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Comparison removal malachite green and methylene blue from aqueous solutions by new adsorbent prepared from *Rosa canina*

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Abstract

In this research, low cost activated carbon simply was prepared from a local , plenty *Rosa canina* tree (AC-RC) in sou'wester of Iran. The potential applicability of AC-RC as useful adsorbent for the removal of Malachite Green(MG) and Methylene Blue(MB) from aqueous solutions. The AC-RC with low cost and toxicity with nano size pore diameter as a good adsorbent for removal dyes MG and MB from aqueous media. The effects of different parameters of pH , contact time, agitation time, initial dye concentration and amount of adsorbent AC-RC on removal MG and MB were evaluated. Increase in pH up to 8 for AC-RC , increase the adsorption capacity and reach equilibrium within 40min of contact time for (MB) dye and 45min for(MG) dye. Experimental data was analyzed by four kinetic models including pseudo first ,second-order, Elovich and the intraparticle diffusion equations. The result shows that adsorption of MG and MB onto AC-RC at all conditions such as versatile adsorbent dosages combination of the pseudo second-order equation.experimental data study for isotherm models like Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich and show results , removal MG and MB dyes by AC-RC conformed from Freundlich isotherm. The adsorption capacity of AC-RC from removal of MG and MB was found to be 30.3 and 27.02mg/g. these results show that adsorbent AC-RC as a low cost adsorbent and high strength for removal Dyes from aqueous media.

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The pollution of drinking water is a great problem due to entrance of hazardous materials include heavy metals, dyes by textile and printing industries. Many industries such as textile, plastic, leather, cosmetics, paper and printing may product dyes that can pollute water media and this process leading to environment dameges. Dyes has complexy structure that enter in the sewage in different process of loom industry and leading to water pullotion, that we shoud removed this dyes from environment (Pavan et al., 2008, Wu et al., 2006, Reza et al., 2010). Between dyes, Methylene blue (MB) is the most commonly used substance for dying cotton, wood and slik. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals (Han et al., 2006). Malachite Green(MG), abasic dye has been widely used for dyeing of leather, silk, wood ,cotton,paper and also in distilleries (Zhang et al., 2008, Mittal, 2006, Culpse et al., 1999). MG dye consist of toxic properties which are known to cause carcinogenesis, mutagenesis, teratogenesis and respiratory toxicity (Singh et al., 1994, Gupta et al., 2004, Beridou et al., 2007). Different methods is for removal pollution as dyes, between this methods, adsorption processes for the reason that low cost, easy design, ease exploit and hyposensitivity to toxic materials, today is a suitable technique for removal dyes pollution and advance quality of surplusewater (Gregorio, 2006, Sudipta et al., 2010). Activated carbon is known as a common and useful adsorbent, but its joineric form by high cost for production and reduction cannot be use as a desired selection. Production of activated carbon from different organic materials is evaluated in several studies that we can point to production activated carbon from slime and plants. Activated carbons has great potential for dyes removal due to properties such as large surface area, microporous structure and cost benefit . The commercial activated carbon are expensive which promotes the search for cheap materials mainly derived from biological origin (Ghaedi et al., 2012, Ghaedi et al., 2011, Ghaedi et al., 2012, Yang et al., 2008). In this work, for production of activated carbon we use *Rosa canina* stalks as a organic adsorbent for removal some dyes. This study was performed for evaluation of activated carbon *rosa cannina* (AC-RC) as natural adsorbent in efficiency for removal dyes MB and MG. Characterization of prepared AC-RC was done by measuring scanning electron microscopy(SEM) and FT- IR analysis.the effect of pH, amount of adsorbent, agitation time ,contact time and initial concentration dyes on removal MB and MG was examined and comparison. Different conventional kinetic models and isotherm models were used and show suitability of new design adsorb for removal MG and MB.

