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Process Optimization and Modeling by Response Surface Methodology of Nitrite Electro-Reduction by Ti/RuO_2 + IrO_2 Electrode

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Abstract

Electrochemical reduction is one of the most suitable methods for the treatment of highly nitrate-contaminated solutions. This work focuses on the optimization of parameters influencing the electrochemical denitrification of water by the Ti/RuO_2 + IrO_2 electrode. The methodological approach used consists in carrying out a series of electrolysis by scrutinizing the reaction selectivity according to the experimental conditions. For this study, the NO_2^- ions concentrations before and after electrolysis were determined by UV-vis absorption spectroscopy. The results of the process optimization showed that the electrochemical reduction of NO_2^- is efficient at neutral pH after 120 mn of electrolysis at −100 mA. In contrast to works found in the literature, this study highlighted the process modeling that could open interesting perspectives to develop new treatment methods of polluted waters.

Keywords

Electrochemical Reduction, Water Treatment, Nitrite, Optimization, Modelling

1. Introduction

Water is the essential element for all living things life [1]. Its availability and abundance play an important role in the development and evolution of societies [2]. Water pollution is a persistent problem threatening both human health and ecosystems [3]-[11]. Industrial development and excessive use of chemical ferti-

lizers in agriculture contribute to the deterioration of its quality [12] [13] [14] [15]. In recent decades, water pollution caused by anions such as nitrites has become a major problems for researchers [16] [17] [18]. Nitrite is formed during the biodegradation of domestic or industrial nitrogenous wastes as well as some fertilizers. Several detection and treatment methods have been developed, such as spectroscopy, electrocoagulation, electrooxidation and electroreduction [19]. Electrochemical methods are an alternative because of their advantages, for example, environmental compatibility, versatility, high energy efficiency and profitability [20] [21] [22]. This work focuses on the optimization of parameters influencing the yield of water electrochemical denitrification by Ti/RuO_2 + IrO_2 electrode. To the best of our knowledge, this electrochemical denitrification method has never been applied to a Ti/RuO_2 + IrO_2 electrode. For this reasons, and with the aim of enhancing the electrochemical method, we examined the nitrite reduction on this choice of electrode at the anode as well as at the cathode. This study will investigate the influence of operating parameters such as electric current intensity, salt concentration and electrolysis time. Moreover, studies of process modeling, supported by the methodology of the response surfaces, lead to a real edification on the efficiency of the process.

2. Materials and Methods

2.1. Chemicals and Apparatuses

All electrochemical manipulations were performed using Ti/RuO_2 + IrO_2 electrode. Electrolyses were carried out in a standard two-electrode cell, with a Voltalab 40 potentiostat, connected to an interfaced computer that employed Voltamaster 4 software. The stock solution, with a concentration of 2 g/L, was prepared by dissolving $NaNO_2$ solid (>99%, Sigma-Aldrich) in distilled water. The other solutions were obtained by successive dilutions up to the desired concentrations. UV-visible absorption spectroscopy was used to determine the NO_2^- concentrations before and after electrolysis, using a Varian UV-vis spectrophotometer Cary-60. In order to control the pH, solutions of NaOH or HCl were added before starting the electrolysis. The pH values were measured with a HI 2211 Ph/ORP Meter pH-meter. For the determination of nitrite ions, the Griess reaction was used. Sulfanilamide (>98%, Sigma-Aldrich) and N-(1-naphthyl) ethylenediamine (>98%, Sigma-Aldrich) were used as received.

2.2. Methods

We first established the UV-vis calibration curve which was then used to evaluate the concentration of all solutions before and after electrolysis. For this purpose, we prepared 4 solutions of nitric acid with concentration ranges of 0.5, 1, 2.5 and 5 mg/L. Removal efficiency for nitrite reduction (R) was obtained by Equation (1):

$$R = \frac{\left(C_i - C_f\right)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final concentration (mg-N/L) of NO_2^-.

Table 1 represents the experimental factors to be optimized and modeled by response surface methodology using Disign-Expert version 13 software.

The matrix consisting of 4 factors, namely electrolysis time, NO_2^- concentration, reduction current and pH, is used to draw up a plan of experiments comprising 30 tests including 6 in the center. This was based on Box-Behnken response surface designs by George Box and Donald Behnken.

