

Simulation of Adsorption kinetics of malachite green onto coffee residues

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Abstract – *In this work, coffee residues were used as a zero-cost adsorbent for the application of adsorption removal of malachite green dye from simulated aqueous solution. Coffee residues were characterized by the point of zero charge (Mass titration). The point of zero charge of coffee residues was 4.37. Adsorption kinetics of malachite green onto coffee residues were studied in a batch system. The effects of pH and contact time were examined. The malachite green maximum adsorption occurred at pH 6 and the lowest adsorption occurred at pH 2. The apparent equilibrium was reached after 240 min. Optimal experimental conditions were determined. In order to determine the best-fit-kinetic adsorption, the experimental data were analyzed using pseudo-first-order, pseudo-second-order, pseudo-third-order, Esquivel, and Elovich models. Linear regressive method and non-linear regressive method were used to obtain the relative parameters. The statistical functions were estimated to find the suitable method which fit better the experimental data. Both methods were suitable to obtain the parameters. The linear elovich(type 1 and 2) model was best to fit the equilibrium data. The present work showed that coffee residues can be used as a low cost adsorbent for the malachite green removal from water.*

Keywords: *coffee residues (CR), linear, non-linear regression, Adsorption kinetics, error estimation, regression coefficient (R^2)*

I. Introduction

The textile industry is one of industrial waste water source. This contaminated water is very toxic for the human and animals [1]. Malachite green is used in coloring paper, dyeing cottons, wools, silk, leather and coating for paper stock. The treatment of effluents containing such dyes is of great interest due to its harmful impacts on receiving waters [2].

Chemical coagulation–flocculation [3] different type of oxidation processes [4] biological process [5], membrane-based separation processes [6] and adsorption [7] were the treatments used in the purification of waters. The best efficient method used for the quickly removal of dyes from the aqueous solution is the physical adsorption [8].

Biosorbents such as: wood sawdust [9], waste-biomass [10], delonix regia [11], agricultural solid waste [12] are able to remove efficiently color from water. However, there are relatively limited studies done on the cationic dyes adsorption by CR (coffee residues) [13]. The potential application of CR as an adsorbent reported for heavy metal ions [14, 15] but few papers have been

published.

This work aims to understand the potential of CR for removal of malachite green dye from simulated aqueous solution in batch mode. The adsorption efficiency of malachite green was investigated in order to optimize the experimental parameters, such as contact time and pH at an agitation speed of 300 rpm, initial adsorbent concentration of 5 mg/L and temperature of 25°C. The statistical functions were used to estimate the error deviations between experimental and theoretically predicted adsorption values, including linear and non-linear method. The optimization procedure required a defined error function in order to evaluate the fit of equation to the experimental data.

II. Experimental

MG (4-(4-(dimethylamino) alpha-phenylbenzylidene)-2,5-cyclohexadien-1-ylidene) dimethylammonium chloride, $C_{23}H_{25}ClN_2$, Mw = 364 g/mol, Figure. 1.) used in the present study was purchased from Merck (Germany) and was selected from the list of dyes normally used in Algeria. The CR (from cafeterias) were

washed several times with deionized water to remove the color and dried at 105 °C for 5 h in a convection oven. The residual organics and lipids were respectively

removed by methanol and petroleum ether. After this procedure, the CR were washed again by distilled water.

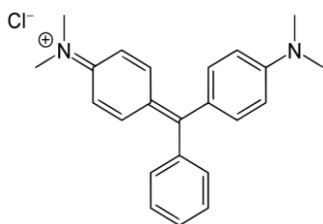


Figure. 1. Structure of malachite green [16].

The CR were characterized by pH measurement of the pH_{PZC} (point of zero charge).

To find out pH_{PZC} , the MT (mass titration) method [17, 18] was used. This method needs only a few instruments such as: balance, magnetic stirrers and a pH-meter [19]. This consists of a simple titration that requires a smaller amount of solid sample than other methods [20].

