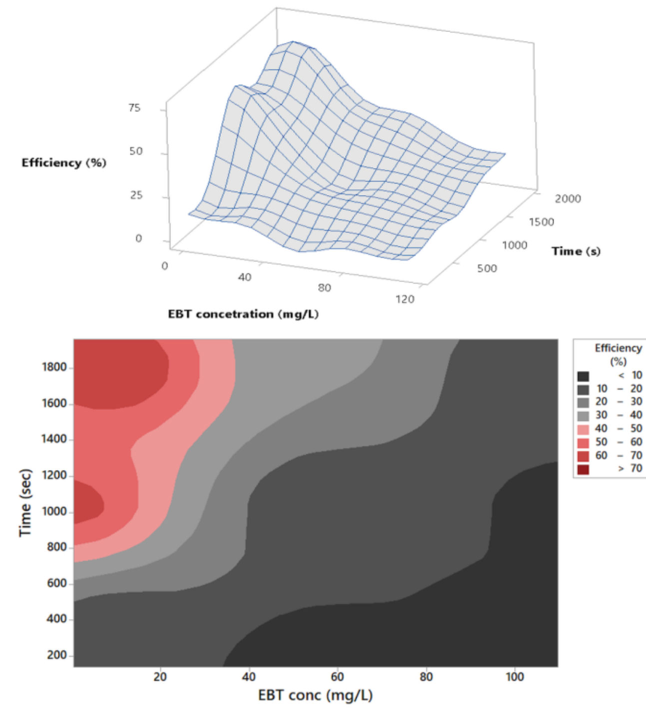

Fig. 5. The effects of EBT concentration and irradiation time on the process efficiency: a – 3D response surface, b – 2D contour plot.

According to Fig.4 the maximum efficacy can be achieved for an amount of TiO_2 between 1 and 1.25 g/L de and an EBT concentration of 10 mg/L.

The influence of irradiation time and EBT concentration upon the photo-decolorization efficacy is presented in Fig. 5.

As expected, the efficacy raises with the increase of irradiation time and with the decrease of EBT concentration.

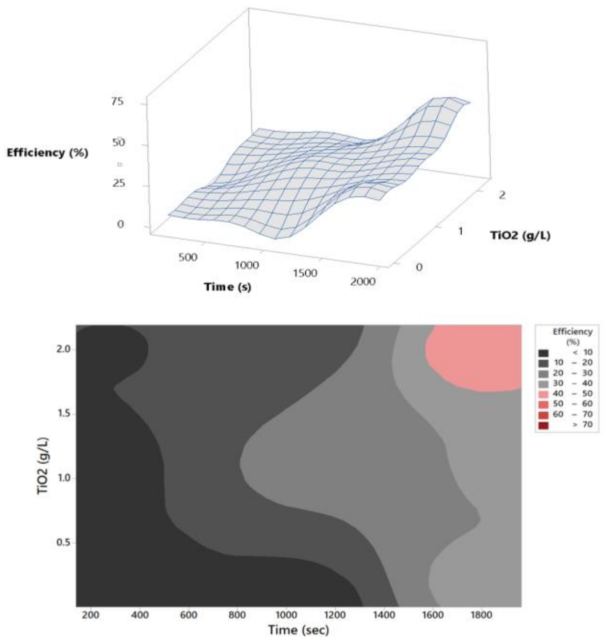

Fig. 6. The effects of irradiation time and amount of catalyst on the process efficiency: a – 3D response surface, b – 2D contour plot.

The influence of the third pair of variables (the irradiation time and the amount of TiO_2) is revealed in Fig. 6. In order to reach more than 50% decolorization efficacy at least 1.5 g/L TiO_2 are required in combination with an irradiation time of at least 1600 s.

Using the RSM based model, the different DE strategies were applied. The control parameters considered were: population dimension: 30, generations: 20. For the classic approach, the F and Cr values were set to 0.5. In case of JADE and SADE, the initial F and CR values were set to 0.5 and adapted using the specific strategy. Taking into account the stochastic nature of the DE algorithm, 10 simulations were performed in each case, the most 3 distinct solutions from each case being presented in Table II.

