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Anionic dye N-2RBL Removal by grape seeds-based activated carbon: A comparative study

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***Abstract*—** This study aims to compare the removal efficiency of Nylosan Red (N-2RBL) dye by adsorbents prepared from grapes seeds and compare it to Aldrich activated carbon. Grapes seeds-based activated carbons were prepared by physical and combined activation. Langmuir and Freundlich isotherms models in their Linear and non-linear forms were applied to assess the removal process. R^2, χ^2 statistic, RMSE measures and APE functions were calculated for isotherms parameters evaluation.

High removal efficiencies of 93.87 % and 92.5 % N-2RBL at conditions of 4 g/L (adsorbent dosage) and 100 mg/L (initial concentration) of were obtained using GC-MA and AAC adsorbents respectively. However, removal efficiency of 92 % and 82.19 % were obtained by GC-PA (4 g/L) and GC-NS (8 g/L) samples respectively at the same concentration.

The best fit for linear and non-linear Langmuir isotherms models was more representative by GC-MA sample corresponding to adsorption capacities of 363.14 and 325.7 mg/g. Also, the non-linear and linear Freundlich isotherm models present good results for GC-MA indicating that the adsorption is favorable with adsorption energies of 40.79 and 26.2 mg/g, while GC-PA is moderate. Samples were classified in terms of adsorption capacity as follow: GC-MA > AAC > GC-PA > GC-NS.

***Keywords*—** Models; Dyes; Adsorbent; Langmuir; Freundlich; grape seeds.

I. INTRODUCTION

Dyes are one of the compounds largely used in the industry especially textile. They are not easily removed from liquid effluents because these compounds are recognized to be toxic ant hardly bio-degradable. In order to reduce effluents coloring issued from the textile industry, various methods were used such as the coagulation-flocculation; adsorption on activated carbon and electro-coagulation among others.

The research was then directed towards the treatment process using natural materials such as clay; sawdust, agricultural wastes and other industrial wastes because of their availability and their low cost, which could participate in the context of materials valorization and especially will contribute to the sustainable development and preserve non-regenerative resources.

The purpose of this work is to compare the uptake capacity of raw grapes seeds, Grapes seeds-based activated carbon and the commercial one from Aldrich to remove Nylosan Red dye from aqueous water. Both forms (Linear and non-linear) of Langmuir and Freundlich isotherms models were used for adsorption process assessment.

We started with, *Section I*, that contains an introduction of adsorption as a technique of separation and mathematical models used. *Section II* deals with the related work of dye capture by different agriculture wastes. *Section III*, talks about the dye specification, adsorbents preparation, experiments and models used. *Section IV* describes results, discussion and comparison of the adsorption of N-2RBL by different prepared samples and Aldrich activated carbon. Separation factors, coefficient of distribution and all forms Langmuir and Freundlich isotherms models were graphically represented. Finally, *Section V* concludes this research work with future perspectives.

II. RELATED WORK

This work is a continuation of the adsorption of N-2RBL by grapes cores-based activated carbon [1], prepared using Calcium chloride ($CaCl_2$), Phosphoric acid (H_3PO_4) and Potassium hydroxide (KOH) as oxidizing agents to enhance their adsorption capacity and intensity this anionic dye.

In order to get a clear idea this raw material as a precursor for adsorbent preparation, it is very important to enhance its porosity by performing chemicals, physicals or combined treatments and assess all isotherms parameters

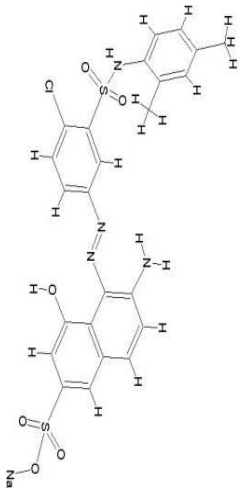
and make a comparison with one commercially available activated carbon. For this purpose, Aldrich activated carbon was chosen for comparison.

III. METHODOLOGY

III. 1. Stock solutions preparation

Nylosan Red belongs to the azo anion acid dyes family, it is a very toxic substance, Table 1 summarizes some of its characteristics [1].