The MT method is based on the fact that pH approaches the limiting value (pH_{∞}) by addition of solid sample to an aqueous solution. The limiting pH_{∞} value, at a high solid content, is then equal to pH_{PZC} [21]. Each addition was 0.1 g of the CR sample to 50 ml of NaCl (0.1M). After each solid addition, the pH was measured and, when equilibration was achieved, a new amount of sample was added to produce a new pH change. This procedure was repeated with a different initial pH until a pH was found where no pH change occurs with the addition of more sample. This is pH where proton adsorption is zero [22]. As shown in Figure. 2., the pH_{PZC} of CR was determined to be 4.37.

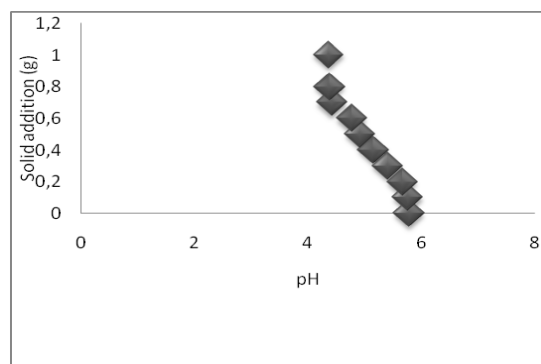


Figure. 2. Mass titration curves of CR, each addition of the solid corresponds to 0.1 g of CR sample.

At $pH < pH_{PZC}$, the surface becomes positively charged, concentrations of H^+ were high and they compete with positively charged MG cation for vacant adsorption sites causing a decrease in dye uptake. At the solution $pH > pH_{PZC}$, the adsorbent surface negatively charged and favors uptake of cationic dyes due to increased electrostatic force of attraction. Thus, MG adsorption onto CR is favoured at pH higher than pH_{PZC} [23]. At pH 5, surface of adsorbent was negatively charged to its maximum extent. Further increase in pH did not increase surface charge intensity as well as adsorption capability. Therefore, pH 5 was used for adsorption studies [2]. These results indicate pH_{PZC} values in the range of 4.37–5 and therefore pH values should be maintained above 5 to ensure a predominant negatively charged surface.

Similar results were found by other authors (Table. 1.).

Material	Aqueous solution	Method	pH_{PZC}	Investigator
CR	0.1 M NaCl	MT	4.37	This study
Greek coffee wastes (COF)	$NaNO_3$ (0.01 M), HNO_3 (0.1 M) and NaOH (0.1 M)	MT	3.3-3.5	[24]
Untreated coffee residues (UCR)	$NaNO_3$ (0.01 M), HNO_3 (0.1 M) and NaOH (0.1 M)	MT	3.5	[13]
Coffee husks (CH)	$NaNO_3$ (0.01 M), HNO_3 (0.1 M) and NaOH (0.1 M)	MT	4.3–4.5	[25, 26]
exhausted coffee wastes (EC)		potentiometric mass titration	3.9	[27]

Table. 1. CR pH_{PZC} values measured in the present study compared to literature.

There is a very good agreement between acid-base potentiometric curves and mass titration curves.

Adsorption Kinetics of MG onto CR was studied in a batch system. The effects of pH and equilibrium time

were examined. The adsorption parameters were optimized. In each experiment pre weighed amount of adsorbent (100 mg) was added to 50 mL of dye solution (5 mg/l) taken in a 250 mL of conical flask and 0.1 M NaOH or 0.1 M HCl were added to adjust the pH. This solution was agitated at 300 rpm and centrifuged. The

$$q = (C_0 - C) \frac{V}{M} \quad (1)$$

where C_0 is the initial MG concentration (mg/L), C is the dye concentration at time t , V is the solution volume (in L) and M is the adsorbent mass (g) [28].