Materials

All chemicals including Hcl, NaOH, HNO₃, MB and MG with the highest purity available are purchased from merck (Darmstadt, Germany). The pH measurements were carried out using pH/Ion meter model -691 (Metrohm, Switzerland, Swiss) and the absorbance measurement were undertaken using Jusco UV-Vis spectrophotometer model V-530 (Jasco, Japan) at 663nm for MB for MG. Fourier transform infrared (FT-IR) analysis for characterization of (AC-IR) was performed using a KBr disk (shimadzu FT-IR 8300 spectrophotometer, shimadzu co., Tokyo, Japan). The morphology of the AC-RC was observed by scanning electron microscopy (SEM: Hitachi S-4160) under an acceleration voltage of 15kv. For prepared AC-RC used of oven (Carbolite-YA505, England). The amount of dyes adsorbed per unit weight of adsorbent at time t, qt (mg.g⁻¹) and percentage dyes removal efficiency, R was calculated as follows:

$Q_t = (C_0 - C_t)V/M$	(1)
$R=((C_0-C_t)/C_0)*100$	(2)

Where C_0 is the initial MB and MG concentration (mg.L⁻¹), C_t is concentration of MB and MG at any time t, V is the volume of solution (L) and M is the mass of adsorbent (g) (AC-RC).

Methods

Methylene Blue with commercial purity(C.I 22120) FW=799.814 gmol⁻¹,with chemical formula C₂₇H₃₃N₂.HO₄S have maximum wavelength of 663nm ;(shanghai chemical reagent Ltd). (e.g.Fig.1)and Malachite Green, FW=364.911g.mol⁻¹,maximum wavelength of 617nm, molecular formula C23H25N2(choloride) was obtained from merck chemicals and used without futher purification(e.g.Fig.2) was used throughout experiments batch experiments were carried out using (500ml) capacity glass beaker. Stock solution of MB and MG (1000mg/L) was prepared by dissolving an accurately weighed quantity (0.5g) of solid dye in 1L of deionized water.while the experimental solutions (in the range of 5-100 mg/L) were obtained by successive dilution of the stock solutions.the effect of solution pH on removal Dyes was studied in pH from 1 to 8(adjusted via 0.1 M Hcl and 0.1M NaoH). Effect agitation time in Rang 5min to 50 min was surveid for both dye. Experimental data optimum show amount of adsorbent for removal MB dye and MG was 0.3g (varying from 0.1 to 0.4 g/50ml). solutions both dyes in concentrations 5 to 40 mg/L prepareded from stocks solution and their removal was study by adsorbent of AC-RC. Results show pH=8 was the optimum percentage removal MB and MG. in the all experimental of removal MG and MB by AC-RC was used stirring speed of 450rpm and pH=8 and at room temperature(25±1°C). In order to study the adsorption isotherm, 0.1g to 0.4g/50ml AC-RC of prepared adsorbent was kept in contact with different concentrations (5-40 mg/L) of dyes solution at pH=8 while stirring the solution at 450 rpm for 40min for MB and 45min for MG (to get confirm that the equilibrium was reached) at temperature of 25±1°C.



Fig. 1.Chemical structure of Methylene Blue. *Preparation of AC from rosa canina*

The first was assembiage amount piece *rosa canina*, then was shard the shells *rosa canina* were washed by de-ionized water and dried in the room temperature, then fix in a oven for 4h in temperature 350°c and heated for remove the water soluble phenolic and other organic compounds , After wards was grouded thereafter in a disk-mill and sieved (80-100 mesh) subsequently. For activation 50g of carbon was abtinad mixed by ratio 1:5 of 4MHcl and 4MHNO₃ for 8h at the room temperature($25\pm1°c$), then was washed by de-ionized water (to reach pH=6.5) and dried(in oven 80°c) for application future.

Results and discussion

Characterization of adsorbent

The morphology of the AC-RC was observed by scanning electron microscopy.The SEM micrograph of AC-RC in(e.g.Fig. 3) shows homogeneous rodlike structure and appearance of different pores in the AC-RC structure that make possible it as useful sites for adsorption process.

The FT-IR spectra of AC-RC shows in(e.g.Fig.4). The FT-IR spectra displayed presence of some absorption peaks attributed to different vibration modes or different functional group including, carbonyl , hydroxyl group and carboxylic acid (Table 1)

Table 1. FT-IR analysis of prepared Activated carbonfrom *Rosa canina*.

Wave num	ber(cm ⁻¹)	Type of vibration	
Group or b	onding		
1150-1200	C-C	out of plane	bending
	C-H	Be	nding
1300	C-O alcohol	or acid (or phenol)	
1580	C-H		Bending
1700	O-H		Bending
2920	C-H aldehyd	e	`
2935	C-H aliphati	с	
2500-3800	o O-H,CooH,	SO_3H	



Fig. 2. Chemical structure of Malachite Green.

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Fig. 3. SEM structure of AC-RC.



Fig. 4. FT-IR spectra of AC-RC.

