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BATCH ADSORPTION AND ISOTHERM STUDIES FOR THE REMOVAL OF MALACHITE GREEN AND REACTIVE RED 4 DYES BY USING AC-MnO_2-NC PREPARED FROM *Typha angustat L.*

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ABSTRACT
The potential of using Typha Angustata L modified AC-MnO_2-NC to eliminate the dyes namely Malachite Green and Reactive Red 4 dyes are studied. The result of more than a few parameters such as adsorbent dosage, contact time, temperature, the initial concentration of the adsorbate and pH has been evaluated. Tempkin, Halsey, Langmuir, Dubinin-Radushkevich and Freundlich isotherms are too studied. The lessons exposed that AC-MnO_2-NC is appropriate to employ as an adsorbent to take away both Malachite Green and Reactive Red 4 dyes.
Keywords: Malachite Green, Reactive Red 4, AC-MnO_2-NC, Isotherm.

INTRODUCTION

In current time, a serious environmental problem was arising due to the vast and increasing the uses of a variety of dyes. So, the water becomes more contaminated. Many industries such as textile, plastics, dyestuff's and paper use dyes so as to color their products and also chomp through a considerable amount of water[1]. The rapid development of the textile industry in developing countries has triggered an increase in pollution of the aquatic environment[2]. A significant quantity of devastating water is generated having sulpHides, heavy metals, chlorine, a highly fluctuating pH salts, COD concentration ,a large number of suspended solids and temperature[3]. Many of the organic dyes are dangerous and may distress food chain and even aquatic life. Discharge of these dyes in a watercourse is aesthetically undesirable. Due to the concentrated color, they diminish sunlight diffusion into water hence disturbing aquatic plants, which eventually upset the aquatic ecosystem; in addition, they are toxic to humans also.

In an effort to crack dye pollution troubles, methods like biological treatments, coagulation, membrane separation, photodegradation, reverse osmosis, chemical oxidation, and adsorption have been used; but the highly effective method is adsorption process. Adsorption procedure is functioning in ordinary chemical, biological and physical systems, and is broadly used in industrial applications such as synthetic resins and activated charcoal. Carbons with brilliant specific functionalities and surface properties must be urbanized to generate a lofty affinity for adsorbate adsorption. An extensive range of materials such as silk cotton fiber [4], black tea leaves[5], cocoa[6], almond shell[7], mango leaves[8], saw dust[9], Jambonut[10],Borassus flabellifer [11], Passiflora Foetida[12] and animal bone [13]are used as a low cost adsorbent. In this current learning, Typha Angustata L was chosen as the confined inexpensive adsorbent and it can be renewed into nanocomposite. The majority of the studies described that the adapted adsorbents are capable in compulsory either the cationic (or) anionic group but not equally. Yet, a combination of dissimilar types of dyes is regularly originated in the manufacturing effluents. In our sustained attempt to

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utilize economical resources for the exclusion of crude pollutants, we have analyzed the presentation of AC-MnO_2-NC from Typha Angustata L as an adsorbent for Malachite Green and Reactive Red dyes.

EXPERIMENTAL

Preparation of Sorbate

A Malachite Green having molecular formula $C_{23}H_{25}N_2Cl$, the molecular weight of 364.92g mol^{-1} with C.I. 42000 and wavelength (λ_{max}) of 617nm was chosen as the adsorbate. A **Reactive Red 4** having molecular formula $C_{32}H_{19}N_8Na_4Cl$, Mol Wt of 995.23 with CI No.18105 and wavelength (λmax) of 517nm was chosen as the adsorbate.

A hoard solution of 1000mg/l was arranged and the functioning solutions were organized by diluting the hoard solution with deionized water as required.