The effect of pH was evaluated by mixing 0.1 g of adsorbent with 50 mL of malachite green simulated aqueous solution of 5 mg/L. The solution pH value was varied from 2 to 12, by adding 0.1M NaOH or 0.1M HCl solutions. The suspension was shaken for 24h at 25°C.

Kinetic experiments were performed by mixing 50 mL of dye solution (5 mg/L) with 100 mg (0.1 g) of adsorbent during different time (5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 180, 240 and 300 min) . The initial pH for each dye solution was set at 6. The suspensions were kept under agitation during 24 hours. Malachite green concentrations in the supernatants were determined and the amount adsorbed of malachite green was calculated.

III. Results and discussion

In order to study the effect of every parameter, it is necessary to fix the values of others. The elimination of pollutant from simulated aqueous solution by adsorption is extremely influenced by the medium of the solution which affects the nature of the adsorbent surface charge, the ionization extent, the aqueous adsorbate species speciation and the adsorption rate. The adsorptive process through functional groups dissociation on the adsorbate and adsorbent were affected by a pH change [29]. The adsorption of malachite green increases with the increasing pH of the solution.

According data presented in Figure. 3., the best value of adsorption capacity, $q_e = 2.15$ mg/g, was recorded at pH 6.

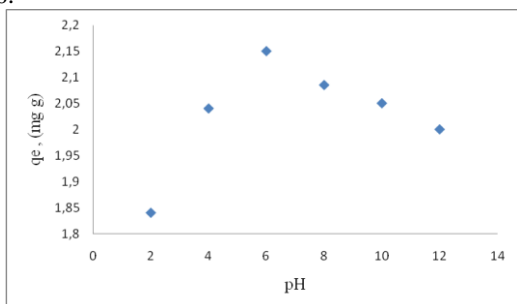


Figure. 3. The initial pH effect on the CR equilibrium adsorption capacity.

From this study, it is obvious that in the basic medium, the negatively charged species tends dominating and the

MG concentration in solution was determined at $\lambda_{max} = 620$ nm by spectrophotometer UV-1700 PHARMA SPEC SHIMADZU. The MG adsorbed amount per mass unit of adsorbent at time t , q (mg/g), (Eq. (1)) was calculated as:

surface began to acquire a negative charge. In this case, the adsorbent surface is negatively charged. The malachite green adsorption increased due to the increasing of electrostatic attractions between the negative charge of CR particles and the positive charge of malachite green species.

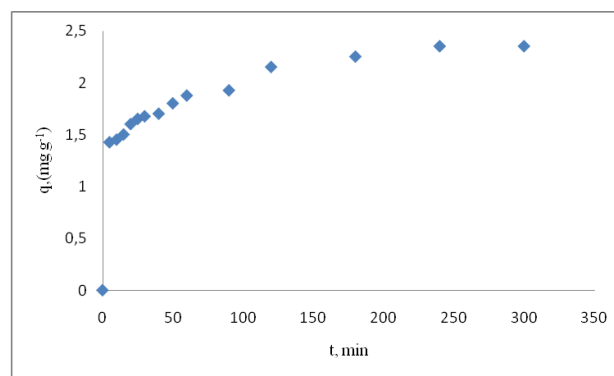


Figure. 4. MG adsorption kinetic on CR.

Figure. 4. illustrates the effect of contact time on decolorization (dye adsorption) with CR. The plot (simulated aqueous solution) could be divided in three zones: (i) 0-30 min, which indicated the fast adsorption of MG, suggesting rapid external diffusion and surface adsorption; (ii) 30-60 min, showed a gradual equilibrium, and (iii) 60-300 min, indicated the plateau of the equilibrium state.

The adsorption was rapid at the initial stage of the contact, but it gradually slowed down until the equilibrium.

The fast adsorption at the initial stage can be attributed to the fact that a large number of surface sites are available for adsorption.

After a lapse of time, the remaining surface sites are difficult to be occupied because of the repulsion between the solute molecules of the solid and bulk phases make it took long time to reach equilibrium.