Effect of contact time on MB and MG removal

The effect of contact time at room temperature on the MB and MG sorption at 10 mg/L for MB and 15 mg/L for MG is depicted in(e.g. Fig 5,6). Equilibrium time is one of the important parameters to design a low cost wastewater treatment system. In this research , first by increase contact time, Recovery was increased in the 40 min for MB and 45 min for MG were high Recovery for removal for dyes , after fixed the proceeding. The initial fast rate of adsorption is attributed to MB and MG adsorption by the exterior surface until surface saturation of AC-RC and finally the MB and MG molecule exerted onto the internal pores of the AC-RC takes relatively long contact time (Ghaedi *et al.*, 2012).

Effect of pH on removal MG and MB

The pH of the system influence on the ability of adsorbent surface of dye molecule tendency and interaction for binding to adsorbent solid.The maximum removal percentage of MG and MB on adsorbent was abserved at pH=8 for MB and MG (e.g.Fig 7,8). At lower pH, the number of positively charged adsorbent surface sites increased an a strong repulsive force occur between MB and MG were protonated at positive charge density decrease at lower pH (Pan *et al.*, 2009, Jabbar *et al.*, 2014). The positively charged surface AC-RC and MG and MB in the low pH increased and lead to decrease in removal percentage of MB and MG on AC-RC with increasing pH in addition the competition of H⁺ with the cationic dye molecules due to the presence of exess H⁺also decreased the adsorption (Apple *et al.*, 2007).



Fig. 5. Effect of contact time of removal MB. (0.1 to 0.4gr/L adsorbent, concentration MB 10mg/L).



Fig. 6. Effect of contact time of removal MG. (0.1 to 0.4gr/L adsorbent, concentration MG 15mg/L).



Fig. 7. Effect of pH on the removal MB (10mg/L,)onto AC-RC, at room temperature(25±1°c), agitation 450rpm for the maximum contact time to reach the equilibrium(40min).



Fig. 8. Effect of pH on the removal MG (15mg/L,) onto AC-RC, at room temperature(25±1°c), agitation 450 rpm for the maximum contact time to reach the equilibrium(45min).

Effect of AC-RC amount on MB and MG removal

The available surface are of adsorbent and its amount show its tendency and capacity for a given initial concentration of dyes solution.The effect of AC-RC amount in the range of 0.1-0.4g/50ml on the MB and MG capacity at 10mg/L MB and 15mg/L MG concentrations is presented in(e.g. Fig 9,10). The optimum value of adsorbent (0.3g/50ml AC-RC and 10mg/L MB and 15mg/L MG). The rate of adsorption becomes slow down. At higher amount of adsorbents , lower dye concentrations remain in solution with respect to large extent of available active surface area.

Effect of initial dye concentration dye on adsorption of MB and MG

The effect of MB and MG concentration in the range of 5-40 mg/L on its adsorption by AC-RC was investigated and the percentage and amount of MB and MG removal at different initial concentration were depicted in(e.g.Fig 11,12). The results show amount of the dyes MB and MG increased with the removal percentage significantly decreased with futher increase in initial MB and MG concentrations that emergen from occupation of the available sites and saturation on the AC-RC at higher MB and MG concentrations, due to increase in its molecule competition for the low vacant reactive sites the adsorption process will increasingly slow down and related to decrease in the mass gradient between the AC-RC and solutions. At lower MB and MG concentrations, solute to adsorbent vacant sites ratio

is high and causes an increase in dye removal (Tuzen *et al.*, 2007).



Fig. 9. Effect of amount of Adsorbent in the range0.1-0.4g on different MB concentration (5-40 mg/L), agitation speed 450 rpm, pH=8 and room temperature($25\pm1^{\circ}c$).



Fig. 10. Effect of amount of Adsorbent in the range 0.1-0.4g on different MG concentration (5-40 mg/L), agitation speed 450 rpm, pH=8 and room temperature($25\pm1^{\circ}c$).



Fig. 11. Effect of initial MB concentration on the adsorption of MB.



Fig. 12. Effect of initial MG concentration on the adsorption of MG.