The number of experiments N to be performed is given by the following relationship [23]:

$$N = 2k(k-1) + r \tag{2}$$

where r is the number of replicates in the centre and k is the number of factors. Thus, the mathematical equation below allowed the calculation of the response according to the factors:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i \right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \tag{3}$$

Y being the predicted response (the degree of conversion); b_0 the constant coefficient; b_i the linear coefficients; b_{ij} the interaction coefficients; b_{ii} the quadratic coefficients and x_i, x_j are the coded factors of the operating parameters.

The analysis of the different models studied (linear, 2FI, quadratic and cubic) shows that the quadratic model with a P = 0.0001 less than 0.05 is the most adequate model to predict the response with a correlation coefficient of 0.9664 according to the predicted R^2 of 0.9220. For the study parameters, the quadratic model was proposed by Design-Expert 13.

3. Results and Discussion

3.1. Diagnostic Model

The results of the comparison between the values obtained by the model (predicted Y) and the experimental data (experimental Y) are summarized in Figure 1. In this case, the correlation between the theoretical response and the experimental one calculated by the model is satisfactory.

3.2. Numerical Optimization of Parameters

Despite its efficiency in determining the optimal parameters of a study, this optimization has some limitations, as the number of experiments to be carried out, and the impossibility of seeing the interaction of the various parameters affecting the yield. To overcome this, the response surface methodology is used. It allows maximum information with a minimum of experience.

In order to better understand the factors influencing this efficiency, we studied the effect of the following parameters: time, current intensity and nitrite concentration. The results obtained after electrolysis at temperatures between 22˚C and 28˚C were carried out at neutral pH. We first optimized the time, in the range of 10 to 180 min. During the reaction, the other parameters such as

nitrite ion concentration (50 mg-N/L), current intensity (−400 mA), pH (7 - 8) and electrode surface area (20 cm^2) remained invariant. In Figure 2, an increase in the efficiency is noted up to an electrolysis time of two hours. From this value, increasing the electrolysis time leads to a decrease in the removal efficiency. This may be due to the absorption of other compounds formed in these conditions. A long electrolysis time is also known to favor secondary reactions. In the course of the electrolysis, the solution becomes yellow, in agreement with this hypothesis. This result indicates an optimal time of 120 min. In the following, we will maintain the electrolysis time at two hours.

The effect of the initial concentration on the elimination yield was investigated at room temperature (27˚C) by fixing the electrolysis time at 120 min, the current intensity at −100 mA and the pH at 7 - 8. The results are shown in Figure 3. Although, the increase in the NO_2^- concentration at high contents leads to a decrease in efficiency, Figure 3 shows that the addition of increasing amounts of nitrites leads to an improvement in efficiency at values below 30 mg-N/L. Beyond this maximum value, any increase in concentration becomes unfavorable to the process. After electrolysis at 30 mg-N/L, we obtained, after analysis by UV-visible spectroscopy, an elimination yield of 97%.

Table 1. Process factors and their levels.

Factors	Unit	Coded variables	Levels	
			Min	Max
Electrolysis time	min	A	10	180
NO_2^- concentration	mg-N/L	B	10	100
Reduction current	mA	C	−700	−50
pH		D	2	14

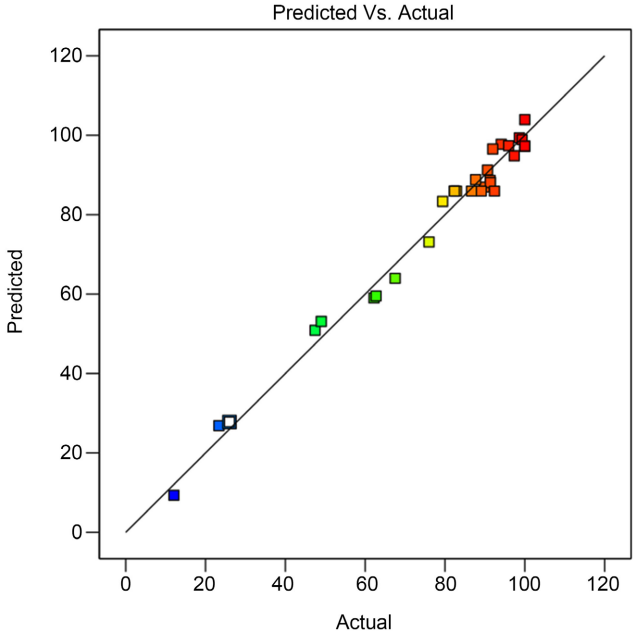

Figure 1. Experimental and predicted response for nitrite removal.