Table 1. Chemical structure and characteristics of N-2RBL

	Characteristics	*Chemical structure*
Molecular formula	$C_{24}H_{21}ClN_4O_6N_2Na$	
Molecular weight	587.97 g/mol	
Max wave length $(\lambda_{max})^*$	500 nm	
LD_{50}(mice)	5000 mg/Kg	
LC_{50}	90 mg/g	
Solubility in H_2O	80 g/L at 90°C	

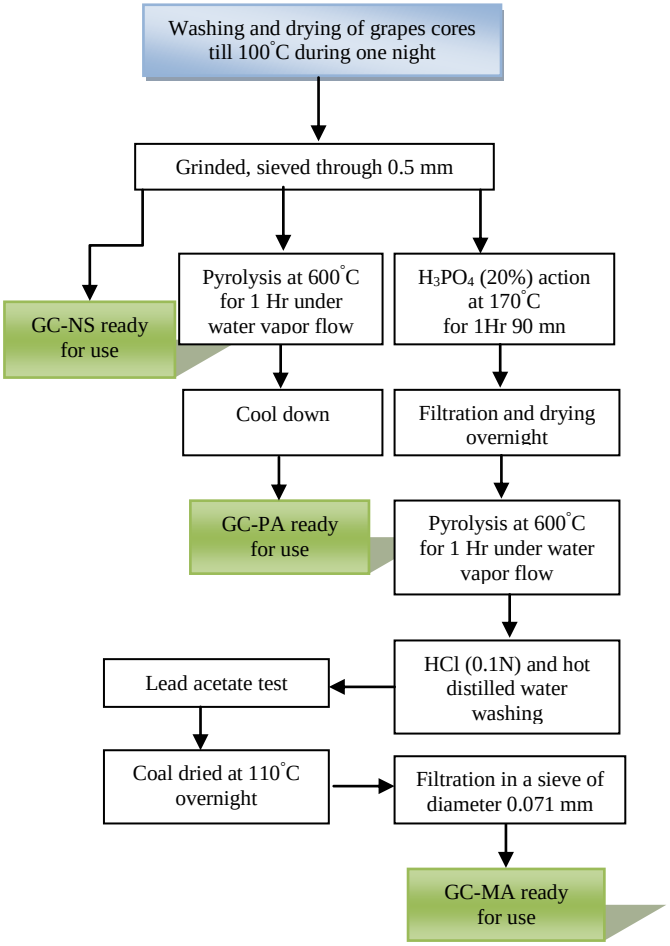
** Experimentally obtained value*

III. 2. Adsorbents preparation

The experimental protocol for activated carbons preparation is shown in scheme 1. The raw material was washed several times with water in order to remove impurities and dust, then dried at 110 °C, the obtained samples were then size reduced in a (Vierzen Crosshop grinde) to increase the contact surface, sieved through 0.5 mm before uses.

In addition, two grape seeds-based activated carbons were prepared in steps process involving a physical activation and mixed activation separately.
The commercially available Aldrich activated carbon was as a reference.

GC-1: Grapes seeds chemically activated with $CaCl_2$
GC-2: Grapes seeds chemically activated with H_3PO_4
GC-3: Grapes seeds chemically activated with KOH
GC-NS: Raw grapes seeds at their natural status
GC-PA: Grapes seeds-physical activation
GC-MA: Grapes seeds-mixed activation
AAC: Aldrich activated carbon
N-2RBL: Nylosan Red-dye



Scheme 1. Steps-process carried out on activated process on grapes cores (Cases: GC-NS/GC-PA/GC-MA preparation)

III. 3. Adsorption experiments

Time, dose and pH, these important parameters were chosen to establish adsorption isotherms for different systems, 25 mL of N-2RBL dye solution with known initial concentrations ranging between 100-2000 mg/L were mixed with an optimal dose of each adsorbent.

The obtained mixture was then agitated at a speed of 200 rpm till equilibrium is reached, separated from solid phase by centrifugation at 4000 rpm and the solution analysed spectrophotometrically at λ_{max} = 500 nm. The following relationships were used to evaluate adsorbent-adsorbate interactions [1].

Table 2. Adsorbents characteristics

Adsorbents	***Iodine index (mg/g)***	***Methylene blue index (mg/g)***	***pHpcz***
GC-NS	420	60	6,3
GC-PA	589	144	7,2
GC-MA	642	209	4,4
AAC	889	297	6,7

Dye uptake $q_e(mg/g)$ and the coefficient of distribution $K_d(L/g)$ are calculated according to the equations (1) and (2)

$$q_e = \frac{(C_0 - C_{eq})}{m*1000} * V \quad (1)$$

$$K_d = \frac{(C_0 - C_{eq})}{C_{eq} * m * 1000} * V \quad (2)$$

Where, C_o and C_{eq} are the initial and the equilibrium concentrations in (mg/L); m the mass of the adsorbent in (g); V the volume in (mL).

The adsorption performance was evaluated using the removal efficiency or elimination rate $R_E(\%)$, according to equation (3):

$$RE(\%) = \frac{(C_0 - C_t)}{C_0} * 100 \quad (3)$$

The equilibrium parameter R_L considered as an important characteristic of Langmuir model is interpreted in table 3. It is defined by equation (4)

$$R_l = \frac{1}{1 + bC_0} \quad (4)$$

Table 3. Nature of the adsorption process

$R_L = 0$	Irreversible process
$0 \langle R_L \langle 1$	Favorable process
$R_L = 1$	Linear process
$R_L \rangle 1$	Unfavorable process

b (L/mg) an equilibrium constant related to the adsorption energy.