Kinetic and isotherm study of MB and MG removal

The behavior of the MB and MG adsorption was analyzed using the four kinetic models such as pseudo first and second order , Elovich and intraparticle diffusion Dubinin, 1960) A linear form of the Lagergren first-order model expression is : Log (q_e-q_t) = Log $q_e - (k_tt/2.303)t$ (3)

Where q_e and q_t (mg.g⁻¹) are the amount adsorbed MB and MG at equilibrium and time t (min), k₁(min⁻¹) is the rate constant of Langergren first-order adsorption(min⁻¹). The respective value of kinetic model is calculated for slop and intercept of obtained line and their value is show in Table (2-9). In pseudo second –order model the plot of t/q_t versus for generally has linear relationship with high correlation coefficient and the k2 and equilibrium adsorption capacity (qe) value, calculated according to the intercept and slope above time. The second-order kinetic model was evaluated from plot and their value is presented in Table (2-9). The adsorbate species are most probably transported from the bulk of the solution in to the solid phase with an intraparticle diffusion process. Which is often the rate- limiting step in many adsorption processes. The possibility of intraparticle diffusion is explored by using the intraparticle diffusion model (Alkan et al., 2008).

 $Q_t = k_{id} t^{1/2} + c \tag{4}$

Where c is the intercept and k_{id} is the intraparticle diffusion rate constant the values of this paremeters are obtain in Table (2-9).

Adsorption equilibrium study

Adsorption equilibrium isotherm represents mathematical relation of amount of adsorbed target per gram of adsorbent (q_e (mg.g⁻¹)) to the equilibrium solution concentration (c_e (mg.L⁻¹)) at fixed temperature (Dogan *et al.*, 2006) . the different isotherms such as Langmuir , Freundlich, Tempkin and Dubinin-Radushkevich is applied in this research for analyzing experimental data for obtain some important information on the surface properties of the AC-RC .The linear from of Langmuir isotherm model may be

$$(C_e/q_e) = (1/k_LQ_m) + (C_e/Q_m)$$
 (5)

Where k_L is the Langmuir adsorption constant (L.mg⁻¹) and Q_m is the theoretical maximum adsorption capacity (mg/g). The linear from of Freundlich isotherm presented as follows:

Log
$$q_e = Log k_F + 1/nLogC_e$$
 (6)
Where k_F ((mg/g)/(mg.L⁻¹)^{1/n}) and n is isotherm
constants indicate the capacity and intensity of the
adsorption, respectively. The 1/n factor also indicate
heterogeneity factor. The well know form of Tempkin
isotherm is given as :

$$Q_e = RT/bLn(k_T C_e)$$
(7)

Eq.can be linearized as: $Q_e = BT Ln k_T + B_T Ln C_e$

Where BT = RT / bT, T is the absolute temperature in k,R is the universal gas constant, 8.314 J.mol⁻¹. K⁻¹, k_T is the equilibrium binding constant (L/mg) and B_T is related to the heat of adsorption and constants value of Tempkin isotherm is show in Table 10,11. The Dubinin-Radushkvich isotherm was also applied to estimate the porosity free energy and the characteristic of AC-RC (Dubinin, 1960, Dubinin *et al.*, 1965).

(8)

In this work, the value of 1/n is found to lie at different amount for AC-RC for removal MB and MG.Data of Table10, 11 obtained the applicability of Freundlich isotherm model for MB and MG with maximum correlation coefficients ($R^2>99\%$) from another models.

Table 2. Kinetic parameters of MB adsorption onto AC-RC conditions: 0.1 g AC-RC over 5-40mg/L at optima conditions of other variables.

Models	parameters	5	10	15	20	30	40
First order kinetic model:	K1	0.094	0.074	0.069	0.062	0.057	0.034
$\log(q_e - q_t) =$	q _e (calc)	2.70	4.86	7.45	9.95	15.31	16.59
$\log(q_e) - (\frac{k_1}{2.303})t$							
	R ²	0.959	0.981	0.988	0.986	0.987	0.979
Second order kinetic model:	K2	0.042	0.0088	0.0045	0.0027	0.0009	0.0069
$d_{qt/dt} = k_2 \; (q_e - q_t)^2$	$q_e(calc)$	2.92	7.09	10.86	15.15	28.57	33.33
	R ²	0.974	0.985	0.991	0.990	0.990	0.994
	h	0.36	0.396	0.533	0.612	0.76	2.21
Intraparticle diffusion	Kdiff	0.408	.812	1.246	1.653	2.433	2.530
$q = k_{id} t^{1/2} + C$	С	0.093	0.036	0.253	0.578	1.227	0.435
	R ²	0.972	0.976	0.977	0.974	0.976	0.973
Elovich	β	1.715	0.863	0.565	0.430	0.296	0.276
$q_{\star} = \frac{1}{2} ln(\alpha\beta) + \frac{1}{2} ln(t)$	α	2.328	4.281	6.321	6.971	6.209	6.106
$\alpha_t \beta^{(\alpha_t, \beta_t)} $	R ²	0.915	0.916	0.908	0.890	0.866	0.844
Experimental date	$q_e(\exp)$	4.954	9.824	14.811	19.761	29.72	36.675