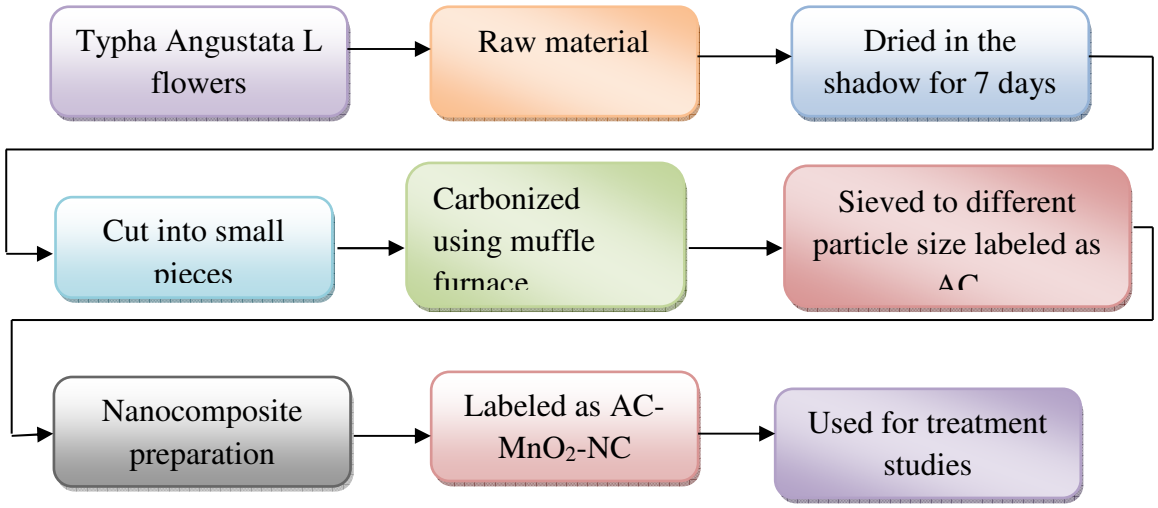


Fig.-1: Flow Chart for the Preparation of AC-MnO_2-NC

Methodology

In each adsorption experiment, 50mL of a dye solution with a known concentration was added to 100mg of AC-MnO_2-NC in a 250ml glass-stoppered flask at 30˚ ± 0.5℃, and the mixture was stirred on a mechanical shaker at 150 rpm min^{-1}. The samples were withdrawn during stirring at preset time intervals, and the adsorbent was separated from the solution by centrifugation (Research centrifuge, Remi Scientific Works, Mumbai) at 4500 rpm min^{-1} for 5min. The absorbance of the supernatant solution was estimated to determine the residual dye concentration, and was measured before and after treatment with doa uble beam spectropHotometer (HITACHI U 2000 SpectropHotometer). All experiments were carried out twice, and the concentrations given are average values. The initial dye concentration in the test solution and the adsorbent dosage were varied to investigate their effect on the adsorption kinetics. The effect of pH was observed by studying the adsorption of dye over the pH range from 3 to 13. The pH of the dye solution was adjusted by using NaOH or HCl solution and a pH meter. The sorption studies were carried out at different temperatures (30˚,40˚, 50˚,60℃). This is used to determine the effect of temperature on the thermodynamic parameters. The amount of adsorption at time t, q_t(mg/g), was designed via the next the principle:

$$q_t = (C_0 - C_t)V / W \quad (1)$$

Where ,C_0(mgL^{-1}) is the initial concentration of the dye in solution. adsorption, C_t(mgL^{-1}) is the liquid pHase concentrations of dye at any time, V is the volume of the solution (L) and W is the mass of dry adsorbent (g).

q_e(mg/g) is the amount of equilibrium was calculated using the formula:

$$q_e = (C_0 - C_e)\ V / W \quad (2)$$

Everyplace $C_e(mgL^{-1})$ and C_0 are the liquid-pHase concentrations of dye initially and at equilibrium. The dye removal percentage can be calculated as follows:

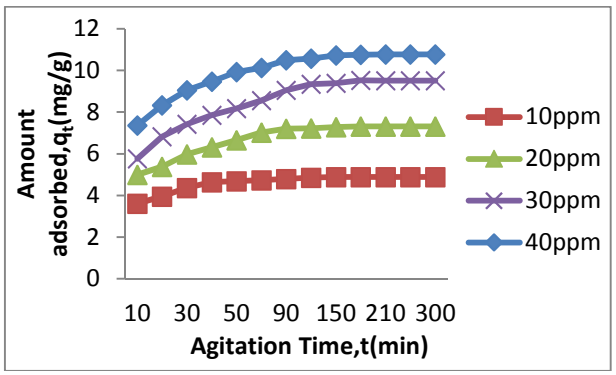
(%) of dye removal = $[(C_0 - C_e) / (C_0)] \times 100$ (3)

Where C_0 and $C_e(mgL^{-1})$ are the initial and equilibrium concentrations of the dye in solution.

