Journal of Materials, Processes and Environment
May edition. Vol.3. N°1. (2015)
ISSN : 2335-1020

Wastewater treatment using extraction industries wastes: Methyl Orange Removal by Bio-sorbent

F. AGOUILLAL[1, 2], H. MOGHRANI[1], N. NASSRALLAH[1], R. MAACHI[1]

1. Laboratoire de Génie de la Réaction, Faculté du Génie Mécanique et du Génie des Procédés, Université des Sciences et de la Technologie Houari Boumediene.
2. Unité de Recherche en Analyse et Développement Technologique en Environnement- Centre de Recherche en Analyses Physico-Chimiques.

ABSTRACT — In this study, as an alternative source of adsorbent for the removal of dyes from wastewaters, the leaves of Lamiacea specie which is a Medicinal and Aromatic Plant were used as an alternative and low cost biomaterial for feasibility study of Methyl Orange (MO) removal from wastewaters.

Experiments were performed to investigate the impact of some parameters such as initial pH, temperature, dye initial concentration and adsorbent S/L ratio on the removal of MO.

The results showed that an optimum of 70% of MO removal is reached at an ambient temperature T=25°C, for a biosorbent concentration of 13 to 16 (g/L) in acidic environments (pH=2).

Kinetic experiments revealed that the adsorption of Methyl Orange onto the Lamiacea leaves can be described with pseudo second-order model and the equilibrium isotherm data were well described by the Langmuir I model. The maximum adsorption capacity of the biomass was found to be 70 mg/g at 25 ◦C.

The proposed waste material collected from aromatic and flavors extraction industries may be proposed as suitable adsorbent for decolorization of industrial effluents due to its low cost; Thus, this preliminary study will be the base of future processes optimization and will be considered as model case studies for investigate other pollutants.

***Keywords**: Biosorption, Solid wastes, Methyl Orange, Dye removal, Wastewater treatment.*

I.Introduction

In recent years, the contamination of environments is growing with the industrial development; the concerned contaminants are multiples including heavy metals, organic pollutants and dyes.

In other hand, the problems resulting of untreated or partially treated industrial effluents have been an increasing interest among scientists and regulators to preserve the public health.

***Corresponding author**: Farid AGOUILLAL,*
Research field: Bio-Process and Environmental Engineering.
Adress. Laboratoire de Génie de la Réaction, Faculté du Génie Mécanique et du Génie des Procédés, Université des Sciences et de la Technologie Houari Boumediene.
E-mail: f.agouillal@gmail.com

It is known that many industries such as paper, plastics, leather and textile, cosmetic and pharmaceutical industries use dyes to color their products. Therefore the major impact of these industries on the environment is to discharge their colored effluents into natural receiving water bodies.

Besides, dyes in aquatic media also affect the biota by reducing light penetration and of course affect photosynthetic activity [1].

Also it is suspected that certain dyes and their degradation products have toxic, carcinogenic and mutagenic effects on living organisms [2].

Since the dye molecules generally have complex molecular structures, they are very resistant to biodegradation [3].

In order to reduce all these harmful effects of dyes, it is necessary to remove dyes from industrial effluents before discharging them into environment.

According to Cheah et al (2013), Methyl Orange (Figure1), or Sodium 4-[[4 (dimethylamino) phenyl] diazenyl] benzene sulfonate (IUPAC) is commonly present in effluent discharges from textile, food, pharmaceutical, priting and paper manufacturing industries. It is a typical water soluble anionic azo dye which can cause a serious threat to physic-chemical properties of fresh water and to aquatic life; therefore, it is necessary to apply suitable technology for the removal of Methyl Orange (MO) from wastewater. [4].

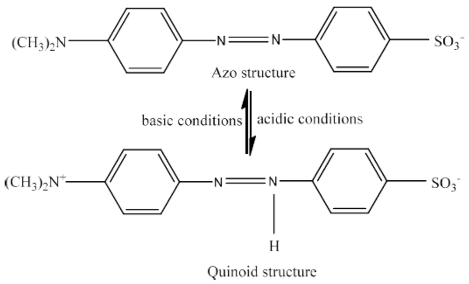

Fig 1.Structural forms of methyl orange under acidic and basic conditions. (Basahel et al 2015).

The conventional available physical, chemical and biological treatments to remove the colored dyes from the textile effluents treatments have various limitations, such as formation of by-products which can be also hazardous; Add to this, the greater energy consumption results in high operational costs [6, 7 , 8].