Parameter values: Concentration dye (ppm)

Table 3. Kinetic parameters of MB adsorption onto AC-RC conditions: 0.2 g AC-RC over 5-40mg/L at optima conditions of other variables.

Models	parameters	5	10	15	20	30	40
First order kinetic model:	K1	0.099	0.078	0.069	0.064	0.062	0.051
$\log(\boldsymbol{q_e} - \boldsymbol{q_t}) =$	q _e (calc)	1.19	2.21	7.45	4.51	6.95	6.62

Parameter values: Concentration dye (ppm)

$\log(q_e) - (\frac{k_1}{2.303})$ t	R ²	0.962	0.967	0.987	0.987	0.990	0.990
Second order kinetic model:	K_2	0.116	0.028	0.0045	0.0095	0.0054	0.019
$d_{qt/dt} = k_2 (q_e - q_t)^2$	q _e (calc)	1.39	3/14	10/87	6/66	10/31	10
	R ²	0.975	0.99	0.990	0.986	0.992	0.999
Intraparticle diffusion	h	0.225	0.276	0.533	0.423	0.58	1.94
	Kdiff	0.178	0.369	1.246	0.763	1.142	1.262
$q_t = k_{id} t^{1/2} + C$	С	0.212	0.272	0.253	0.188	0.139	1.903
	R ²	0.970	0.970	0.973	0.974	0.977	0.975
Elovich	β	3.94	1.89	0.966	0.92	0.622	0.527
$q_t = \frac{1}{2} ln(\alpha\beta) + \frac{1}{2} ln(t)$	α	5.612	8.48	7.649	7.491	7.301	6.921
$f_t \beta \beta \beta$	R ²	0.914	0.913	0.916	0.905	0.895	0.882
Experimental date	q _e (exp)	2.4845	4.947	7.411	9.8995	14.893	19.855

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Table 4. Kinetic parameters of MB adsorption onto AC-RC conditions: 0.3 g AC-RC over 5-40mg/L at optima conditions of other variables.

Models	parameters	5	10	15	20	30	40
First order kinetic model:	Kı	0.113	0.089	0.088	0.067	0.062	0.057
$\log(\boldsymbol{q_e} - \boldsymbol{q_t}) =$	qe(calc)	1.27	1.43	2.18	2.85	4.29	3.74
$\log(q_e) - (\frac{k_1}{2.303})t$							
	R ²	0.971	0.964	0.974	0.992	0.993	0.99
Second order kinetic model:	K_2	0.188	0.051	0.0318	0.018	0.011	0.0077
$d_{qt/dt} = k_2 (q_e - q_t)^2$	$q_e(calc)$	0.94	2.05	3.012	4.22	6.37	8.55
	\mathbb{R}^2	0.978	0.99	0.990	0.997	0.996	0.993
	h	0.166	0.217	0.288	0.321	0.45	0.563
Intraparticle diffusion	Kdiff	0.112	0.234	0.362	0.472	0.707	0.949
$q t = k_{id} t^{1/2} + C$	С	0.190	0.293	0.317	0.371	0.441	0.419
	\mathbb{R}^2	0.962	0.964	0.973	0.981	0.985	0.982
Elovich	β	6.21	3.003	1.931	1.49	0.99	0.748
$q_t = \frac{1}{2}ln(\alpha\beta) + \frac{1}{2}ln(t)$	α	3421	1447	681	597	502	439
β	R ²	0.908	0.902	0.916	0.915	0.911	0.899
Experimental date	q _e (exp)	1.2462	3.3093	4.958	6.6146	9.932	13.940

Parameter values: Concentration dye (ppm)

Table 5. Kinetic parameters of MB adsorption onto AC-RC conditions: 0.4 g AC-RC over 5-40mg/L at optima conditions of other variable.