Adsorption is a complex process whereby it is influenced by several parameters related to adsorbent and to the physicochemical conditions under which the process is carried out [30]. In order to understand the mechanism of the adsorption process, the following equations: pseudo-first order (Lagergren Model) [2], pseudo-second order [31], esquivel [32], pseudo-third order [24], and elovich [33] were selected to fit the experimental kinetic data. Equations of these models were illustrated in Table. 2.

Applied model	Non Linear form	Linear form	Reference
Pseudo-first order			
Pseudo-first order (type1)	$q = q_e(1 - e^{-k_1 t})$	$\log(q_e - q) - \log(q_e) = -\frac{k_1 t}{2.303}$	[34]
Pseudo-first order (type2)		$\ln(q_e - q) - \ln(q_e) = -k_1 t$	[35]
Pseudo-first order (type3)	$C = C_0 e^{-k_1 t}$	$\ln\left(\frac{C}{C_0}\right) = -k_1 t$	[36]
Pseudo-first order (type4) Helfrich		$\ln\left[1 - \frac{C_0 - C}{C_0 - C_e}\right] = -k_1 t$	[37]
Pseudo-second order			
Pseudo-second order type 1		$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	[38]
Pseudo-second order type 2		$\frac{1}{q} = \frac{1}{k_2 q_e^2 t} + \frac{1}{q_e}$	[1]
Pseudo-second order type 3	$q = q_e \left[1 - \frac{1}{1 + k_2 t}\right]$	$\left(\frac{1}{q} - \frac{1}{q_e}\right) q_e^2 = \frac{1}{k_2 t}$	[39]
Pseudo-second order type 4		$q = q_e - \left(\frac{1}{k_2 q_e}\right) \frac{q}{t}$	[40]
Pseudo-second order type 5		$(q - q_e) q_e = -\left(\frac{1}{k_2}\right) \frac{q}{t}$	[41]
Pseudo-second order type 6		$\frac{q}{t} = k_2 q_e^2 - k_2 q q_e$	[42]
Pseudo-second order type 7		$\frac{1}{q_e - q} - \frac{1}{q_e} = k_2 t$	[43]
Pseudo-second order type 8		$\frac{1}{t} = k_2 q_e^2 \left(\frac{1}{q}\right) - k_2 q_e$	[44]
Pseudo-second order type 9		$\frac{q_e}{q_e - q} - 1 = k_2 t$	[45]
Pseudo-second order type 10		$\frac{\theta}{1 - \theta} = k_2 t$	[46]

Pseudo-second order type 11		$C - \frac{1}{C_0} = k_2 t$	[47]
Pseudo-second order type 12		$\frac{1}{C} - \frac{1}{C_0} = k_2 t$	[41]
Pseudo-second order type 13		$\frac{1}{C_0 - C} = k_2 t + b$	[48]
Esquivel model (type 1)	$q = q_e \left(\frac{t}{t + K_E} \right)$	$\frac{1}{q} = \left(\frac{K_E}{q_e} \right) \frac{1}{t} + \frac{1}{q_e}$	[32]
Esquivel model (type 2)	$q = q_e \left(\frac{t}{t + K_E} \right)$	$\left(\frac{1}{q} - \frac{1}{q_e} \right) q_e = K_E \frac{1}{t}$	[32]
Pseudo-third order	$q = q_e \left[1 - \frac{1}{(1 + 2k_3 t)^{1/2}} \right]$	$\frac{1}{q^2} = \frac{1}{q_e^2} + k_3 t$	[24]
Elovich (type1)	$\frac{dq}{dt} = k_4 \exp(-k_5 q)$	$q = k_5 \ln(k_5 k_4) + k_5 \ln(t)$	[33]
Elovich (Roginsky-Zeldovich) (type 2)	$\frac{dq}{dt} = k_7 \exp(k_6 q)$	$q = (1/k_6) \ln(k_6 k_7) + (1/k_6) \ln(t)$	[49]