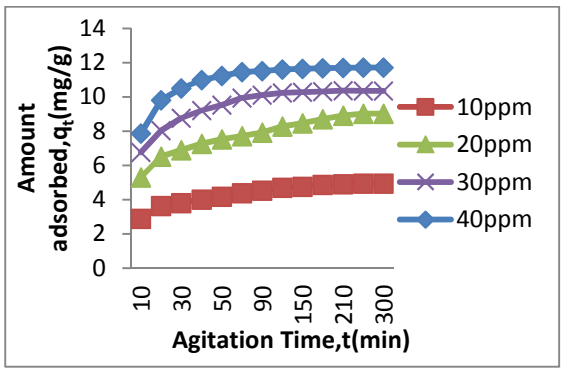
RESULTS AND DISCUSSION

Effects of Initial Dye Concentration Vs Agitation Time

Belongings of initial dye concentration (10, 20, 30 and 40 mg/L) and agitation time on the elimination of MG and RR 4 by adsorbent are offered in Graph-1(a&b). The removal percentage of MG increased with increase in agitation time and it will be decreased from 97.59 to 53.89 as the initial dye concentration was increased from 10 to 40 mg/L with a fixed carbon concentration of 100mg/50mL at room temperature (30°C) respectively. In the case of RR4 it will be decreased from 99.05 to 58.58 percentage. It is lucid that the exclusion of the dye depends on the initial concentration. The deletion curves are smooth, single and continuous leading to saturation.



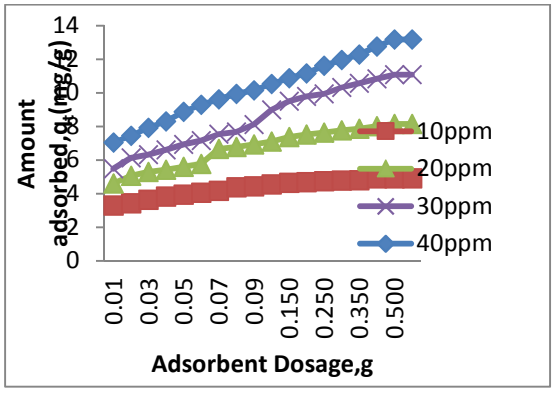
Graph-1a:Effects of initial dye concentration and agitation time on the removal of Malachite Green onto AC-MnO_2-NC



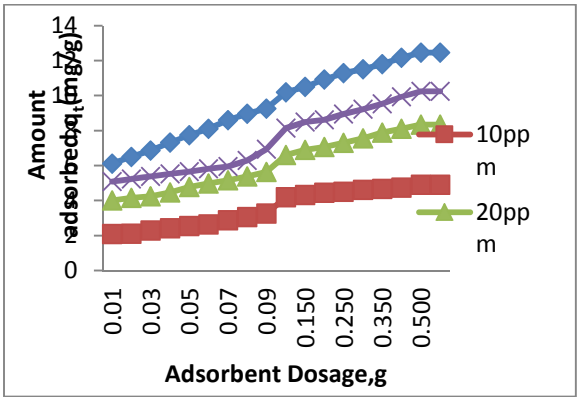
Graph-1b: Effects of initial dye concentration and agitation time on the removal of Reactive Red 4 onto AC-MnO_2-NC

Effect of Adsorbent Quantity

The different adsorbent quantity was tested for the dye concentrations 10, 20, 30 and 40 mg/L to the elimination of MG and RR4 by adsorbent are presented in Graph-2(a&b) (10mg to 600mg/50ml). Increasing adsorbent concentration the adsorption also increases; this is owing to the availability of more adsorption site and increase in surface area. So the finest amount of adsorbent dose was 100mg/50ml.



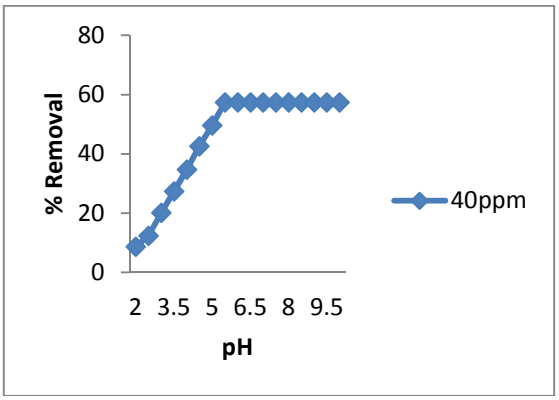
Graph-2a:Effect of adsorbent quantity on the removal of Malachite Green against AC-MnO_2-NC