III. 4. Langmuir and Freundlich isotherms models

Langmuir and Freundlich isotherms models in their both forms (Linear and non-linear) are usually used to fit experimental data for any adsorption process. The Langmuir isotherm assumes that the adsorption process takes place at specific homogeneous sites within the adsorbent [2].

The Freundlich isotherm is generally used to describe adsorption tests taking place on heterogeneous adsorbents and to define the exponential distribution of active sites and their energies [3],[4].

Where, n and K_F (mg/g) are Freundlich constants respectively related to the adsorption intensity and adsorption energy, q_m (mg/g) represents the maximum adsorption capacity.

In table 5 are mentioned expressions of both models.

Range values significance of the adsorption intensity "n" is given in table 4.

Table 4. The adsorption intensity

Adsorption intensity versus the adsorption capacity	
$n \langle 1$	Capacity of adsorption is low.
$1 \langle n \langle 2$	The adsorption capacity is moderated
n in the range of 2 to 10	Favorable adsorption

Table 5. Forms of Langmuir and Freundlich isotherms models

Isotherms	***Non-linear***	***Linear***	***Plots***
Freundlich	$q_e = K_F C_{eq}^{1/n}$	$\ln(q_e) = \ln K_F + (1/n) * \ln(C_e)$	$\ln(q_e)$ *VS* $\ln(C_e)$
Langmuir-type I	$q_e = \frac{q_m b C_e}{1 + bC_e}$	$C_e/q_e = (C_e/q_m) + (1/b * q_m)$	C_e/q_e *VS* C_e
Langmuir-type II		$1/q_e = (1/b * q_m) * (1/C_e) + (1/q_m)$	$1/q_e$ *VS* $1/C_e$
Langmuir-type III		$q_e = q_m - (1/b) * (q_e/C_e)$	q_e *VS* q_e/C_e
Langmuir-type IV		$q_e/C_e = b * q_m - b * q_e$	q_e/C_e *VS* q_e

III. 5. Error functions analysis

The statistical aspect is very important to assess the convergence of models, R^2 is part of the error function, higher value of this coefficient means the model is well represented, in the other hand, it is very important also to calculate error functions such as: the *APE* (Average percentage error), the *RMSE* (Root mean square error) and the χ^2 (Chi-square), lowest values found from these errors functions mean that the experimental and the calculated data are in good agreement; better is the curve fitting and best model convergence becoming then favorable.

$$Chi - SquareStatistic = x^2 = \sum \frac{(q_{e,\exp} - q_{e,cal})^2}{q_{e,cal}} \quad (5)$$

$$RMSE = \sqrt{(1/N-2) * \sum_1^N (q_{e,\exp} - q_{e,cal})^2} \quad (6)$$

$$APE = (\sum_1^N (|q_{e,\exp} - q_{e,cal}| / q_{e,\exp}) / N) * 100 \quad (7)$$

With, N is the number of observations in the experimental data.

It has been reported that using R^2 alone is not enough to predict best-fitting solution of different isotherms [5-6], that is why the study other error function is very important.

IV. RESULTS AND DISCUSSION

IV. 1. Adsorption of N-2RBL by GC-NS

Results of the adsorption isotherm using an adsorbent dose of 0.1g are:

- The highest values of K_d and R_E are equal to 2.91 L/g and 92.1 % respectively at C_o = 500 mg/L and an uptake q_e = 115.13 mg/g. In the other hand, the lowest values of K_d and R_E are obtained at the highest initial concentration C_0.

- The highest equilibrium factors R_L values for linear and non-linear Langmuir isotherms models correspond to the lowest initial and equilibrium concentrations, models are favorable because the separation factor is between $0 < R_L < 1$.

- The linear Langmuir isotherm (type-I) is a valid model, its coefficient of determination is equal to 0.969; it has an adsorption energy and a maximum adsorption capacity equal to 0.0204 L/mg and 156.433 mg/g respectively.

- The non-linear Langmuir isotherm model is also valid, its adsorption energy is higher than the linear Langmuir isotherm type-I it is equal to 0.0301 L/mg.

- Both forms of Freundlich isotherms (linear and non-linear) are favorable, their intensities and adsorption energies are equal to 3.599, 2.535 and 27.69/15.228 mg/g respectively.
All isotherm models fittings are represented in Figure-2

IV. 2. Adsorption of N-2RBL by GC-MA
- The lowest elimination rate and the lowest coefficient of distribution correspond to higher C_o, the highest value of the R_E (%) is 97.7 % obtained at C_o=500 mg/L and GC-MA adsorbent dose of 4 g/L.