Table. 2. Adsorption kinetics model and their linear and non linear forms

where k_1 is pseudo-first order rate constant (min^{-1}), k_2 is pseudo-second order rate constant ($\text{g}/(\text{mg min})$), k_3 is pseudo-third order rate constant ($\text{g}^2/(\text{mg}^2 \text{min})$), K_E is esquivel rate constant (min), k_4 is elovich rate constant ($\text{mg}/(\text{g min})$), k_5 is extent of surface coverage and activation energy of the process (g/mg), k_6 extent of surface coverage and activation energy of the process

(g/mg), k_7 elovich rate constant ($\text{mg}/(\text{g min})$), q_e is amount of adsorption at equilibrium (mg/g), and θ dimensionless parameter ($=q/q_e$).

A non-linear and linear fitting procedure using Excel and Origin software were used respectively. The constants of all models were given in Table. 3.

Model	Linear Method	Non-linear Method
Pseudo-first order (type 1)		
q_e	2.352	1.328
k_1	0.023	637.406
R^2	0.898	-0.687
Equation	$\log(q_e - qt) - \log(q_e) = -0.010 * t$	$q = 1.328 * (1 - \exp(-637.406 * t))$
Pseudo-first order (type 2)		
q_e	2.352	
k_1	0.024	
R^2	0.898	
Equation	$\ln(q_e - qt) - \ln(q_e) = -0.024 * t$	
Pseudo-first order (type 3)		
C_0	5	5

k_1	0.012	0.046
R^2	0.294	0.487
Equation	$\ln(C/C_0)=-0,012*t$	$C=5*\exp(-0,032*t)$
Pseudo-first order (type 4)		
C_0	5	
k_1	0.015	
R^2	0.668	
Equation	$\ln(1-((C_0-C)/(C_0-C_e))=-0,015*t$	
Pseudo-second order (type 1)		
q_e	2,427	2.157
k_2	0,032	0.188
R^2	0,996	0.903
Equation	$(t/q) = 0.412*t + 5,233$	$q=2.157*(1-(1/(1+0,188*t)))$
Pseudo-second order (type 2)		
q_e	1,996	
k_2	0.178	
R^2	0,621	
Equation	$1/q = 1.408*(1/t) + 0,501$	
Pseudo-second order (type 3)		
q_e	1.990	
k_2	0.180	
R^2	0.621	
Equation	$((1/q)-(1/q_e))*(q_e^2) = 5.539*(1/t)$	
Pseudo-second order (type 4)		
q_e	3.068	
k_2	0.026	
R^2	0.661	
Equation	$q = - 12.470*(q/t) + 3.068$	
Pseudo-second order (type 5)		
q_e	2.034	
k_2	0.157	
R^2	0.537	
Equation	$(q-q_e)*q_e = -6.372*(q/t)$	
Pseudo-second order (type 6)		
q_e	2.233	
k_2	0.074	
R^2	0.537	
Equation	$(q/t) = -0.167*q + 0.373$	
Pseudo-second order (type 7)		
q_e	2.505	
k_2	0.021	
R^2	0.962	
Equation	$(1/(q_e-q))-(1/q_e) = 0.021*t$	
Pseudo-second order (type 8)		
q_e	2.146	
k_2	0.095	
R^2	0.621	
Equation	$1/t=0.440*(1/q)-0.205$	
Pseudo-second order (type 9)		
q_e	2.505	
k_2	0.053	
R^2	0.962	
Equation	$(q_e/(q_e-q))-1 = 0.053*t$	
Pseudo-second order (type 10)		
q_e	2.505	
k_2	0.053	
R^2	0.962	