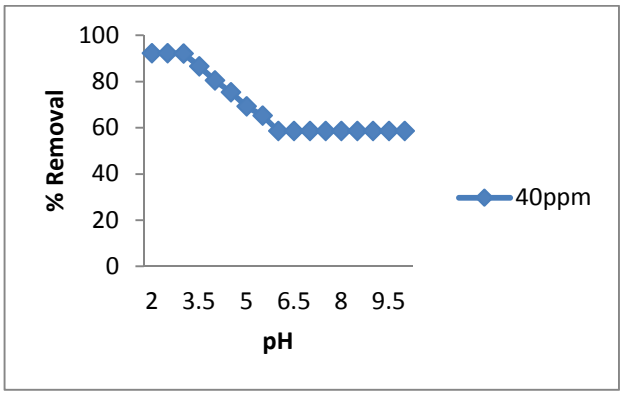
GrapH-2b: Effect of adsorbent dose on Removal of Reactive Red 4 on Adsorbent

Effect of pH

The adsorption of dye solution on the adsorbent surface is highly influenced by the solution pH. The adsorption capability of AC-MnO_2-NC against the solution pH is studied by varying the pH of the solution from 2.0 to 12.0 using dil. HCl and NaOH solutions for a fixed MG and RR 4 concentration of 40 ppm. The surface properties of the activated carbon also play a significant role in the pH-dependent adsorption of dye in solution.The percent elimination of MG increases from 8.65 to57.36% (Graph-3a); of initial dye concentration of 40ppm with the increase in initial pH of dye solutions from 2 to 10 with fixed AC-MnO_2-NC. In that case for AC-MnO_2-NC removal of reactive dye, RR 4 decreased from 92.25 to 58.58% (Graph-3b) with an initial dye concentration of 40ppm. It is revealed from GrapHs an appreciable removal of dyes occurred at acidic pH for the anionic dyes (Reactive dyes) and at alkaline pH for basic dyes (Malachite Green) suggests that the adsorption is chemisorptive in nature.



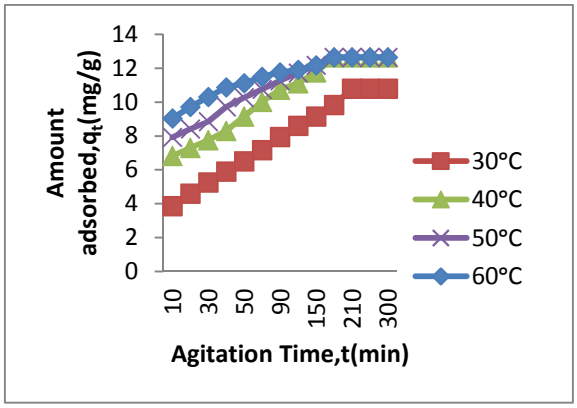
Graph-3a: Cause of pH of dye solution on the removal of Malachite Green on AC-MnO_2-NC



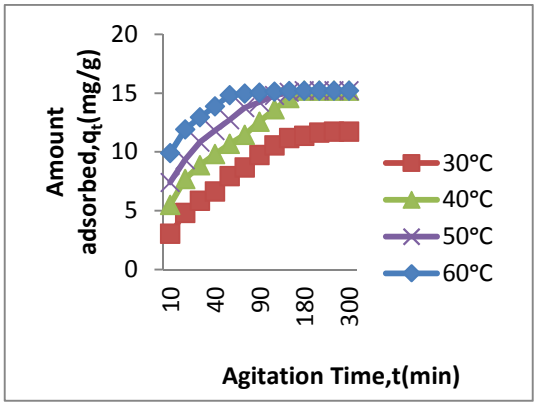
Graph-3b: Cause of pH of dye solution on the removal of Reactive Red 4 on AC-MnO_2-NC

Cause of Temperature

The influence of temperature on the adsorption of MG and RR4 by AC-MnO_2-NC is shown in Graph-4(a&b).The uptake of MG and RR4 by AC-MnO_2-NC increases from 53.89 to 63.18% and 58.28 to 76.04% when the solution temperature increased from 30 to 45°C. The enhanced adsorption at the high temperature indicated the endothermic nature of MG and RR4 adsorption onto the AC-MnO_2-NC surface. At high temperature, the pores of the adsorbent are widened, which can accommodate more solutes. Another fact is that, at high temperature, the mobility of the MG and RR4 dyes increases. In these study, the amount of dye removed at equilibrium, with increases with increase in temperature indicates it is endothermic in nature.[14]



Graph-4a: The outcome of temperature on the removal of Malachite Green onto AC-MnO_2-NC



Graph-4b: The outcome of temperature on the removal of Reactive Red 4 onto AC-MnO_2-NC