TABLE II: THE SOLUTIONS OBTAINED WITH THE 3 DE BASED VARIANTS

Variant	Z1	Z2	Z3	Efficiency (%)
Classic DE	1.533	1961.250	0.325	98.901
	1.249	1961.250	0.325	97.853
	0.735	1961.250	0.325	92.924
JADE	1.722	1961.250	0.325	98.934
	1.094	1958.317	0.325	96.642
	1.260	1876.835	0.325	93.961
SADE	1.706	1961.250	0.325	98.951
	1.480	1961.250	0.325	98.797
	1.301	1961.250	0.325	98.135

The best solution found (in case of Classic DE- 98.9%) was experimentally validated, the efficiency obtained being 97.92%.

IV. CONCLUSIONS

In this work, EBT was decolorized using a photochemical approach. Based on DOE approach, a series of experiments were performed with the scope of studying the influence of various parameters on the process performance. Moreover, a RSM methodology was used to determine the process model and to the optimal conditions. In addition, the process was further optimized using a bio-inspired metaheuristic represented by DE. The results obtained indicated that the DE based approaches were able to identify various conditions around the global optima that could be used to optimize the process up to 98.9%.

REFERENCES

[1] Slokar, Y.M. and Majcen Le Marechal, A., *Methods of decoloration of textile wastewaters.* Dyes and Pigments, 1998. **37**(4): p. 335-356, ISSN:0143-7208. https://doi.org/10.1016/S0143-7208(97)00075-2

[2] Hao, O.J., Kim, H., and Chiang, P.-C., *Decolorization of Wastewater.* Critical Reviews in Environmental Science and Technology, 2000. **30**(4): p. 449-505, ISSN:1064-3389. https://doi.org/10.1080/10643380091184237

[3] Forgacs, E., Cserháti, T., and Oros, G., *Removal of synthetic dyes from wastewaters: a review.* Environment International, 2004. **30**(7): p. 953-971, ISSN:0160-4120. https://doi.org/10.1016/j.envint.2004.02.001

[4] Zaharia, C., Suteu, D., and Muresan, A., *Options and solutions for textile effluent decolorization using some specific physico-chemical treatment steps.* Environmental Engineering and Management Journal, 2012. **11**(2): p. 493-509, ISSN:1843-3707. https://doi.org/10.30638/eemj.2012.062

[5] Samsami, S., et al., *Recent advances in the treatment of dye-containing wastewater from textile industries: Overview and perspectives.* Process Safety and Environmental Protection, 2020. **143**: p. 138-163, ISSN:0957-5820. https://doi.org/10.1016/j.psep.2020.05.034

[6] Collivignarelli, M.C., et al., *Treatments for color removal from wastewater: State of the art.* Journal of Environmental Management, 2019. **236**: p. 727-745, ISSN:0301-4797. https://doi.org/10.1016/j.jenvman.2018.11.094

[7] Slama, H.B., et al., *Diversity of Synthetic Dyes from Textile Industries, Discharge Impacts and Treatment Methods.* Applied Sciences, 2021. **11**(14): p. 6255, ISSN:2076-3417. https://doi.org/10.3390/app11146255

[8] Bafana, A., Devi, S.S., and Chakrabarti, T., *Azo dyes: past, present and the future.* Environmental Reviews, 2011. **19**(NA): p. 350-371, ISSN:1181-8700. https://doi.org/10.1139/a11-018

[9] Ejhieh, A.N. and Khorsandi, M., *Photodecolorization of Eriochrome Black T using NiS–P zeolite as a heterogeneous catalyst.* Journal of Hazardous Materials, 2010. **176**(1): p. 629-637, ISSN:0304-3894. https://doi.org/10.1016/j.jhazmat.2009.11.077

[10] Mittal, A. and Gupta, V.K., *Adsorptive removal and recovery of the azo dye Eriochrome Black T.* Toxicological & Environmental Chemistry, 2010. **92**(10): p. 1813-1823, ISSN:0277-2248. https://doi.org/10.1080/02772248.2010.485998

[11] Nezamzadeh-Ejhieh, A. and Khorsandi, M., *Heterogeneous photodecolorization of Eriochrome Black T using Ni/P zeolite catalyst.* Desalination, 2010. **262**(1): p. 79-85, ISSN:0011-9164. https://doi.org/10.1016/j.desal.2010.05.047

[12] Kazeminezhad, I. and Sadollahkhani, A., *Photocatalytic degradation of Eriochrome black-T dye using ZnO nanoparticles.* Materials Letters, 2014. **120**: p. 267-270, ISSN:0167-577X. https://doi.org/10.1016/j.matlet.2014.01.118

[13] Vaiano, V., et al., *Photocatalytic removal of eriochrome black T dye over ZnO nanoparticles doped with Pr, Ce or Eu.* Chemical Engineering Transactions, 2017. **57**: p. 625-630, ISSN:2283-9216.