To response for these limitations, many adsorption methods using biosorbents are recently studied and proposed as a low-cost and environmentally friendly means of the textile effluents treatment [9, 10, 11].

Therefore, recently, there has been an increasing interest to find cheap and easily provided natural adsorbents. Certain natural materials such as banana pith, rice husk, papaya seeds, orange peel, banana peel, have been used for the treatment of wastewaters [11].

Functional groups of amino, carboxyl, thiol and phosphate present on the lignocellulosic cell wall of the biosorbent (fig 2.) are responsible for bonding of dyes molecules [12]. Then, several dyes from the textile effluents, which exist as cationic or anionic molecules in solutions, are respectively attracted by carboxyl and other negatively charged groups or amine groups via electrostatic interaction and/or hydrogen bonding.

In this work, methyl orange dye (MO) was selected as model of anionic pollutant to investigate adsorption kinetics of pollutant onto a typical low cost wastes and by-products biomaterial under different experimental conditions, such as the effect of temperature, initial pH, MO initial concentration, and adsorbent concentration on the adsorption process.

The kinetic data was analyzed by pseudo-first order and pseudo-second order models so that we can estimate the adsorption mechanism and different models such as Langmuir and Freundlich equations are applied to fit the experimental data. This informations may be useful for further study and practical applications of the adsorbent in future processes optimization and will be proposed as case studies for investigate other pollutants.

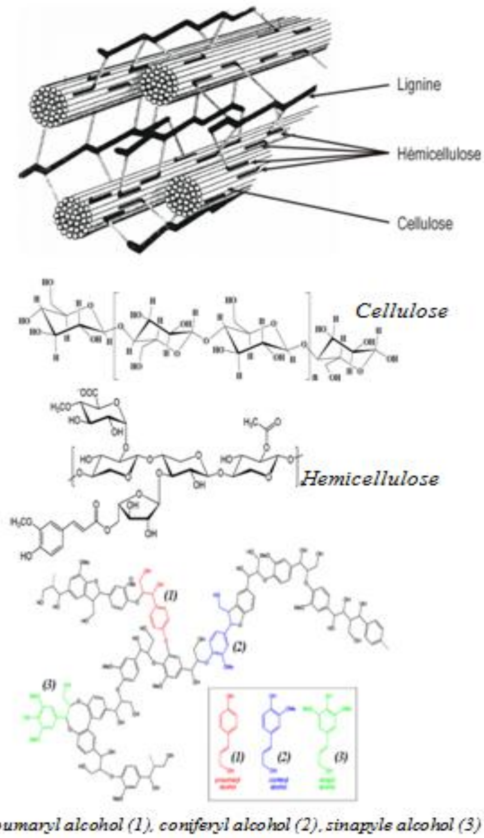

Fig. 2 Hemicellulosic and Ligno-cellulosic structure in the cell walls of the wastes biomass.

II. Material and Methods

II.1. Preparation of biosorbent

The used leaves of the plant were collected and firstly washed with tap water, then washed with distilled water;

Finally, it was dried in an oven at 110°C for 24 h then powder form of this biomaterial was obtained. The resulting Lamiacea biomaterial powder with a mean particle size of 200 µm was used in further experiments.

II.2. Physicochemical characterization of the biosorbent and pHpzc determination

The physical properties of biosorbent used in this study are measured following the solide porosity and density characterizations.

In order to determine the isoelectric point of biosorbent, 0.1 g of bisorbent was added into 50 mL, 0.01 M NaCl solutions at different pH values from 2 to 10. All prepared suspensions were mixed at 400 rpm and 25 ◦C for 24 h and the final pH was reported.

II.3. Adsorption protocol and analysis

Methyl Orange (MO), was used as a dye model. 1 g of MO was dissolved in distilled water to prepare stock solution (1000 mg/L) and other desired concentrations for further experiments were prepared by dilutions. According to the results of spectral analysis, the wavelength for maximum absorption of MO was determined as 506 nm at pH2 and pH4, the Optical Density of the solution were evaluated with UV–vis spectrophotometer. pH adjustments were done by using hydrochloric acid and sodium hydroxide solutions.

Adsorption experiments were carried out in batch conditions by using required concentration of adsorbate and adsorbent in glass vessels. While the samples were agitated in the temperature controlled by magnetic stirrer, test samples were withdrawn at particular time intervals. These test samples were centrifuged at 5000 rpm for 10 min and the remaining dye concentrations in supernatants were analyzed at 506 nm in the UV–vis spectrophotometer. All experiments were performed in duplicate and the results were shown as the means.