Adsorption Isotherm

Adsorption equilibrium statistics and properties, generally notorious as adsorption isotherms, Which explain how adsorbate (pollutant) work together with the adsorbent resources and demonstrate how they are decisive in optimizing the value of adsorbents. As a result, the association of equilibrium data by any hypothetical or experimental equation is fundamental to the matter-of-fact plan and process of adsorption scheme. So as to optimize the intend of the adsorption arrangement to eliminate dyes from effluents, it is significant to create the main suitable connection for the equilibrium arch [15]. Even though these isotherms discard no light on the method of the adsorption, they are helpful for evaluating results from different starting place on a quantitative origin, given that in order on the adsorption potential of a substance with effortlessly interpretable constants. At hand a number of isotherm equations obtainable for scrutinizing trial adsorption equilibrium statistics. In this job, the trial statistics were tested in Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich, and Halsey isotherm models.

Langmuir Isotherm

Langmuir isotherm [16] is signify by the subsequent equation:

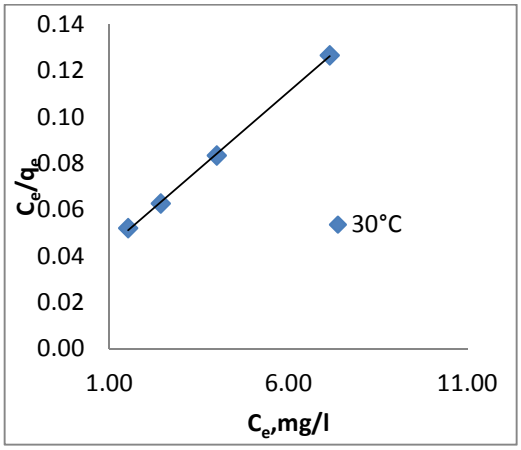
$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \qquad (4)$$

Wherever, the energy of adsorption (Lmg^{-1}) is related to the b, C_e is the equilibrium dye concentration in solution (mgl^{-1}) and Q_0 is a constant related to monolayer adsorption capacity (mgg^{-1}). A plot (Graph-5a&b) of C_e/Q_e versus C_e should indicate a straight line of slope $1/Q_0$ and an intercept of $1/(K_L. Q_0)$ and are presented in Table.- 1 and 2. The essential characteristics of Langmuir Isotherm can also be described by a dimensionless separation factor R_L which is defined by the following equation-

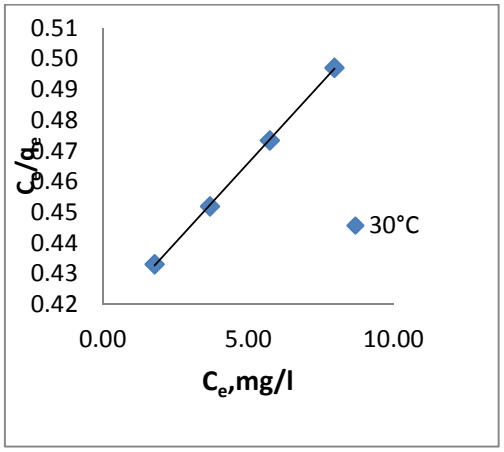
$$R_L = \frac{1}{1 + K_L C_0} \qquad (5)$$

Where C_0 is the initial dye concentration (mgL^{-1}) and K_L is the Langmuir constant. R_L value among 0 to 1 designate favorable adsorption.

$R_L > 1$	Unfavourable adsorption
$0 < R_L < 1$	Favourable adsorption
$R_L = 0$	Irreversible adsorption
$R_L = 1$	Linear adsorption



Graph-5a: Langmuir plot for the Malachite Green onto AC-MnO_2-NC



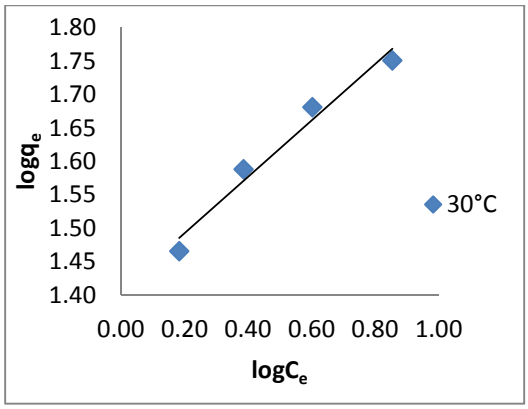
Graph-5b: Langmuir plot for the Reactive Red 4 onto AC-MnO_2-NC