Models	parameters	5	10	15	20	30	40
First order kinetic model:	K1	0.115	0.089	0.081	0.069	0.059	0.058
$\log(\boldsymbol{q_e} - \boldsymbol{q_t}) =$	qe(calc)	2.118	1.18	1.303	1.73	2.63	3.74
$\log(q_e) - (\frac{k_1}{2.303})t$							
	R ²	0.968	0.984	0.973	0.991	0.992	0.995
Second order kinetic model:	K_2	0.423	0.136	0.11	0.054	0.032	0.0197
$d_{qt/dt} = k_2 (q_e - q_t)^2$	qe(calc)	.6680	1.39	2	2.79	4.15	5.618
	R ²	.9920	0.997	0.987	0.993	0.997	0.996
	h	.1910	0.263	0.439	0.42	0.548	0.627
Intraparticle diffusion:	Kdiff	0.070	0.145	0.229	0.318	0.478	0.654
$q t = k_{id} t^{1/2} + C$	С	0.231	0.413	0.526	0.588	0.751	0.785
	R ²	0.961	0.964	0.96	0.965	0.968	0.978
Elovich:	β	9.708	4.716	3.003	2.146	1.43	1.057
$q_{\perp} = \frac{1}{2} ln(\alpha\beta) + \frac{1}{2} ln(t)$	α	2*10 ⁵	1.01 [*] 10 ⁵	881.09	732.14	462.74	441.63
$a_t \beta \beta \beta$	R ²	0.958	0.955	0.932	0.957	0.948	0.943
Experimental date	q _e (exp)	1.2462	2.4875	3.7247	4.9642	7.450	9.9405

Parameter values: Concentration dye (ppm)

Table 6. Kinetic parameters of MG adsorption onto AC-RC conditions: 0.1 g AC-RC over 5-40mg/L at optima conditions of other variables.

		Parameter values: Concentration dye (ppm)						
Models	parameters	5	10	15	20	30	40	
First order kinetic model:	K1	0.076	0.035	0.037	0.037	0.038	0.034	
$\log(\boldsymbol{q}_{e} - \boldsymbol{q}_{t}) = \log(\boldsymbol{q}_{e}) - (\frac{\boldsymbol{k}_{1}}{\boldsymbol{k}_{1}})t$	$q_e(calc)$	1.603	2.673	4.742	7.014	11.94	16.59	
log(q _e)-(<u>2.303</u>)(\mathbb{R}^2	0.975	0.785	0.86	0.933	0.963	0.979	
Second order kinetic model:	K_2	0.088	0.078	0.032	0.018	0.0089	0.0069	
$d_{qt/dt} = k_2 (q_e - q_t)^2$	q e(<i>calc</i>)	2.66	4.38	6.76	9.09	14.08	33.33	
	\mathbb{R}^2	0.994	0.998	0.991	0.989	0.971	0.962	
	h	0.62	1.457	1.462	1.57	1.572	2.21	
Intraparticle diffusion	Kdiff	0.323	0.516	0.854	1.18	1.892	2.530	
$q = k_{id} t^{1/2} + C$	С	0.649	1.399	1.452	1.376	0.764	0.435	
	\mathbb{R}^2	0.931	0.851	0.92	0.969	0.976	0.983	

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Elovich	β	2.066	1.238	0.78	0.574	0.37	0.276
$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln(t)$	α	1.972	4.37	4.212	4.217	4.19	4.86
	\mathbb{R}^2	0.962	0.963	0.956	0.966	0.936	0.927
Experimental date	q _e (exp)	4.99	9.997	14.60	19.997	29.997	39.997

Table 7. Kinetic parameters of MG adsorption onto AC-RC conditions: 0.2 g AC-RC over 5-40mg/L at optimaconditions of other variables.

Models	parameters	5	10	15	20	30	40
First order kinetic model:	K1	0.078	0.078	0.062	0.06	0.053	0.051
$\log(\boldsymbol{q_e} - \boldsymbol{q_t}) =$	$q_e(calc)$	1.718	1.903	2.14	3.03	4.71	6.62
$\log(q_e) - (\frac{k_1}{2.303})t$	R ²	0.981	0.98	0.971	0.983	0.981	0.954
Second order kinetic model:	K2	0.352	0.145	0.079	0.052	0.031	0.019
$d_{qt/dt} = k_2 (q_e - q_t)^2$	q _e (calc)	1.271	2.56	3.76	5	7.46	10
	R ²	0.997	0.995	0.99	0.988	0.991	0.993
	h	0.568	0.953	1.126	1.32	1.72	1.94
Intraparticle diffusion	Kdiff	0.113	0.243	0.376	0.528	0.865	1.262
$q = k_{id} t^{1/2} + C$	С	0.6	1.089	1.399	0.0642	1.957	1.903
	R ²	0.914	0.938	0.958	0.969	0.95	0.948
Elovich	β	4.78	2.73	1.78	1.28	0.77	0.527
$q_t = \frac{1}{R} ln(\alpha\beta) + \frac{1}{R} ln(t)$	α	3.70	7.52	7.29	7.305	6.25	5.47
ч ч	R ²	0.993	0.981	0.983	0.976	0.981	0.987
Experimental date	$q_e(\exp)$	2.49	4.9985	7.4575	9.9985	14.9985	19.9985