[14] Aly-Eldeen, M.A., et al., *The uptake of Eriochrome Black T dye from aqueous solutions utilizing waste activated sludge: Adsorption process*

optimization using factorial design. The Egyptian Journal of Aquatic Research, 2018. **44**(3): p. 179-186, ISSN:1687-4285. https://doi.org/10.1016/j.ejar.2018.09.001

[15] Sabre, W., Mohammed, S.A., and Ali, A.H., *Effect of Operating Parameters on Degradation of Eriochrome black T Dye.* Engineering and Technology Journal, 2019. **37**(1C): p. 163-167. https://doi.org/10.30684/etj.37.1C.26

[16] Najjar, M., et al., *Green chemical approach for the synthesis of SnO_2 nanoparticles and its application in photocatalytic degradation of Eriochrome Black T dye.* Optik, 2021. **242**: p. 167152, ISSN:0030-4026. https://doi.org/10.1016/j.ijleo.2021.167152

[17] Sumadevi, K.R., et al., *Photocatalytic degradation of Eriochrome black-T and Evan's blue dyes under the visible light using PVA capped and uncapped Ag doped ZnS nanoparticles.* Emergent Materials, 2021. **4**(2): p. 447-456, ISSN:2522-574X. https://doi.org/10.1007/s42247-020-00153-7

[18] Kansal, S.K., et al., *Photocatalytic degradation of Eriochrome Black T dye using well-crystalline anatase TiO_2 nanoparticles.* Journal of Alloys and Compounds, 2013. **581**: p. 392-397, ISSN:0925-8388. https://doi.org/10.1016/j.jallcom.2013.07.069

[19] Zhu, J. and Jiang, Z., *Electrochemical Photocatalytic Degradation of Eriochrome Black T Dye Using Synthesized TiO_2@ CNTs Nanofibers.* Int. J. Electrochem. Sci, 2021. **16**: p. 210318. https://doi.org/10.20964/2021.03.55

[20] Kaur, J., et al., *Spherical MoO_3 Nanoparticles for Photocatalytic Removal of Eriochrome Black T.* ACS Applied Nano Materials, 2021. **4**(11): p. 12766-12778. https://doi.org/10.1021/acsanm.1c03433

[21] Lee, K.M., Abdul Hamid, S.B., and Lai, C.W., *Multivariate analysis of photocatalytic-mineralization of Eriochrome Black T dye using ZnO catalyst and UV irradiation.* Materials Science in Semiconductor Processing, 2015. **39**: p. 40-48, ISSN:1369-8001. https://doi.org/10.1016/j.mssp.2015.03.056

[22] Grassi, P., et al., *Water treatment plant sludge as iron source to catalyze a heterogeneous photo-Fenton reaction.* Environmental Technology & Innovation, 2020. **17**: p. 100544, ISSN:2352-1864. https://doi.org/10.1016/j.eti.2019.100544

[23] Box, G.E. and Hunter, J.S., *Multi-factor experimental designs for exploring response surfaces.* The Annals of Mathematical Statistics, 1957: p. 195-241, ISSN:0003-4851. https://doi.org/10.1214/aoms/1177707047

[24] Mayam, *Mayam organic & pure cosmetic ingredients, http://www.mayam.eu, 2021.*

[25] Atomi, A.I., et al., *Experimental study on TiO_2 promoted photo-degradation of methylene blue.* Bulletin of Romanian Chemical Engineering Society, 2018. **5**(1): p. 68-74, ISSN:2360-4697.

[26] Nechita, M.T., et al., *Differential evolution-based optimization of corn stalks black liquor decolorization using active carbon and TiO_2/UV.* Scientific Reports, 2021. **11**(1): p. 1-12, ISSN:2045-2322. https://doi.org/10.1038/s41598-021-98006-8

[27] Feoktistov, V., *Differential evolution: in search of solutions*. 2006, Berlin: Springer.

[28] Van Thieu, N. *The state-of-the-art MEta-heuristics ALgorithms in PYthon (MEALPY)*. 2021 [cited 2021 08.02.2021]; Available from: https://pypi.org/project/mealpy/