Freundlich Isotherm

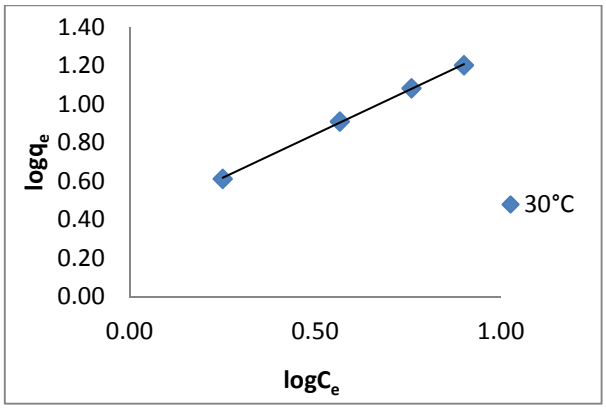
The Freundlich isotherm [17] model is an exponential equation that applies to the adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and is not restricted to the formation of a monolayer. This isotherm is symbolized by the equation:

$$\log q_e = \left(\frac{1}{n}\right)\log C_e + \log k_f \qquad (6)$$

Where, C_e is the equilibrium dye concentration in solution (mgL^{-1}), q_e is the amount of dye adsorbed (mg) at equilibrium, k_f[$mg/g(L/g)^{1/n}$] is the Freundlich constant, k_f is related to the binding energy and n is the heterogeneity factor (n is a measure of deviation from linearity of the adsorption). It indicates the degree of non-linearity between solution concentration and adsorption. The value of k_f and n were calculated from the linear plot (Graph-6a&b) of "log qe" versus "log Ce" and are presented in Table.-1and 2.



Graph-6a: Freundlich plot for the Malachite Green onto AC-MnO_2-NC



Graph-6b: Freundlich plot for the Reactive Red 4 onto AC-MnO_2-NC

Tempkin Isotherm

Tempkin isotherm[18] takes into account the effect of indirect adsorbate-adsorbate interaction on adsorption and suggests that the heat of adsorption of all molecules in the adsorbent surface layer would decrease linearly with coverage. The Tempkin isotherm can be articulated in its linear form as-

Tempkin isotherm is represented by the following equation:

$$q_e = RT/b \ln A + RT/b \ln C_e \qquad (7)$$

$$q_e = B \ln A + B \ln C_e \qquad (8)$$

Where B=RT/b

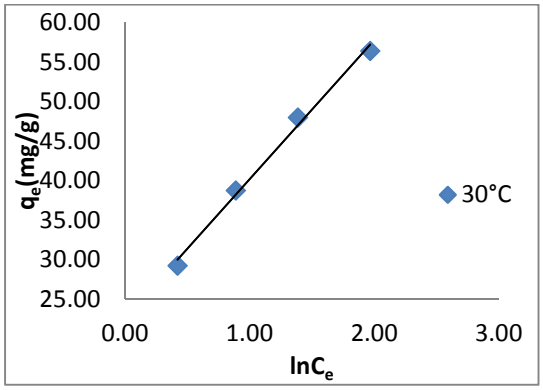
The adsorption data can be investigated as said by equation (8). A plot of q_e versus $\ln C_e$ facilitate the purpose of the isotherm constants A and B and it is revealed in Graph-7a&b. Constant B is related to the heat of adsorption and A is the equilibrium binding constant (1/mol) corresponding to the maximum binding energy and values of the factor are agreed in Table-1and 2.

Dubinin-Radushkevich (D-R) Isotherm

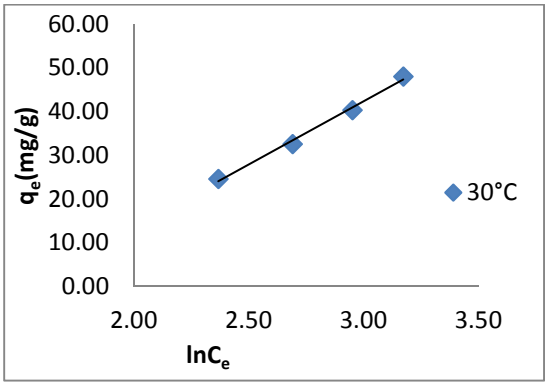
The D-R[19] model was also applied to determine the nature of the adsorption processes as either physical or chemical. The (D-R) isotherm is used to estimate the adsorption energy. This isotherm model is more general than Langmuir because it does not assume a heterogeneous surface or a constant adsorption potential. D-R model has commonly been applied in the following form-

$$\ln q_e = \ln q_D - B_D\varepsilon^2 \qquad (9)$$

Where q_D is the D-R constant representing theoretical saturation capacity (monolayer adsorption capacity) (mg/g), and B_D is the D-R isotherm constant of the sorption energy (mol^2/ KJ^2), which is related to the (ε) average energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from an infinite distance in the solution [20] , q_e is the amount of dye adsorbed in the adsorbent at equilibrium (mg/g).