- By comparison between linear Langmuir isotherms models, the model type-I presents the highest coefficient of determination and maximum adsorption capacity, they are equal to 0.973 and 363.139 mg/g respectively and its errors functions values were found very low, the non-linear Langmuir isotherm model is also valid because its adsorption energy and capacity are important and R^2 =0.9249, separation factors are less than 1 which mean that Langmuir models are favorable.

- Taking into consideration the adsorption intensity values we can say that both forms of Freundlich isotherms are favorable with an advantage for the non-linear model, its coefficient of determination and the maximum adsorption capacity are equal to 0.9466 and 40.79 mg/g respectively.
All isotherm models fittings are represented in Figure-4

IV. 3. Adsorption of N-2RBL by GC-PA
By using 0.2 g of grapes cores activated physically with a solution of N-2RBL at initial concentration equal to 400 mg/L; the removal efficiency and the coefficient of distribution are the highest and respectively equal to 94.25 % and 2.05 L/g.

- The highest maximum adsorption capacity and a high R^2 are obtained from the linearized Langmuir isotherm model type-II. They are respectively equal to 424.87 mg/g and 0.952. The model describes well the equilibrium data because values of *RMSE* ; *APE* and Chi-square χ^2 are very low, which is a sign of convergence between experimental and calculated values.

The non-linear Langmuir isotherm model presents positive results; the maximum adsorption capacity is equal to 229 mg/g, the coefficient of determination and the adsorption energy are equal to 0.877 and 0.0076 L/mg respectively and the *APE* is about 26 %.

- The linear and non-linear Freundlich isotherms models have an acceptable R^2 , errors functions values of the non-linear model are greater than the linear isotherm, the adsorption intensities are ranked between $1\langle n\langle 2$ which significates that the adsorption capacities are moderate.
All isotherm models fittings are represented in Figure-6

IV. 4. Adsorption of N-2RBL by AAC
- By using 0.1 g of Aldrich activated carbon and at initial N-2RBL concentration equal to 500 mg/L, the removal percentage reached 96.05 %, in parallel with a coefficient of distribution equal to 6.08 L/g.

- The best fit found for linear Langmuir isotherms models is related to the model type-I, errors functions values are very low and its R^2 =0.974 and the adsorption energy is equal to 0.0218 L/mg, the non-linear model is favorable, the adsorption intensity found is equal to 0.032 L/mg.

- Linear and non-linear Freundlich isotherms models are favorable because their adsorption intensities are equal to 2.155 and 3.17 respectively
All isotherm models fittings are represented in Figure-8

IV 5. Adsorption of N-2RBL by GC-1/GC-2/GC-3
- The activation of grapes cores-based activated carbons by H_3PO_4 or by KOH presents good results in the non-linear and linear Langmuir isotherms models. The linear Langmuir isotherm model type-II applied for the adsorption of N-2RBL by GC-3, gives the best correlation between the calculated data and experimental one, with maximum adsorption capacity of 336.951 mg/g and a value of 0.0395 L/mg as adsorption energy [1].

- Linear Freundlich isotherms models for the adsorption of N-2RBL by GC-2 or by GC-1 are moderate because the adsorption intensities are less than 1, in the other hand, the adsorption of the same dye by GC-3 is good [1].

- Non-linear Langmuir isotherm gives the maximum adsorption capacity to be 410.4 mg/g onto GC-3 with an *APE* =16.19 % and R^2 = 0.9585

Table 6. Parameters of Langmuir and Freundlich isotherms models for GC samples [1]

Isotherms	GC-1		GC-2		GC-3	
Langmuir	b	q_m	b	q_m	b	q_m
Langmuir- I	-	-	0.0074	509.17	-	-
Langmuir- II	0.0035	339.75	-	-	0.0395	336.95
Non-Linear	-	-	0.01004	470.6	0.0203	410.4
Freundlich	n	K_F	n	K_F	n	K_F
Non-Linear	0.989	0.9097	2.302	27.5	2.65	42.57
Linear	1.13	1.57	1.696	12.304	2.128	28.15

