

Enhanced Removal of Malachite Green from aqueous solution by Fruit Waste pretreated with Phosphorous (V) Oxy Chloride

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Abstract: In the present study fruit waste pretreated with Phosphorous (V) Oxy chloride is used for adsorption of Malachite Green (MG). In order to investigate the effects of pretreatment on the cationic dye adsorption, kinetics and capacities of raw fruit waste (RFW) and Phosphorous (V) Oxy Chloride treated fruit waste (TFW) to remove MG from aqueous solutions were compared. The effects of various experimental parameters (e.g., Initial pH, dye concentration, contact time) were also studied. According to the maximum adsorption capacity obtained, adsorption capability of fruit waste is significantly increased after phosphorous (V) Oxy Chloride treatment. Both adsorption isotherms of RFW and TFW fitted the Langmuir model well. The processes of uptake followed pseudo-second order rate kinetics. The results in this study indicated that treated fruit waste is a promising adsorbent for remaining MG from aqueous solution.

Keywords: Malachite Green, Fruit Waste, Adsorption, Phosphorous (V) Oxy Chloride, Waste water.

1. INTRODUCTION

Dyes are used widely in many modern industries such as food, paper, rubber, plastic, cosmetics and textiles, in order to colour their products [1]. Many developing countries discharge the effluent to surface water without any treatment because of technological and economical limitations [2]. Because most of the dyes are stable to light and oxidizing agents, the elimination of colour from dye-bearing wastewater is one of the most economical and efficient treatment techniques for the elimination of dyes. Many of them are cellulose based [3] and can be used with or without any previous thermal or chemical treatment, such as wood sawdust, wheat straw, orange peel, banana pith, peanut hull, rice husk, water hyacinth roots, guava seeds, etc.

In this study, it is proposed to use the waste residues obtained from juice processing industry as biosorbent for the removal of basic dye (Basic Green 4) from aqueous solution.

2. MATERIALS AND METHODS

Waste Fruit residues (FR) obtained from the fruit juice processing industry after the removal of impurities (washed with dil. HCl, distilled water and dried) is mixed with Phosphorous (V) Oxy Chloride in 1:3 ratio boiling with stirring on a water bath for half an hour, cooled, washed with water to remove excess Phosphorous (V) Oxy Chloride and finally dried at 383K for 12 hours in a hot air oven.

MG (Basic Green 4) is used as the adsorbate in this study. It has molecular weight 365 with Colour Index Number 42000. The wavelength of maximum absorption (λ_{max}) of this dye is 618.5 nm.

The dye stock solutions were prepared by dissolving accurately weighed dyes in distilled water to the concentration of 1000 mg/l. The experimental solutions were obtained by diluting the stock solutions in accurate proportions to different initial concentrations.

Adsorption procedures of TFW

and 29°C using 100 ml conical flasks containing 50 ml of different concentrations and initial pH values of dye solutions. The initial pH values of the solutions were previously adjusted with 0.1 M NaOH. Different doses of adsorbent

were added to each flask and then the flasks were sealed to prevent change in volume of the solution during experiments. After shaking the flasks for pre-determined time intervals, the samples were taken out from the flasks and the MG solutions were separated from the adsorbent by filtration and centrifuged. Dye concentrations maximum wavelength 618.5nm using a UV-VISIBLE Spectrophotometer 119 (Systronics).

IR spectra study

The IR spectra of and FW were performed on a Fourier Transform Infrared Spectrophotometer (systronics) to elucidate the functional groups presenting in fruit waste before and after treatment .

3. RESULTS AND DISCUSSION

The adsorption experiments were carried out at different experimental (Table-1) conditions. The results obtained are discussed below.

Effect of initial concentration

The effect of initial concentration of Malachite Green (interms of percentage removal and amount adsorbed (q_t)) are given in Tables. The percentage removal was found to decrease exponentially, while the amount of dye adsorbed increased exponentially with the increase in initial concentration of MG. This indicates a decrease in adsorption, which is attributed due to the lack of available active sites required of the high initial concentration of MG. Similar results have been reported in literature on the extent of removal of dyes[4], [5] and carboxylic acids[6], [7] . The optimum initial concentration of dye solution (MG) was fixed for various adsorption systems and given in Table. 1(Fig.1) and Table. 2(Fig.2).

Table 1: Effect of agitation time and initial concentration on the removal of Malachite Green with FR adsorbent

Agitation Time, t (min)	10mg/L		20mg/L		30mg/L		40mg/L	
	% Removal	q_t mg/g	% Removal	q_t mg/g	% Removal	q_t mg/g	% Removal	q_t mg/g
30	35.70	1.785	30.30	3.030	24.00	3.600	15.20	3.040
60	42.10	2.105	38.40	3.840	30.60	4.590	29.70	5.940
90	45.40	2.270	43.10	4.310	34.40	5.160	32.20	6.440
120	50.60	2.530	47.60	4.760	39.80	5.970	35.10	7.020
135	54.20	2.710	51.30	5.130	44.80	6.720	40.00	8.000
150	62.10	3.105	56.40	5.640	48.20	7.230	44.50	8.900
165	62.60	3.130	58.80	5.880	51.90	7.785	47.60	9.520
180			59.10	5.910	52.40	7.860	50.20	10.040
195							51.40	10.280