Graph-7a: Tempkin plot for the Malachite Green onto AC-MnO_2-NC



Graph-7b: Tempkin plot for the Reactive Red 4 onto AC-MnO_2-NC

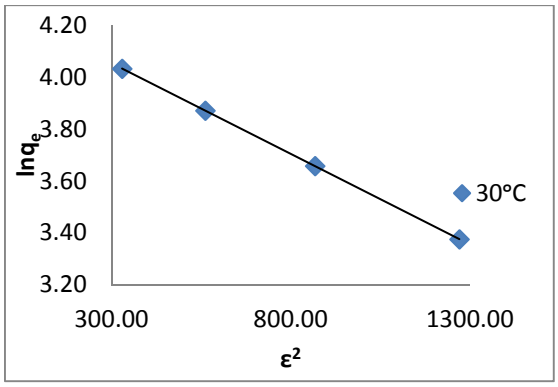
The parameter ε is the Polanyi [21] potential, which can be attained by:

$$\varepsilon = RT \ln\left(1+\frac{1}{C_e}\right) \quad (10)$$

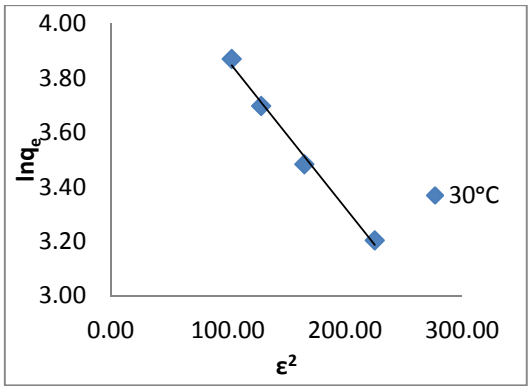
Where R is the gas constant, which is equal to 8.314 J/mol K and T is the solution temperature(K).
The average energy, ε (kJ/mol), can be calculated by using the D-R parameter B_D:

$$\varepsilon = \frac{1}{\sqrt{2B_D}} \quad (11)$$

Based on this energy of activation one can predict whether an adsorption is a pHysisorption or chemisorption. If the value of E lies between 8 and 16kJ/mol the sorption process is a chemisorption one, while values of below 8kJ/mol indicate a physical adsorption process [22]. The plot of $\ln q_e$ against ε^2 is revealed in Graph-8a and 8b. and the constants q_D and B_D were intended from the slope and intercept correspondingly. The D-R isotherm parameters are set in Table-1and 2. This plot also indicated from the regression parameter (R^2). The high-value q_D show high adsorption capacity.



Graph-8a: D-R plot for the Malachite Green onto AC-MnO_2-NC



Graph-8b: D-R plot for the Reactive Red 4 onto AC-MnO_2-NC

Halsey Isotherm

Halsey planned an expression for the concentration of a multilayer at a moderately huge distance from the surface[23],

$$q_e = \left[\frac{K_H}{C_e}\right]^{1/n} H \quad (12)$$

This can be linearised as:

$$\ln q_e = \frac{1}{n_H \ln K_H} - \frac{1}{n_H \ln C_e} \quad (13)$$

The plot of $\ln q_e$ vs $\ln C_e$ is exposed in Graph-9a and b. and the constants K_H and n_H were premeditated from the slope and intercept correspondingly. This equation is apt for multilayer adsorption. Principally, the correct of the trial statistics to this equation prove to the hetero porous nature of the adsorbent. The Halsey isotherm parameter is specified in Table-1and 2.

Analysis of Isotherms

Langmuir Isotherm

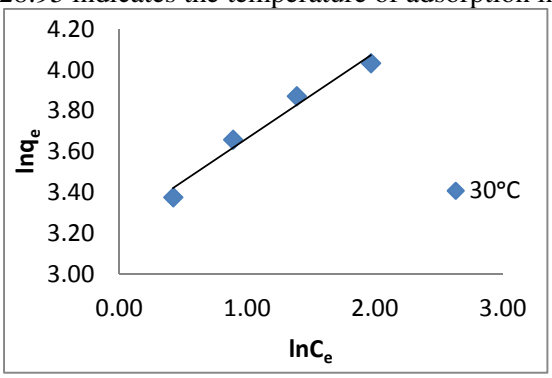
In the current study, Q_o value for MG is 90.9090 and RR4 is 100.00. The separation factor R_L value among 0 to 1 designate the suitable adsorption. The R^2 evaluation is close to unity which reached to good fitting into Langmuir isotherm.