Table 7. Parameters Langmuir and Freundlich isotherms models

Models	Isotherm Type	R^2	b (L/mg)	q_m (mg/g)	n	K_F (mg/g)	χ^2	RMSE	APE
Adsorption isotherm of N-2RBL by Grapes cores in their natural status GC-NS									
$q_e = 0.205 * C_e + 67.83$	Experimental	0.584	–	–	–	–	83.084	28.5	42.68
$C_e/q_e = 0.314 + 0.0064 * C_e$	Linear Langmuir – I	0.969	0.0204	156.43	–	–	0.617	0.188	20.3
$1/q_e = 0.0029 + 0.534 * 1/C_e$	Linear Langmuir – II	0.673	0.0054	343.89	–	–	0.025	0.008	43.25
$q_e = 124.79 - 18.15 * (q_e/C_e)$	Linear Langmuir – III	0.204	0.0551	124.79	–	–	130.66	39.45	63.23
$q_e/C_e = 2.52 - 0.011 * q_e$	Linear Langmuir – IV	0.204	0.0112	224.56	–	–	5.61	0.981	81.31
$q_e = \frac{4.63 * C_e}{1 + 3.08E-02 * C_e}$	Non – Linear Langmuir	0.8287	0.0301	151	–	–	40.93	18.3	25.33
$q_e = 27.68 * C_e^{0.277}$	Non – Linear Freundlich	0.7301	–	–	3.6	27.69	60.08	22.97	32.73
$\ln(q_e) = 2.723 + 0.394 * \ln(C_e)$	Linear Freundlich	0.619	–	–	2.535	15.23	0.332	0.408	6.86
Adsorption isotherm of N-2RBL by grapes cores-based activated carbon-Mixed activation GC-MA									
$q_e = 0.666 * C_e + 104.62$	Experimental	0.8168	–	–	–	–	177.41	44.6	49.96
$C_e/q_e = 0.138 + 0.0028 * C_e$	Linear Langmuir – I	0.973	0.0199	363.14	–	–	0.21	0.064	25.14
$1/q_e = 0.0014 + 0.155 * 1/C_e$	Linear Langmuir – II	0.715	0.0092	700.46	–	–	0.02	0.006	39.73
$q_e = 274.69 - 21.006 * (q_e/C_e)$	Linear Langmuir – III	0.553	0.0476	274.7	–	–	383.63	69.65	80.17
$q_e/C_e = 9.29 - 0.026 * q_e$	Linear Langmuir – IV	0.553	0.0263	352.89	–	–	12.77	2.47	48.01
$q_e = \frac{9.75 * C_e}{1 + 2.99E-02 * C_e}$	Non – Linear Langmuir	0.9249	0.0299	325.7	–	–	72.85	28.56	21.05
$q_e = 40.79 * C_e^{0.355}$	Non – Linear Freundlich	0.9466	–	–	2.814	40.79	75.43	24.08	28.47
$\ln(q_e) = 3.265 + 0.45 * \ln(C_e)$	Linear Freundlich	0.804	–	–	2.222	26.2	0.354	0.354	5.472
Adsorption isotherm of the N-2RBL by grapes cores-based activated carbon-physical activation GC-PA									
$q_e = 0.441 * C_e + 33.813$	Experimental	0.929	–	–	–	–	60.38	16.1	32.08
$C_e/q_e = 0.556 + 0.0044 * C_e$	Linear Langmuir – I	0.83	0.0079	225.117	–	–	0.72	0.27	19.4
$1/q_e = 0.0024 + 0.616 * 1/C_e$	Linear Langmuir – II	0.952	0.0038	424.875	–	–	0.02	0.004	26.16
$q_e = 178.63 - 72.44 * (q_e/C_e)$	Linear Langmuir – III	0.598	0.0138	178.631	–	–	208.62	38.42	72.13
$q_e/C_e = 1.94 - 0.008 * q_e$	Linear Langmuir – IV	0.598	0.0082	234.631	–	–	2.06	0.41	38.23
$q_e = \frac{1.75 * C_e}{1 + 7.63E-02 * C_e}$	Non – Linear Langmuir	0.877	0.0076	229	–	–	57.28	21.26	18.43
$q_e = 7.32 * C_e^{0.544}$	Non – Linear Freundlich	0.9253	–	–	1.838	7.326	42.5	16.57	21.81
$\ln(q_e) = 1.755 + 0.592 * \ln(C_e)$	Linear Freundlich	0.899	–	–	1.689	5.784	0.251	0.264	5.51
Adsorption isotherm of the N-2RBL by the Aldrich activated carbon AAC									
$q_e = 0.487 * C_e + 106.08$	Experimental	0.68	–	–	–	–	225	49.85	55.79
$C_e/q_e = 0.15 + 0.0033 * C_e$	Linear Langmuir – I	0.974	0.0218	305.49	–	–	0.23	0.079	18.83
$1/q_e = 0.0002 + 0.25 * 1/C_e$	Linear Langmuir – II	0.851	0.0007	5697.32	–	–	0.04	0.004	40.98
$q_e = 260.37 - 28.16 * (q_e/C_e)$	Linear Langmuir – III	0.459	0.0355	260.37	–	–	309.7	64.88	82.24
$q_e/C_e = 6.18 - 0.016 * q_e$	Linear Langmuir – IV	0.459	0.0163	379.49	–	–	7.64	1.56	60.82
$q_e = \frac{9.24 * C_e}{1 + 3.2E-02 * C_e}$	Non – Linear Langmuir	0.9271	0.03205	288.4	–	–	52.19	23.82	23.76
$q_e = 43.73 * C_e^{0.315}$	Non – Linear Freundlich	0.8382	–	–	3.17	43.73	123.75	35.49	39.33
$\ln(q_e) = 3.09 + 0.464 * \ln(C_e)$	Linear Freundlich	0.736	–	–	2.155	21.99	0.397	0.399	6.825