At equilibrium, the amount of adsorbed MO onto the LBP (qe) was calculated as given below:

$$q_e = \frac{C_0 - C_e}{M} V \quad (1)$$

where C0 and Ce are the initial and equilibrium liquid phase concentration of MO (mg/L), respectively. V is the volume of the dye solution (L) and M is the amount of biosorbent (g).

The percentage of dye removal was expressed as:

$$\text{dye removal}\,\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

In order to determine the effects of the experimental parameters on the efficiency of adsorption, the experiments were carried out by altering the pH, the temperature of the medium, the dye concentration and adsorbent ratio.

The effect of pH on adsorption was analyzed for 2, 4 and 6 while the initial dye concentration and the adsorbent ratio, RSL, were fixed to 10 mg/L and 16 g/L, respectively at 25 ◦C. The temperature effect was investigated at 15, 25, 35, 45 and 55 °C by using 8 g/L adsorbent at pH 2. To determine the impact of initial dye concentration on adsorption efficiency, four different concentrated dye solutions were used. pH and the adsorbent ratio were fixed to 2 and 16 g/L at 25 °C during this experiment.

The effect of the adsorbent ratio on dye removal was determined for 150 mg/L initial dye concentration, at pH 2 and 25 ◦C with various adsorbent ratios ranging from 5 to 20 g/L.

II.3. Kinetic modeling

Since the determination of adsorption kinetics is of great importance for predicting the control mechanism of adsorption process, a kinetic investigation was conducted. Two kinetic models (pseudo first-order kinetic model and pseudo second-order kinetic model) were used to fit the experimental data of MO adsorption by LBP.

The linearized forms of pseudo first-order and pseudosecond order kinetic equations are given as follows, respectively [13]:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where qe and q are the amount of dye adsorbed at equilibrium and at time t, respectively (mg/g), and k1(1/min) and k2 (g/mg min) are the pseudo first-order and the pseudo second-order rate constant, respectively.

II.4. Isotherm modeling

Due to the fact that adsorption isotherms help to understand the mechanism of adsorption process Langmuir I, II, and Freundlich isotherm models were used to analyze the sorption equilibrium data.

Langmuir model identifies the adsorption process on a homogeneous surface assuming the monolayer coverage of adsorbent [13].

The linear form of the Langmuir isotherm model is given by the following equation:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{bq_m} \times \frac{1}{C_e} \qquad (6)$$

where qm is the maximum adsorption capacity (mg/g), b is the Langmuir constant (L/mg), Ce is the equilibrium concentration of adsorbate in the solution (mg/L) and q is the solid phase concentration of adsorbate at equilibrium (mg/g).

The Langmuir parameters can also be used to predict the adsorption process is favorable or unfavorable. In order to describe this, the dimensionless equilibrium constant must be calculated by using the equation below:

$$R_L = \frac{1}{1 + bC_0} \qquad (7)$$

where b is the Langmuir isotherm constant (L/mg) and C0 is the initial dye concentration (mg/L). It was stated that RL > 1 represents unfavorable, RL = 1 represents linear, 0 < RL < 1 represents favorable and RL = 0 represents irreversible characteristic of adsorption process.

Freundlich model describes the multilayer adsorption on heterogeneous surfaces [13]. The linear form of the Freundlich isotherm model is given by the following equation:

$$\log q = \log K_f + \frac{1}{n}\log C_e \qquad (8)$$

where Kf is the relative adsorption capacity, nf (1/n) is the

Freundlich constant related to adsorption intensity, Ce is the equilibrium concentration of adsorbate in the solution (mg/L) and q is the solid phase concentration of adsorbate at equilibrium (mg/g).

III. Results and discussion

III.1. Characterization of the Lamiacea biosorbent powder:

The reported pHpzc value of the tested Lamiacea biosorbent powder (LBP), as shown in fig3, proves that the surface charge of this materials is overall positive for pH values lower than the pHpzc=6,3.