Parameter values: Concentration dye (ppm)

Table 8. Kinetic parameters of MG adsorption onto AC-RC conditions: 0.3 g AC-RC over 5-40mg/L at optima conditions of other variables.

		Parameter values: Concentration dye (ppm)					
Models	parameters	5	10	15	20	30	40
First order kinetic model:	K1	0.108	0.074	0.059	0.051	0.046	0.044
$\log(\boldsymbol{q_e} - \boldsymbol{q_t}) =$	qe(calc)	6.88	3.419	1.663	1.06	1.76	2.78
$\log(q_e) - (\frac{k_1}{2.303})$ t	R ²	0.96	0.907	0.935	0.918	0.901	0.912
Second order kinetic model:	K2	2.102	0.949	0.406	0.23	0.132	0.078

$d_{qt/dt} = k_2 (q_e - q_t)^2$	$q_e(calc)$	0.842	1.663	2.47	3.23	4.78	6.29
	\mathbb{R}^2	0.999	0.999	0.999	0.997	0.997	0.997
	h	1.49	2.61	2.47	2.33	2.84	3.08
Intraparticle diffusion:	Kdiff	0.034	0.074	0.137	0.207	0.351	0.544
$q t = k_{id} t^{1/2} + C$	С	0.654	1.262	1.704	2.012	2.746	3.089
	R ²	0.787	0.768	0.809	0.854	0.814	0.869
Elovich:	β	17.85	8.33	4.54	3.07	1.79	1.176
$a = \frac{1}{-\ln(\alpha R)} + \frac{1}{-\ln(t)}$	α	5912.3	3859.7	458.47	149.7	14.9	31.003
$q_t = \beta \left(\frac{\alpha p}{\beta} \right) + \beta \left(\frac{\alpha p}{\beta} \right)$	R ²	0.935	0.935	0.957	0.972	0.951	0.978
Experimental date	q _e (exp)	1.665	3.3332	4.9826	6.6656	9.99	13.322

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Table 9. Kinetic parameters of MG adsorption onto AC-RC conditions: 0.4 g AC-RC over 5-40mg/L at optima conditions of other variables.

Models	parameters	5	10	15	20	30	40
First order kinetic model:	K1	0.109	0.074	0.055	0.048	0.048	0.044
$\log(\boldsymbol{q_e} - \boldsymbol{q_t}) =$	$q_e(calc)$	21.33	10.16	5.16	2.6	1.54	1.054
$\log(q_e) - (\frac{k_1}{2.303})t$	R ²	0.891	0.829	0.817	0.854	0.903	0.93
Second order kinetic model:	K2	6.87	3.029	1.59	0.76	0.265	0.159
$d_{qt/dt} = k_2 (q_e - q_t)^2$	q _e (<i>calc</i>)	0.627	1.25	1.86	2.45	3.65	4.76
	R ²	1	1	1	0.999	0.999	0.998
	h	2.7	4.83	5.52	0.47	3.53	3.59
Intraparticle diffusion	$\mathbf{K}_{\mathrm{diff}}$	0.014	0.03	0.052	0.089	0.204	0.292
$q = k_{id} t^{1/2} + C$	С	0.551	1.092	1.579	1.960	2.487	3.052
	R ²	0.7	0.715	0.748	0.795	0.847	0.881
Elovich 1 1 1 2	β	41.66	20	11.76	6.94	3.1	2.21
$\boldsymbol{q}_{t} = -\lim_{\beta} (\alpha\beta) + -\ln(t)$	α	1.8*10 ⁹	1.3 [*] 10 ⁹	2 [*] 10 ⁵	1.04 [*] 10 ⁵	674.07	373.61
	\mathbb{R}^2	0.898	0.908	0.932	0.954	0.974	0.985
Experimental date	q _e (exp)	1.24	2.4992	3.7412	4.9992	7.4992	9.992