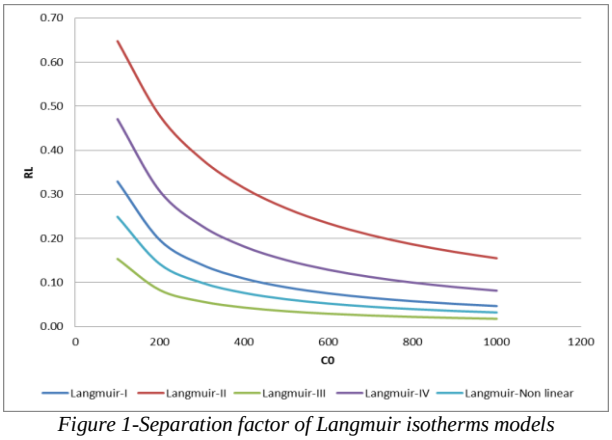


Figure 1-Separation factor of Langmuir isotherms models (GC-NS case)

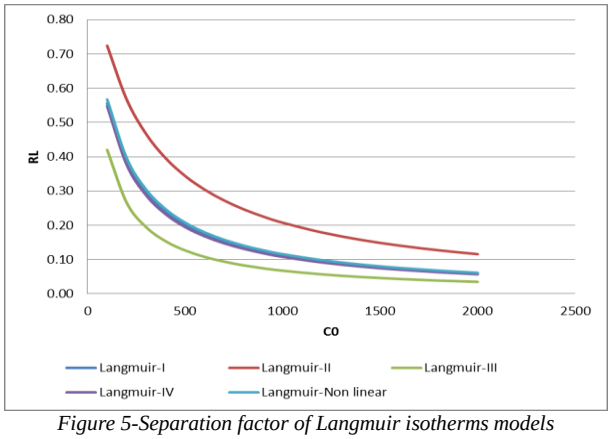


Figure 5-Separation factor of Langmuir isotherms models (GC-PA case)

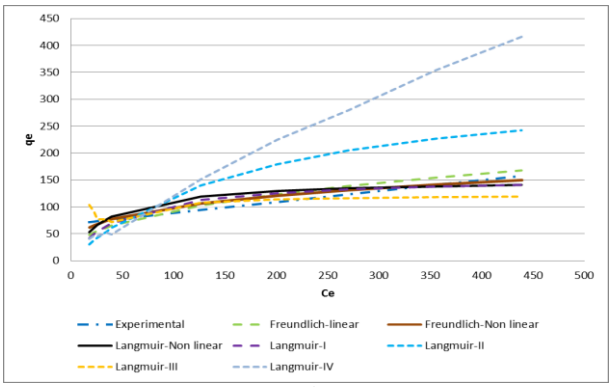


Figure 2-Representations of Langmuir and Freundlich isotherms models for GC-NS

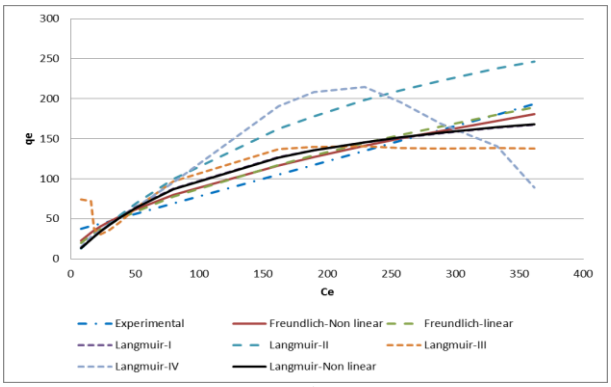


Figure 6-Representations of Langmuir and Freundlich isotherms models for GC-PA

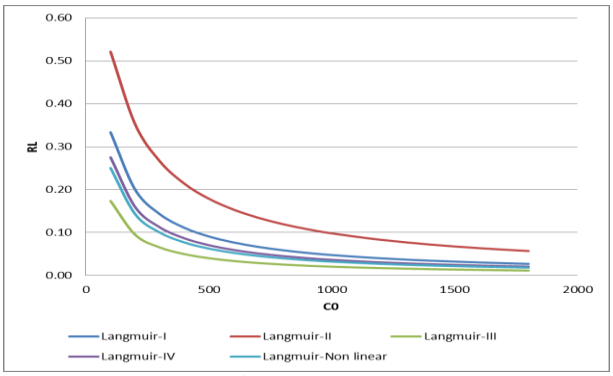


Figure 3-Separation factor of Langmuir isotherms models (GC-MA case)