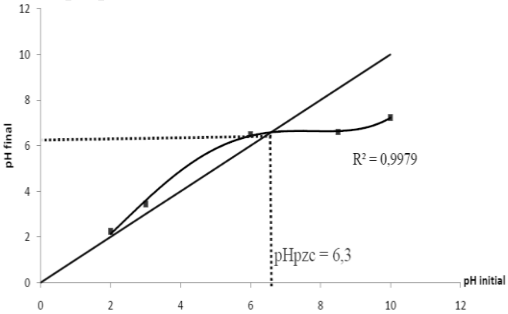

Fig3. Final pH versus initial pH for the used LBP.

For that, in the preliminary experiment, we adjust the initial pH of the solutions with a low value of pH (about 2: acid medium).

Table1. Physicochemical properties of the LBP

parameters	value
Real Density	0,76
Porosity	0,405
Total Porous Volume	1,66
pH pzc	6,3

The physical properties of biosorbent used in this study are measured following the solide porosity and density characterizations and listed in Table 1.

The real density is 0.76 and the porosity of the biosorbent is 0.405 with a Total Porous Volume of 1.66.

III.2. Effect of the dye initial concentration on the adsorption yield of LBP:

The relative variation of the observed adsorption yield for the concentrations in MO is presented in Fig.4; for concentrations going from 5mg/l to 15mg/l the adsorption yield passed from 40% to 70% what represents an improvement of 30%.

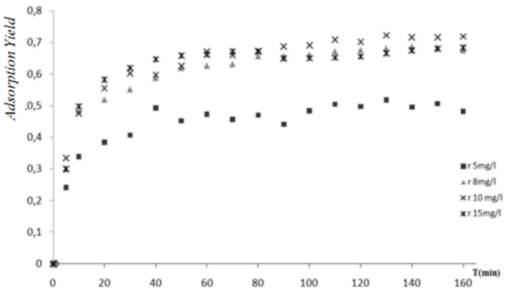

Fig 4. Effect of the initial orange methyl concentration on the adsorption yield (pH=2, RSL = 16 (g/L), stirring speed (ss) =600 tr/min, T=25C°)

Then, it appears that in MO initial concentration has a low effect on the biosorption yield for concentration from 8 to 15 mg/L.

III.3. Effect of the temperature

The temperature has a major effect on the process of adsorption; generally, increasing temperature enhances the molecules diffusion through the external layer and the internal pores of the adsorbent particles, this increase would have also a positive or negative effect on the adsorption capacity. Figure 5 and 6 shows the effect of the temperature on the MO adsorption capacity on LBP.

Adsorption yield passes from 44% at 15°C to an optimum yield of 70% at 25 °C and decreases gradually up to 45% at 55°C.

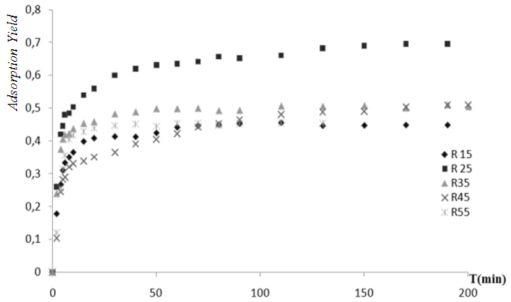

Fig5. Effect of the temperature on the MO adsorption yield (pH=2, RSL = 8 (g/L), ss =600 tr/min, C_0=10mg/l).

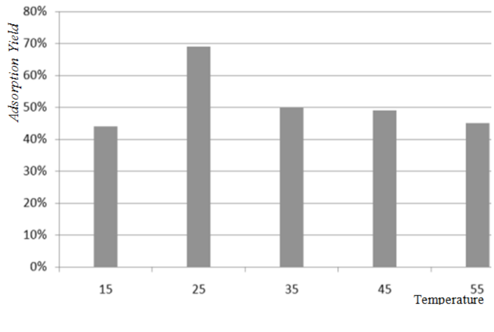

Fig6. Maximum MO adsorption yield according to the temperature (pH=2, RSL = 8 (g/L), ss =600 tr/min, C_0=10mg/l)

According to the obtained results, we note that the capacity of adsorption is optimal at an ambient temperature T=25°C.

III.4. Effect of the biosorbent ratio

In this experiment, we fix the initial pH solutions as well as the initial concentration and temperature (25C°), the adsorbent mass is varied.

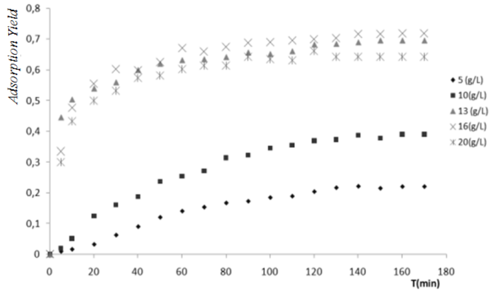

Fig7. Effect of the LBP ratio on the MO adsorption capacity; (pH = 2, T=25C°, C=10mg/l, va=600 tr/min).