Equation	$(\theta/(1-\theta)) = 0.053*t$	
Pseudo-second order (type 11)		
C_0	5	
k_2	0.002	
R^2	-1.47	
Equation	$(C-(1/C_0)) = 0.002*t$	
Pseudo-second order (type 12)		
C_0	5	
k_2	0.011	
R^2	0.961	
Equation	$((1/C)-(1/C_0)) = 0.011*t$	
Pseudo-second order (type 13)		
C_0	5	
k_2	$-1 \cdot 10^{-4}$	
R^2	0.792	
Equation	$(1/(C_0-C)) = -1 \cdot 10^{-4}*t+0.318$	
Esquivel Model (type 1)		
q_e	1.996	2.157
k_E	2.810	5.324
R^2	0.621	0.903
Equation	$1/qt = 1.408*(1/t)+0.501$	$q=2.157*(t/(t+5.324))$
Esquivel Model (type 2)		
q_e	1.990	
k_E	2.783	
R^2	0.621	
Equation	$((1/qt)-(1/q))*q_e = 2.783*(1/t)$	
Pseudo-third order (type 1)		
q_e	1.571	
k_3	$-1 \cdot 10^{-3}$	
R^2	0.739	
Equation	$(1/q^2)=-1*10^{-3}*t+0.405$	
Elovich (type 1)		
k_4	98.178	
k_5	0.260	
R^2	0.984	
Equation	$q = 0.259*\ln(t) + 0.841$	
Elovich (type 2)		
k_6	6.624	
k_7	3.850	
R^2	0.984	
Equation	$q = 0.259*\ln(t) + 0.841$	

Table. 3. A linear and non-linear Pseudo-first order, Pseudo-second order, Esquivel, Pseudo-third order and Elovich kinetics isotherms constants related to the

adsorption of MG onto CR.

The optimization procedure has required a defined error function in order to evaluate the fit of equation to the experimental data. The best-fitting equation is determined using the well-known special functions to

calculate the error deviation between experimental and predicted data. The mathematical equations of these error functions were illustrated in Table. 4.

Error functions	Equations	References
ARED	$ARED = \frac{100}{n} \sum_{i=1}^n \left \frac{q_{exp} - q_{calc}}{q_{exp}} \right _i$	[50]
ARE	$ARE = \frac{\sum q_{calc} - q_{exp} }{n \cdot q_{exp}}$	[51]

$$SAE = EABS \quad SAE = EABS = \sum_{i=1}^n |q_{exp} - q_{calc}| \quad [52]$$

$$ARS \quad ARS = \sqrt{\frac{\sum \left[\frac{(q_{exp} - q_{calc})}{q_{exp}} \right]^2}{(n-1)}} \quad [53]$$

$$MPSD \quad MPSD = 100 \sqrt{\frac{\sum \left[\frac{(q_{exp} - q_{calc})}{q_{exp}} \right]^2}{n-p}} \quad [54]$$

$$\Delta q(\%) = 100 * ARS \quad \Delta q(\%) = 100 \sqrt{\frac{\sum \left[\frac{(q_{exp} - q_{calc})}{q_{exp}} \right]^2}{(n-1)}} \quad [55]$$

$$SSE \quad SSE = \sum (q_{calc} - q_{exp})^2 \quad [56]$$

$$MPSED \quad MPSED = \sqrt{\frac{\sum \left[\frac{(q_{exp} - q_{calc})}{q_{exp}} \right]^2}{(n-p)}} \quad [57]$$

$$HYBRID \quad HYBRID = \frac{1}{(n-p)} \sum_{i=1}^n \left| \frac{q_{exp} - q_{calc}}{q_{exp}} \right|_i \quad [58]$$

Table. 4. Mathematical equations of error functions.