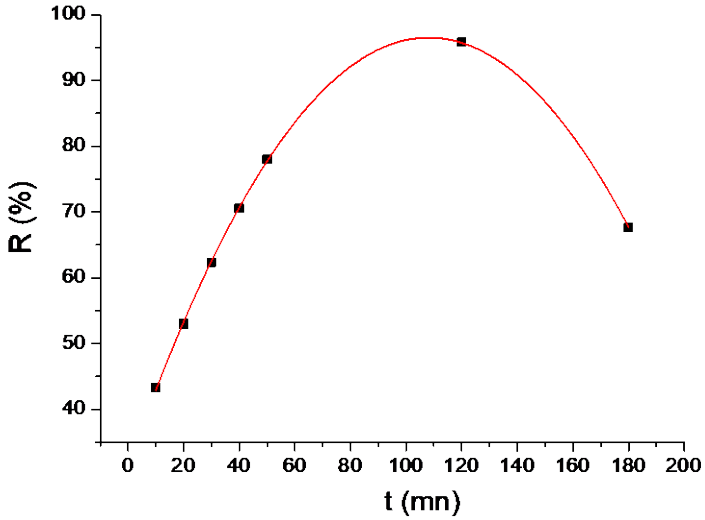

Figure 2. Influence of time on the removal efficiency.

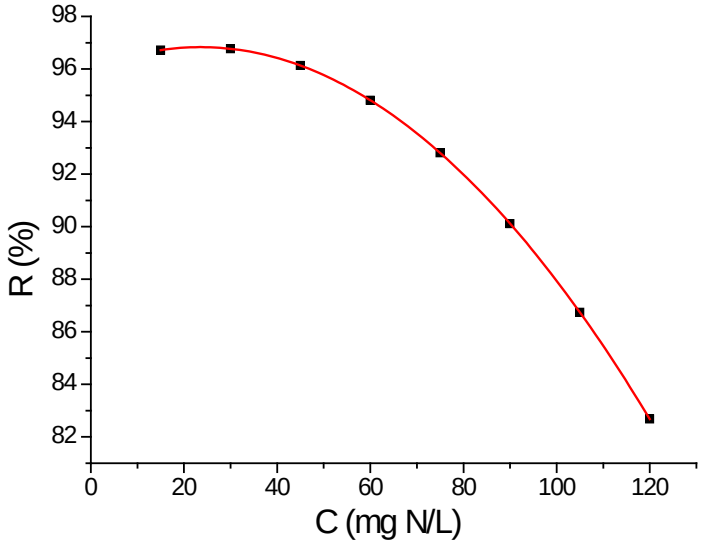

Figure 3. Influence of concentration on the removal efficiency.

For any wastewater treatment process, the applied current intensity is one of the most important parameter. The current intensity was varied between −50 to −700 mA to test a wide range of reducing current. The effect of the current, as a function of the removal efficiency, is represented in (b). Electrolysis was carried out in the following conditions: current intensity = −100 mA, pH = 7 and electrolysis time = 120 min. From **Figure 4**, it appears that the nitrite removal efficiency approaches a limiting value close to zero for a wide range of current. This result could be explained by the use of two $Ti/RuO_2 + IrO_2$ electrodes in a single compartment, allowing a higher electron production and facilitating nitrite reduction.

Initial pH is an important parameter for wastewater treatment. Starting with 30 mg-N/L of $NaNO_2$, the current was set at −100 mA. **Figure 5** shows the degree of conversion in the pH range of 2.0 - 14. In contrast to the situation ob-

served in acid medium, an efficiency of 100% was observed for nitrite reduction. In the literature, it was notably established that the protons are reduced near 0.00 V/SHE in our conditions, all possibly contributing to limiting the faradaic yield of the desired reaction. The results of this work consistently indicate that the ideal pH range for the reduction of nitrite ions is located in the basic range.

3.3. Analysis of Variance

For the choice of model, the Desirability Function Approach (DFA) was used and applied with the help of the Design Expert software to overcome this ambiguity in order to examine the optimal operating conditions for the electro-reduction of nitrite in the chosen experimental field. In order to help with the optimal parameters, a graphical visualization over the entire design space seems more interesting to us than the values of the design parameters that maximize desirability. Table 2 summarizes the parameters for response modeling and optimization by response surface methodology. Analysis of variance is used to describe the significance of the curvature of response at a 95% confidence interval. Indeed, significant process variables are usually decided on the basis of the F-value or P-value [24] [25]. The F-value of the model of 60.6 implies that the model is significant. There is only a 0.01% chance that such a large F-value is due to noise. P-values below 0.05 also indicate that the model terms are significant.