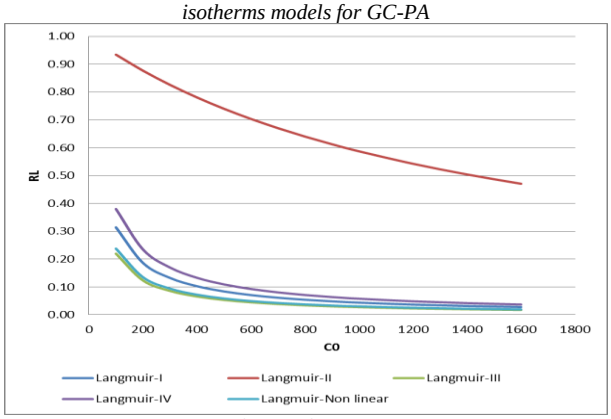


Figure 7-Separation factor of Langmuir isotherms models (GC-AAC case)

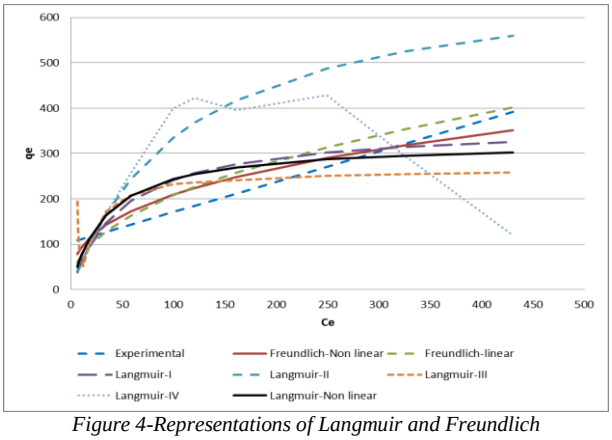


Figure 4-Representations of Langmuir and Freundlich isotherms models for GC-MA

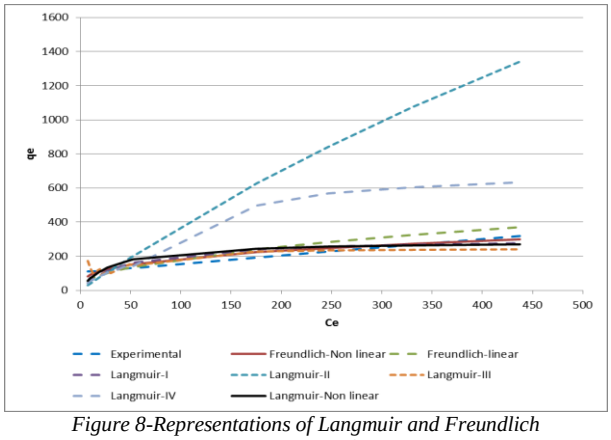


Figure 8-Representations of Langmuir and Freundlich isotherms models for AAC

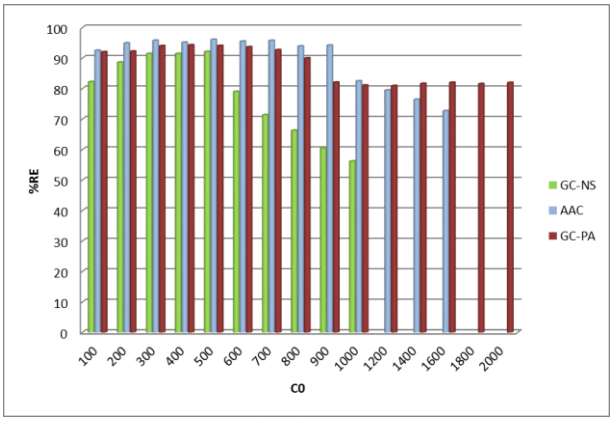


Figure 9-Evolution of R_E for the adsorption isotherms of N-2RBL (/GC-NS/GC-PA /AAC cases)

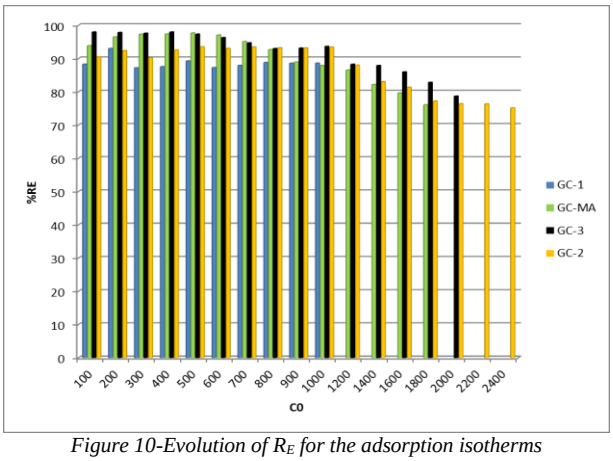


Figure 10-Evolution of R_E for the adsorption isotherms of N-2RBL (GC-1/GC-2/GC-3/GC-MA cases)