According to the results presented in figure 7, the MO adsorption yield increases with the mass of the adsorbent. Thus, yield passes from 20% for a LBP ratio of 5 (g/L) to 40% for a doubled LBP ratio of 10 (g/L) and reached an optimum yield of 70% for LBP ratio 13 and 16 (g/L); noting that for a ratio 20 (g/L), the yield is 64%.

III.5. Effect of the pH

pH acts both on solubility and on the ionization state of the adsorbent.
Thus, the effect of pH varying from 2, 4 and 10 was investigated and the results were shown in Fig. 8. The removal of dye was a bit higher in acidic environments than neutral counterparts. At acidic pH (pH=2), the adsorption yield reaches maximum value of 70%, for a slightly acidic pH (pH=4) and a pH near to neutrality (pH=6), the adsorption yield decrease to 40%.

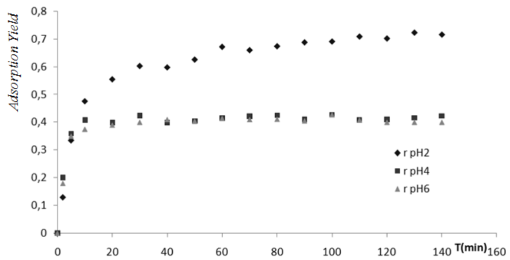

Fig8. Effect of pH on the MO adsorption yield (Temperature = 25°C, RSL = 16 (g/L), stirring speed=600 tr/min, C0=10mg/l)

Obtained better yield with acidic pH can be allotted to the fact that the surface of the used biomaterial seems to be charged positively (H+ ions) at pH below pHpzc (6,3) enhancing the adsorption of MO.

III.6. Adsorption isotherm modeling

Mathematical modeling allows obtaining certain number of qualitative and quantitative information such as the interaction kind, the saturation phenomenon or the thermodynamic of the adsorption.

Various isotherm models can be used in order to investigate the interaction between adsorbate and adsorbent and also to predict the mechanism of adsorption. The results of the isotherm modeling studies were used to evaluate the adsorption parameters and these parameters were given in Table 2.

Since the correlation coefficient obtained for Langmuir II equation is very low than the other two models, it can be said that Langmuir II isotherm model is not convenient for the adsorption of MO onto LBP. Beside this, although the correlation coefficients observed for the other two models are very close to each other and close to 1, it can be concluded from the results that the adsorption of MO onto LBP is better defined by the Langmuir I model than the Frendlich model. The maximum adsorption capacity was observed to be 70 mg/g at 25°C and it decreased with increasing temperature.

Table 2.Langmuir and Frendlich parameters for MO adsorption

Isotherme		Linear form	Fonction	Linear transformation	
Langmuir	$\frac{q_e}{q_m} = \frac{b.C_e}{1+b.C_e}$	$\frac{1}{q_e} = \frac{1}{C_e}\frac{1}{bq_m} + \frac{1}{q_m}$ I	$\frac{1}{qe} = f(\frac{1}{C_e})$	q_m	5.3410
				B	0.0300
				R_L	0.7690
				R^2	0.9958
		$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{bq_m}$ II	$Ce/qe = f(Ce$	q_m	3.5430
				B	0.0470
				R_L	0.6800
				R^2	0.6555
Freundlich	$q_e = K_F.C_e^{1/n_f}$	$Ln\,q_e = lnK_F + \frac{1}{n_f} lnC_e$	$Ln\,qe = f(Ln\,Ce)$	K_F	0.1600
				$1/n_f$	0.9116
				n_f	0.9600
				R^2	0.9914

The Langmuir parameters can also be used to calculate the dimensionless equilibrium constant which contribute to predict that the adsorption process is favorable or unfavorable. Since the value of RL calculated for the studied temperature (25°C) is between 0 and 1, it can be concluded that the adsorption of MO onto LBP occurred favorable.

III.7. Adsorption kinetics modeling

Both pseudo first-order and pseudo-second order models were tested for the adsorption of MO onto LBP and the kinetic parameters derived from these models were summarized in Table 3.