Table 10. Isother	n constant parameters and	d correlation coefficient	s calculated for the	adsorption MB.
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Isotherm	Equation	parameters	Adsorbent (g)			
			.10	.20	.30	.40
Langmuir	$C_e/q_e = 1/K_aQ_m +$	Qm (mg g ⁻¹)	250	66.66	30.3	15.38
	C_e/Q_m	Ka (L mg ⁻¹)	.0750	.1830	0.268	0.671
		R ²	0.973	0.972	0.951	0.957
Freundlich	$\mathrm{Ln}\mathrm{q_e} = \ln\mathrm{K_F} + (1/n)\mathrm{ln}$	1/n	0.533	0.498	0.436	0.434
	C_{e}	K _F (L mg ⁻¹)	527.23	139.64	56.1	43.55
		R ²	0.985	0.992	0.991	0.993
Tempkin	$q_e = B_l \ln K_T + B_l \ln C_e$	Bı	7.853	3.864	2.251	1.687

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		K _T (L mg ⁻¹)	10.48	13.41	21.77	31.09
		R ²	0.848	0.829	0.816	0.867
Dubinin and	$Ln \; q_e = ln \; Q_s - K \epsilon^2$	Q _s (mg g ⁻¹)	21.69	10.99	7.32	6.00
Radushkevich		В	4*10 ⁻⁸	4*10 ⁻⁸	3*10 ⁻⁸	2*10 ⁻⁸
		E (kJ/mol)= 1/(2K) ^{1/2}	3.5 [*] 10 ³	$3.5^{*10^{3}}$	4 . 1*10 ³	5000
		R ²	0.737	0.732	0.744	0.792

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Table 11. Isotherm constant parameters and correlation coefficients calculated for the adsorption MG.

Isotherm	Equation	narameters	Adsorbent (g)			
isotnerm		parameters	.10	.20	.30	.40
Langmuir	$C_e/q_e = 1/K_aQ_m +$	Qm (mg g ⁻¹)	200	50	27.02	21.73
	C_{e}/Q_{m}	Ka (L mg ⁻¹)	0.022	.435	0.787	1.09
		R ²	0.974	0.978	0.992	0.956
Freundlich	$\mathrm{Ln} \ \mathrm{q_e} = \ln \ \mathrm{K_F} + (1/n) \mathrm{ln}$	1/n	0.472	0.525	0.388	0.378
	C_{e}	K _F (L mg ⁻¹)	188.36	155.81	7.62	6.63
		\mathbb{R}^2	0.991	0.978	0.996	0.993
Tempkin	$q_e = B_l \ln K_T + B_l \ln C_e$	B_1	4.324	3.893	2.3	1.706
		K _T (L mg ⁻¹)	8.83	15.11	47.16	77.61
		R ²	0.82	0.957	0.896	0.878
Dubinin and	$Ln \ q_e = ln \ Q_s - K \epsilon^2$	Q _s (mg g ⁻¹)	14.75	12.88	9.08	7.16
Radushkevich		В	6*10 ⁻⁸	5*10 ⁻⁸	2*10 ⁻⁸	1*10 ⁻⁸
		$E (kJ/mol) = 1/(2K)^{1/2}$	2.8*10 ³	$3.2^{*}10^{3}$	5000	7123
		R ²	0.937	0.888	0.79	0.816

Conclusion

The results of this research show : the new adsorbent AC-RC as a good , low-cost , green with high adsorption capacity adsorbent (30.3 mg/g) for the removal of MG and (27.02 mg/g) for the removal of MB , by using 0.3g/L (AC-RC) could remove of 10 mg.L⁻¹ of MB and 15 mg.L⁻¹ of MG at short times, 40min of contact time for MB and 45 min for removal MG (<60min), that their optimum point. The effective pH was 8 for removal both Dyes. The four kinetic models show, the kinetic study of MB and MG on these new adsorbent AC-RC conformed pseudo second-order model. Fitting the experimental data for AC-RC show good fit to the Freundlich isotherm for MB and MG by new adsorbent of AC-RC. This work confirms that Activated Carbon from Rosa Canina is a new adsorbent as low cost, economic with simple preparation for removal MB and MG from aqeous media.

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