Table 2. Analysis of variance (ANOVA) for the quadratic response surface model.

Source	Squares	DF	Mean Square	F-value	P-value	Remarks
Model	16811.34	14	1200.81	60.60	<0.0001	significant
A	8766.12	1	8766.12	442.41	<0.0001	
B	799.69	1	799.69	40.36	<0.0001	
C	873.56	1	873.56	44.09	<0.0001	
D	2321.52	1	2321.52	117.16	<0.0001	
AB	59.32	1	59.32	2.99	0.1041	
AC	215.78	1	215.78	10.89	0.0049	
AD	1293.12	1	1293.12	65.26	<0.0001	
BC	60.64	1	60.64	30.06	0.1006	
BD	193.01	1	193.01	9.74	0.0070	
CD	59.32	1	117.99	5.95	0.0276	
A^2	215.78	1	1969.43	99.39	<0.0001	
B^2	1293.12	1	65.24	3.39	0.0896	
C^2	19.80	1	19.80	0.9992	0.3333	
D^2	3.58	1	3.58	0.1807	0.6768	
Residual	297.22	15	19.81			
Lack of Fit	209.66	10	20.97	1.20	0.4465	Not significant
Pure Error	87.56	5	17.51			
Cor Total	17108.56	29				

DF: Degree of freedom.

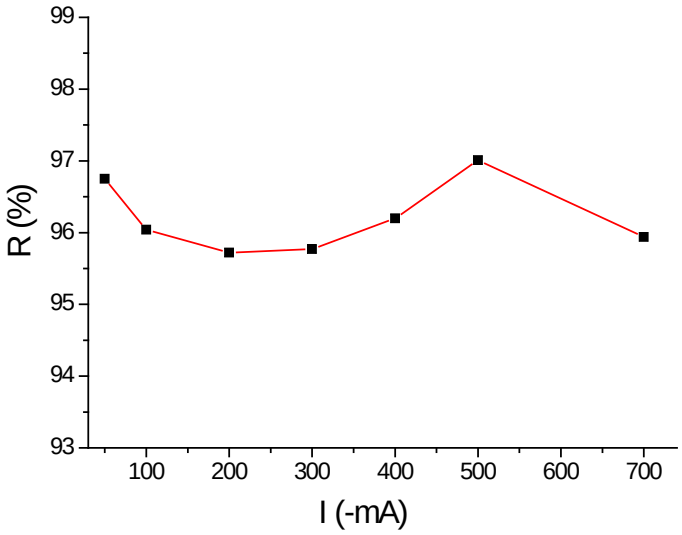

Figure 4. Influence of current on the removal efficiency.

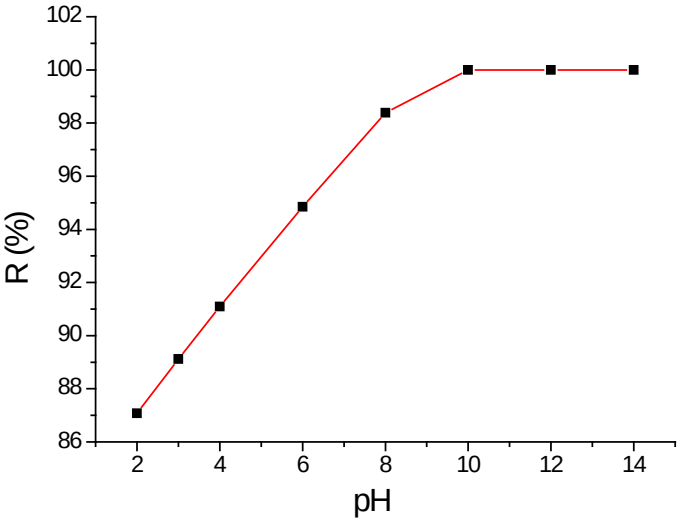

Figure 5. Influence of pH on the removal efficiency.

Table 2 shows that only the cross-effects AD is significant on the response (the degree of conversion). They suggest that the neutral pH was more favorable for the removal of nitrites.