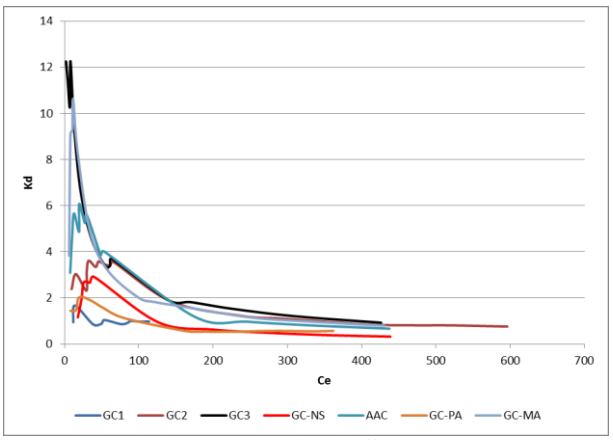


Figure 11-Distribution coefficient curves (GC-1/GC-2/GC-3/GC-NS/GC-PA/GC-MA/AAC cases)

IV 4. Comparative study of Langmuir and Freundlich isotherms models in their both forms

- Langmuir linear isotherms models type-I are the most favorable for the adsorption of N-2RBL by GC-NS/GC-MA/AA, their adsorption energies are very close and equal to 0.02 L/g, the highest maximum adsorption of N-2RBL onto GC-MA is equal to 363.14 mg/g and the lowest one was 156.43 mg/g using GC-NS.
Langmuir linear isotherm model type II gave also good result for GC-PA case.

- For the non-linear isotherms models, the highest maximum adsorption capacity was 325.7 mg/g using GC-MA sample, the lowest is related to the adsorption of the same dye by GC-NS

- All the linear Freundlich isotherms models are favorable except the case of the adsorption of N-2RBL by the GC-PA which is moderate in addition its energy is equal to 5.78 mg/g which is the lowest.
The adsorption of N-2RBL by GC-MA presents the highest energy of adsorption, in the other hand, the lowest heterogeneity factor relates for the case of GC-NS.

- All the non-linear Freundlich isotherms models are favorable except the case of the adsorption of N-2RBL by the GC-PA which is moderate and its energy is the lowest.
The most important adsorption intensity is related to the adsorption of N-2RBL by AAC it is equal to 3.17 , errors functions values are significant and the coefficient of determination is equal to 0.8382, in the other hand, the adsorption of N-2RBL by the GC-MA presents the highest R^2 and the lowest APE.

V. CONCLUSION AND FUTURE SCOPE

At initial N-2RBL concentration equal to 100 mg/L and 0.1 g of the adsorbent, the removal efficiency was 98 % for GC-3 case; 93.87 % for GC-MA; 92.5 % for AAC; 90.5 % for GC-2; 88.31 % for GC-1 and 82.19 % for GC-NS, however it was 92 % for 0.2 g of GC-PA.

Except for the linear Langmuir isotherm model type-II regarding the adsorption of N-2RBL by the GC-PA, all the other favorable isotherms models are type-I and the best fits are related to GC-MA and AAC, their R^2 tend to the unit and the adsorption capacities are equal to 363.14 and 305.49 mg/g respectively.

The non-linear Langmuir isotherms models present important adsorptions energies compared to the linear Langmuir isotherms, best fits are related to GC-MA and AAC, the adsorption intensities and capacities are equal to 0.03/0.032 L/mg and 325.7/288.4 mg/g respectively.

Non-linear Freundlich isotherms models present better coefficients of determination compared to the linear Freundlich models, adsorptions are favorable for GC-NS; GC-MA and AAC and it is moderate for the case of GC-PA, best fits are related to GC-MA and AAC.

Adsorption energies and capacities found from the non-linear Freundlich isotherms models are much higher than those found from the linear Freundlich isotherms models.

There is a need to study the statistical aspect of equation and to do not be limited on R^2.
Non-linear isotherms models describe very well the adsorption process and they are close to the reality, that is why it worth to study these equations.

In this study we have used an agriculture waste which is the grapes cores as an adsorbent, this raw material was chemically & physically treated in order to ameliorate its structure especially in matter of porosity and capillarity, we have also used raw grapes cores at their natural status, for the mean reason, which is to select the best adsorbent, in parallel we have studied an industrial adsorbent which is Aldrich activated carbon, results were compared and best models were justified.

For the capture of azo anion acid dyes such as Nylosan Red, we recommend to use activate chemically grapes cores-based activated carbons by KOH or acid H_3PO_4 or proceed for mixed activation.

The abandonment of the agriculture wastes is not a good process, we have confirmed that they can be recovered treated enhanced for future use, by this manner we will preserve the other natural resources and contribute in the sustainable development and protect the environment.

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