Where n is the number of experimental data points, q_{calc} is the predicted (calculated) quantity of MG adsorbed onto CR, q_{exp} is the experimental data, p is the number of parameters in each kinetic model, ARED is the average relative error deviation (dimensionless parameter), ARE the is average relative error (dimensionless parameter), ARS is the average relative standard error (dimensionless parameter), HYBRID is the hybrid fractional error function (dimensionless

parameter), $MPSD$ Marquardt's is the percent standard deviation (dimensionless parameter), $MPSED$ Marquardt's is the percent standard deviation (dimensionless parameter), $SAE=EABS$ is the sum of absolute error (mg/g), SSE is the sum of the squares of the errors (mg/g)², and $\Delta q(\%)$ is the normalized standard deviation (mg/g). The constants of all error analysis were represented in Table. 5.

Error functions	ARED	SAE = EABS	MPSED	SSE	HYBRID	ARE	ARS	$\Delta q(\%)=100*ARS$	MPSD
Linear Pseudo-first order type 1	25,865	5,649	0,398	4,288	0,302	0,258	0,382	38,233	48,725
Linear Pseudo-first order type 2	24,944	14,527	5,443	0,388	4,052	0,291	0,249	0,372	37,249
Linear Pseudo-second order type 1	26,761	6,095	0,368	3,797	0,312	0,267	0,354	35,392	45,421
Linear pseudo-second order type 7	73,65	46,593	0,805	156,499	0,859	0,736	0,774	77,394	170,351
Linear pseudo-second order type 9	64,113	40,56	0,701	118,388	0,748	0,641	0,673	67,351	148,193
Linear pseudo-second order type 10	64,113	40,56	0,701	118,388	0,748	0,641	0,673	67,351	148,193
Linear pseudo-second order type 12	295,634	16,838	3,293	28,906	3,449	2,956	3,049	304,926	200,85
Non linear pseudo-second order	8,712	2,185	0,111	0,436	0,101	0,087	0,107	10,704	14,437
Non linear esquivel	8,71	2,184	0,111	0,436	0,101	0,087	0,107	10,706	14,438
Linear elovich model type 1	3,308	0,823	0,046	0,07	0,038	0,033	0,044	4,415	5,886
Linear elovich model type 2	3,308	0,823	0,046	0,07	0,038	0,033	0,044	4,415	5,886

Table. 5: Error deviation data related to the MG adsorption onto CR using most commonly used functions.

Adsorption kinetic data are the basic requirements for the design of adsorption systems. In order to optimize the design of a specific sorbate/sorbent system to remove malachite green from aqueous solution, it is important to establish the most appropriate correlation for the experimental kinetic data. Applicability of some statistical tools to predict optimum adsorption kinetics of malachite green onto CR after linear regression analysis showed that the highest R^2 value and the lowest ARED, ARE, SAE, ARS, MPSD, Δq , SSE, MSPED, and HYBRID values could be suitable and meaningful tools to predict the best-fitting equation models.

The best fitting is determined based on the use of these functions to calculate the error deviation between experimental and predicted equilibrium adsorption kinetic data, after linear analysis. Hence, according to Table. 5., it seems that the linear elovich (type 1 and type 2) models were the most suitable models to describe satisfactorily the studied adsorption phenomenon. Therefore, based on these mentioned results, the best useful error estimation statistical tools should point out the linear elovich (type 1 and type 2) followed by non linear esquivel model and non linear pseudo- second order as the best-fitting models.

IV. Conclusion

CR were characterized by the $pH_{PZC} = 4.37$ and used for the MG adsorption in simulated aqueous solution. In batch mode, the adsorption was highly dependent on various operating parameters (pH, contact time).

The obtained results revealed the following optimal conditions: pH value of 6 and 240 min of contact time, which lead to 94 % malachite green removal.

The adsorption kinetic of malachite green onto CR can be better fitted by the linear elovich (type 1 and type 2) as compared to the non-linear pseudo-second-order, linear pseudo-second-order, non linear pseudo first order, linear pseudo first order, pseudo third order, and Esquivel models. On the whole, the experimental results showed that CR is suitable adsorbent for the removal of malachite green.

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