The result of electrolysis in the same condition shows that the predicted value (100%) is very close to the experimental one (99.32%). This result highlights a valid and applicable model for the prediction of the response.

4. Conclusion

In this work, it was shown that optimization of the operating parameters such as $NaNO_2$ concentration, electrolysis time and current intensity significantly improves the efficiency of the process. The necessity to improve the nitrite removal process led us to parameters modeling (reaction time, pH, $NaNO_2$ concentration and current intensity). In this study, we were able to show the significant inte-

raction between pH and duration of electrolysis. The results indicate a real correlation between the optimal value (100) predicted by the mathematical model and that obtained experimentally (99.32). In this study, the choice of working electrode, Ti/RuO_2 + IrO_2 is justified on several levels but it would be interesting to locate the trend of other electrodes and guide further research, aiming at the design of an electrode on this process.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Wang, Q. and Yang, Z. (2016) Industrial Water Pollution, Water Environment Treatment, and Health Risks in China. *Environmental Pollution*, **218**, 358-365. https://doi.org/10.1016/j.envpol.2016.07.011

[2] Tran, T.K., Chiu, K.F., Lin, C.Y. and Leu, H.J. (2017) Electrochemical Treatment of Wastewater: Selectivity of the Heavy Metals Removal Process. *International Journal of Hydrogen Energy*, **42**, 27741-27748. https://doi.org/10.1016/j.ijhydene.2017.05.156

[3] Picetti, R., Deeney, M., Pastorino, S., Miller, M.R., Shah, A., Leon, D.A., Dangour, A.D. and Green, R. (2022) Nitrate and Nitrite Contamination in Drinking Water and Cancer Risk: A Systematic Review with Meta-Analysis. *Environmental Research*, **210**, Article ID: 112988. https://doi.org/10.1016/j.envres.2022.112988

[4] Chen, B., Wang, M., Duan, M., Ma, X., Hong, J., Xie, F., Zhang, R. and Li, X. (2019) In Search of Key: Protecting Human Health and the Ecosystem from Water Pollution in China. *Journal of Cleaner Production*, **228**, 101-111. https://doi.org/10.1016/j.jclepro.2019.04.228

[5] Mousavi, S.A., Mehralian, M., Khashij, M. and Ibrahim, S. (2018) Effect of Air Flow Rate and C/N Ratio on Biological Nitrogen Removal through the CANON Process Treating Reject Water. *Environmental Technology*, **39**, 2891-2899. https://doi.org/10.1080/09593330.2017.1369578

[6] Ghernaout, D. and Elboughdiri, N. (2020) Electrochemical Technology for Wastewater Treatment: Dares and Trends. *Open Access Library Journal*, **7**, 1-17. https://doi.org/10.4236/oalib.1106020

[7] Saravanan, A., Kuma, P.S., Varjani, S., Karishma, S., Jeevanantham S. and Yaashika, P.R. (2021) Effective Removal of Cr(VI) Ions from Synthetic Solution Using Mixed Biomasses: Kinetic, Equilibrium and Thermodynamic Study. *Journal of Water Process Engineering*, **40**, Article ID: 101905. https://doi.org/10.1016/j.jwpe.2020.101905

[8] Khanal, S.K., Varjan, I.S. and Awasthi, M.K. (2020) Waste-to-Resources: Opportunities and Challenges. *Bioresource Technology*, **317**, Article ID: 123987. https://doi.org/10.1016/j.biortech.2020.123987

[9] Dimé, A.K.D., Diouf, G., Sarr, M.M. and Fall, M. (2020) Caractérisation Physico-Chimique de la Nappe Phréatique Située dans une Zone à Forte Pollution Industrielle: Cas de la Commune de Rufisque. *Revue Ivoirienne des Sciences et Technologie*, **35**, 163-174.