Freundlich Isotherm

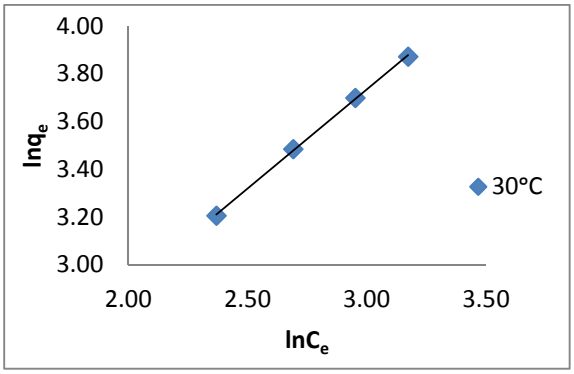
For both dyes, the values of n were among 1 to 10 point out cooperative adsorption [24]. R^2 value is close to unity which reached to good fitting into Freundlich isotherm.

Temkin Isotherm

B_T – Heat of adsorption is related to the Temkin constant. The B_T value for together the dyes are 20.94 and 28.95 indicates the temperature of adsorption increased.



Graph-9a: Halsey plot for the Malachite Green onto AC-MnO_2-NC



Graph-9b: Halsey plot for the Reactive Red 4 onto AC-MnO_2-NC

Table. -1: Calculated isotherms parameters for the adsorption of MG onto AC-MnO_2-NC

Isotherm Models	Initial dye concentration	Parameters and their results			
		R_L	b	Q_o(mg/g)	R^2
Langmuir	60	0.1812	0.0753	90.9090	0.999
	80	0.1423			
	100	0.1172			
	120	0.0996			
Freundlich	Initial dye concentration	n	K_F (mg/g(L/mg)$^{1/n}$)		R^2
	60	1.3642	11.0407		0.997
	80				
	100				
	120				
Temkin	Initial dye concentration	B_T	A_T	b_T	R^2
	60	20.94	0.6262	118.317	0.999

	80				
	100				
	120				
Dubinin-Radushkevich	Initial dye concentration	B_D	q_D	E	R^2
	60	$2x10^{-3}$	71.0227	15.8113	0.999
	80				
	100				
	120				
Halsey	Initial dye concentration	n_H	K_H		R^2
	60	2.3752	1.1386		0.970
	80				
	100				
	120				

Table.- 2: Results of isotherm study for the adsorption of RR4 onto AC-MnO_2-NC

Isotherm Models	Initial dye concentration	Parameters and their results			
		R_L	b	Q_o(mg/g)	R^2
Langmuir	60	0.4088	0.0241	100.00	0.999
	80	0.3424			
	100	0.2932			
	120	0.2569			
Freundlich	Initial dye concentration	n	K_F $(mg/g(L/mg)^{1/n})$		R^2
	60	1.0989	2.4490		0.999
	80				
	100				
	120				
Temkin	Initial dye concentration	B_T	A_T	b_T	R^2
	60	28.95	4.5643	85.5810	0.994
	80				
	100				
	120				
Dubinin-Radushkevich	Initial dye concentration	B_D	q_D	E	R^2
	60	$5X10^{-3}$	81.8591	10.000	0.992
	80				
	100				
	120				
Halsey	Initial dye concentration	n_H	K_H		R^2
	60	1.2062	0.5138		0.999
	80				
	100				
	120				

Dubinin-Radushkevich Isotherm

The activation energy E value of MG is15.8113 and RR4 is 10.000. B_D value is $2x10^{-3}$ and $5X10^{-3}$ indicates the chemisorption.

Halsey Isotherm

The R^2 value is close to unity which reached to good fitting into Halsey isotherm.

CONCLUSION

The current research illustrates that AC-MnO_2-NC able to be used as an adsorbent for removal of Malachite Green and Reactive Red 4. The quantity of dye adsorbed varied with temperature, initial concentration, pH and adsorbent dose. The adsorption isotherm data well described by the following order: MG is Langmuir> Temkin> Dubinin-Radushkevich> Freundlich> Halsey and RR4 is Langmuir> Freundlich> Halsey > Temkin > Dubinin-Radushkevich. This isotherm constant predicted that the high-level monolayer adsorption and low-level multilayer adsorption. The study reveals to facilitate AC-MnO_2-NC is more efficient adsorbent for removing the Malachite Green and Reactive Red 4.

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