The low correlation coefficient values obtained for pseudo firstorder model (0,962) presents that the adsorption of MO onto LBP cannot be explained by this model.

Table3. Parameters characterizing the kinetics of adsorption of the three dyes for various ratios RS/L used. Va=600 tr/min and T = 25°C

$R_{S/L}$ (g/L)		MO C_0 = 10mg/L			
		5	10	13	16
Pseudo-First Order Kinetic	q_e (mg/g)	0.791	0.462	0.318	1.202
	K_1 (min^{-1})	0.005	0.023	0.029	0.050
	R^2	0.975	0.991	0.962	0.983
Pseudo-Second Order Kinetic	q_e (mg/g)	0.843	0.625	0.555	0.465
	K_2 (min^{-1})	0.080	0.017	0.146	0.163
	R^2	0.971	0.976	0.998	1

However the correlation coefficient values of pseudo second-order model were very close to 1 (0,998), and these results indicated that the adsorption of MO onto LBP occurred in accordance with this kinetic model. Since this model expresses the chemisorption behaviour of the reaction.

IV. Conclusions

The present study aims to use a solid industrial waste material into an alternative solution for overcoming another environmental problem. Therefore, the used leaves of the Lamiacea plant as an alternative and low cost biomaterial for the treatment of colored wastewaters.

The results of the kinetic and equilibrium experiments are also well in line with this observation, thus, it can be concluded that the adsorption of MO onto the biosorpent occurred favorable and follow a chemisorption process.

In conclusion, this waste material may be a suitable adsorbent for decolorization of industrial effluents due to its low cost and sufficient adsorption capacity. Although the present study offers an alternative usage of Medicinal and Aromatic Plant harvested after the industrial extraction, the collection of the live form of this plant is not recommended because of its vital importance for the ecosystem health.

References

[1] H. Ali, S.K. Muhammad, Biosorption of crystal violet from water on leaf biomass of Calotropis procera, J. Environ. Sci. Technol. 1 (2008) 143–150.

[2] M. Ramakrishnan, S. Nagarajan, Utilization of waste biomass for the removal of basic dye from water, World Appl. Sci. J. 5 (2009) 114–121.

[3] S. Mona, A. Kaushik, C.P. Kaushik, Waste biomass of Nostoc linckia as adsorbent of crystal violet dye: optimization based on statistical model, Int. Biodeter. Biodegr. 65 (2011) 513–521.

[4] Willie Cheah, Soraya Hosseini, Moonis Ali Khan, T.G. Chuah, Thomas S.Y. Choong, Acid modified carbon coated monolith for methyl orange adsorption, Chemical Engineering Journal, Volumes 215–216, 15 January 2013, Pages 747-754, ISSN 1385-8947.

[5] Basahel, S. N. et al. Influence of crystal structure of nanosized ZrO2 on photocatalytic degradation of methyl orange. Nanoscale Res Lett. 10, 73 (2015).

[6] P. Nigam, G Armour, I.M Banat, D Singh, R Marchant, Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues, Bioresource Technology, Volume 72, Issue 3, May 2000, Pages 219-226, ISSN 0960-8524.

[7] Enric Brillas, Carlos A. Martínez-Huitle, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, Applied Catalysis B: Environmental, Volumes 166–167, May 2015, Pages 603-643, ISSN 0926-3373.

[8] Esther Forgacs, Tibor Cserháti, Gyula Oros, Removal of synthetic dyes from wastewaters: a review, Environment International, Volume 30, Issue 7, September 2004, Pages 953-971, ISSN 0160-4120.

[9] Tim Robinson, Geoff McMullan, Roger Marchant, Poonam Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresource Technology, Volume 77, Issue 3, May 2001, Pages 247-255, ISSN 0960-8524.

[10] T. Robinson, B. Chandran, P. Nigam, Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk, Environment International, Volume 28, Issues 1–2, April 2002, Pages 29-33, ISSN 0160-4120.

[11] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal – A review, Journal of Environmental Management, Volume 90, Issue 8, June 2009, Pages 2313-2342, ISSN 0301-4797.

[12] Asha Srinivasan, Thiruvenkatachari Viraraghavan, Decolorization of dye wastewaters by biosorbents: A review, Journal of Environmental Management, Volume 91, Issue 10, October 2010, Pages 1915-1929, ISSN 0301-4797.

[13] Xunjun Chen, Modeling of Experimental Adsorption Isotherm Data; Information 2015, 6, 14-22.