[10] Ağca, N., Karanlık, S. and Ödemiş, B. (2014) Assessment of Ammonium, Nitrate,

Phosphate, and Heavy Metal Pollution in Groundwater from Amik Plain, Southern Turkey. *Environmental Monitoring and Assessment*, **186**, 5921-5934. https://doi.org/10.1007/s10661-014-3829-z

[11] Choomyen, P.B., Muangmeesri, B. and Maneetham, D. (2022) Management of Water Treatment Systems Automatically via the Internet of Things. *Engineering*, **14**, 385-397. https://doi.org/10.4236/eng.2022.149030

[12] Zongo, I., Leclerc, J.P., Maiga, H.A., Wethe, J. and Lapicque, F. (2009) Removal of Hexavalent Chromium from Industrial Wastewater by Electrocoagulation: A Comprehensive Comparison of Aluminium and Iron Electrodes. *Separation and Purification Technology*, **66**, 159-166. https://doi.org/10.1016/j.seppur.2008.11.012

[13] Florke, M., Kynast, E., Barlund, I., Eisner, S., Wimmer, F. and Alcamo, J. (2013) Domestic and Industrial Water Uses of the Past 60 Years as a Mirror of Socio-Economic Development: A Global Simulation Study. *Global Environmental Change*, **23**, 144-156. https://doi.org/10.1016/j.gloenvcha.2012.10.018

[14] Dimé, A.K.D., Diouf, G., Dramé, E.T. and Fall, M. (2018) Caractérisation Physico-Chimique de la Nappe Phréatique Située dans une Zone à Forte Pollution Industrielle: Cas de la Commune de Ngoundiane. *Journal de la Société Ouest-Africaine de Chimie*, **46**, 23-28.

[15] Aydın, A., Ercan, O. and Tascioglu, S. (2005) A Novel Method for the Spectrophotometric Determination of Nitrite in Water. *Talanta*, **66**, 1181-1186. https://doi.org/10.1016/j.talanta.2005.01.024

[16] Umar, A.S. and Iqbal, M. (2007) Nitrate Accumulation in Plants, Factors Affecting the Process, and Human Health Implications. A Review. *Agronomy for Sustainable Development*, **27**, 45-57. https://doi.org/10.1051/agro:2006021

[17] Yang, H. and Cheng, H. (2007) Controlling Nitrite Level in Drinking Water by Chlorination and Chloramination. *Separation and Purification Technolonogy*, **56**, 392-396. https://doi.org/10.1016/j.seppur.2007.05.036

[18] Zhou, Y., Oehmen, A., Lim, M., Vadivelu, V. and Ng, W.J. (2011) The Role of Nitrite and Free Nitrous Acid (FNA) in Wastewater Treatment Plants. *Water Research*, **45**, 4672-4682. https://doi.org/10.1016/j.watres.2011.06.025

[19] Ianoul, A., Coleman, T. and Asher, S.A. (2002) UV Resonance Raman Spectroscopic Detection of Nitrate and Nitrite in Wastewater Treatment Processes. *Analytical Chemistry*, **74**, 1458-1461. https://doi.org/10.1021/ac010863q

[20] Santana, M.M.D., Zanoelo, E.F., Beninca, C. and. Freire, F.B. (2018) Electrochemical Treatment of Wastewater from a Bakery Industry: Experimental and Modeling Study. *Process Safety and Environmental Protection*, **116**, 685-692. https://doi.org/10.1016/j.psep.2018.04.001

[21] Diouf, G., Dimé, A.K.D., Boye, M.B. and Baldé, I. (2022) Optimisation des Paramètres Influençant le Rendement de la Dénitrification Electrochimique de l'Eau par l'Electrode de Ti/RuO_2 + IrO_2. *Afrique Science*, **20**, 1-10.

[22] Baldé, I., Dimé, A.K.D. and Kane, C. (2023) Production Electrochimique de la Soude: Optimisation et Modélisation du Procédé par la Méthodologie de Surface de Réponse. *Afrique Science*, **22**, 29-41.

[23] Auta, M. (2012) Optimization of Tea Waste Activated Carbon Preparation Parameters for Removal of Cibacron Yellow Dye from Textile Waste Waters. *International Journal of Advanced Engineering Research and Studies*, **1**, 50-56.

[24] Gebresemati, M., Gabbiye, N. and Sahu, O. (2017) Sorption of Cyanide from Aqueous Medium by Coffee Husk: Response Surface Methodology. *Journal of Applied Research and Technology*, **15**, 27-35. https://doi.org/10.1016/j.jart.2016.11.002

[25] Elmoubarki, R., Taoufik, M., Moufti, A., Tounsadi, H., Mahjoubi, F.Z., Bouabi, Y., Qourzal, S., Abdennouri, M. and Barka, N. (2017) Box-Behnken Experimental Design for the Optimization of Methylene Blue Adsorption onto Aleppo Pine Cones. *Journal of Materials and Environmental Sciences*, **8**, 2184-2191.