Conditions: Adsorbent dose: 100mg/50ml; Initial pH: 6.8; Temp.: 302 K

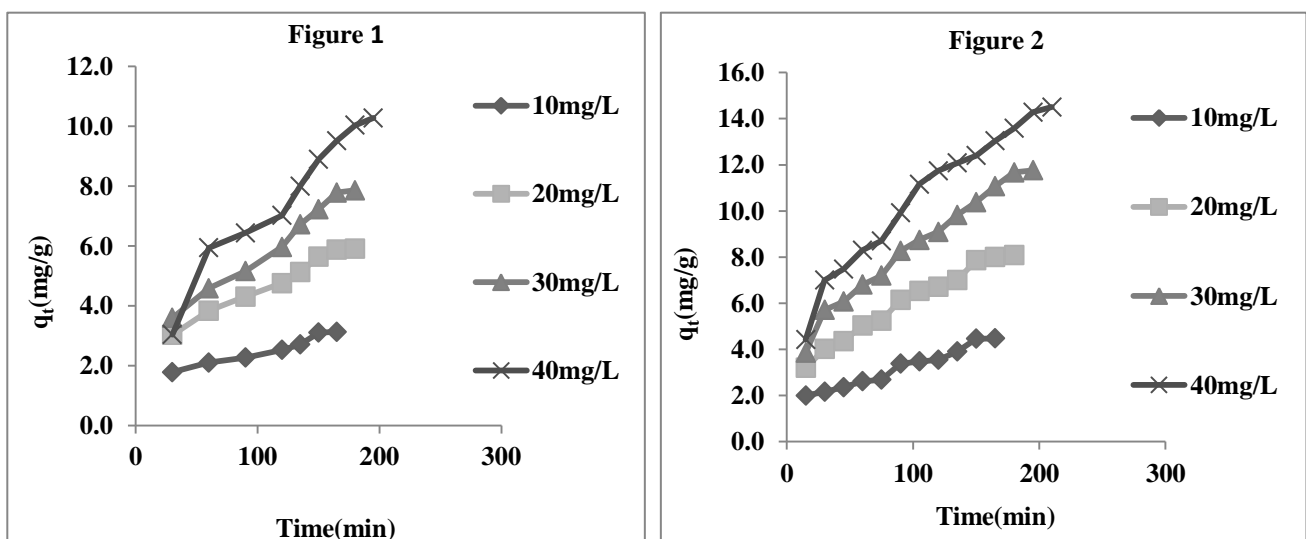


Fig.1,2 Effect of agitation time and initial concentration on the removal of Malachite Green with FR and PFR adsorbent

Table 2: Effect of agitation time and initial concentration on the removal of Malachite Green with PFR adsorbent

Agitation Time, t (min)	10mg/L		20mg/L		30mg/L		40mg/L	
	% Removal	q _t mg/g	% Removal	q _t mg/g	% Removal	q _t mg/g	% Removal	q _t mg/g
15	40	2.000	32.00	3.200	25.70	3.855	22.10	4.420
30	43.2	2.160	40.20	4.020	38.10	5.715	35.00	7.000
45	47.2	2.360	43.60	4.360	40.50	6.075	37.40	7.480
60	52.4	2.620	50.40	5.040	45.40	6.810	41.50	8.300
75	53.7	2.685	52.50	5.250	48.00	7.200	43.50	8.700
90	67.6	3.380	61.40	6.140	55.10	8.265	49.60	9.920
105	69.5	3.475	65.30	6.530	58.30	8.745	55.80	11.160
120	70.9	3.545	67.20	6.720	60.60	9.090	58.70	11.740
135	78.2	3.910	70.10	7.010	65.50	9.825	60.40	12.080
150	89.2	4.460	78.60	7.860	69.20	10.380	62.00	12.400
165	89.6	4.480	80.10	8.010	73.80	11.070	65.20	13.040
180			80.90	8.090	77.80	11.670	67.90	13.580
195					78.40	11.760	71.40	14.280
210							72.50	14.500

Conditions: Adsorbent dose: 100mg/50ml; Initial pH: 7.2; Temp.: 302 K

Adsorption isotherms

The adsorption data were analysed with the help of the following linearised forms of Freundlich and Langmuir isotherms[8] .

Freundlich isotherm : $\log q_e = \log K + 1/n \log C_e$

Langmuir isotherm: $C_e / q_e = 1/Q_0 b + C_e / Q_0$

Where

K=adsorption capacity

(1/n)=order/intensity of adsorption

q_e =amount of MG adsorption per unit mass of adsorbent (mg/g)

C_e =equilibrium concentration of dye (ppm)

Q₀=monolayer (maximum) adsorption capacity (mg/g)

b=Langmuir constant related to energy of adsorption (l/mg)

The values of Freundlich and Langmuir parameters have been obtained respectively,from the linear correlation between the values of (i) log q_e and log c_e and (ii) (c_e / q_e) and c_e (Figure -3,4).

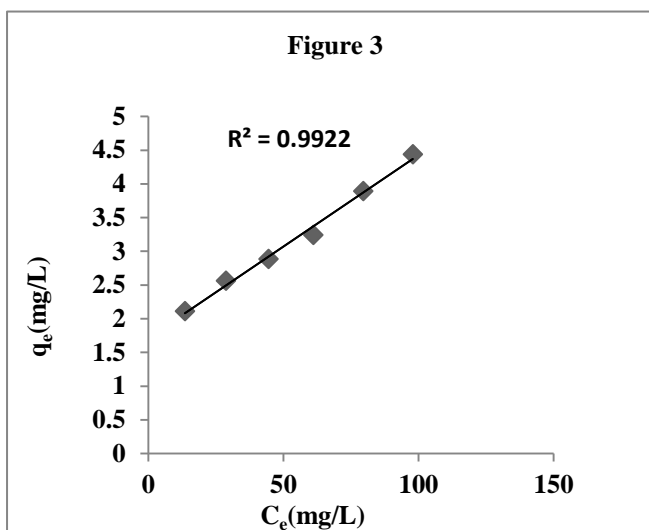


Fig.3 Langmuir Isotherm

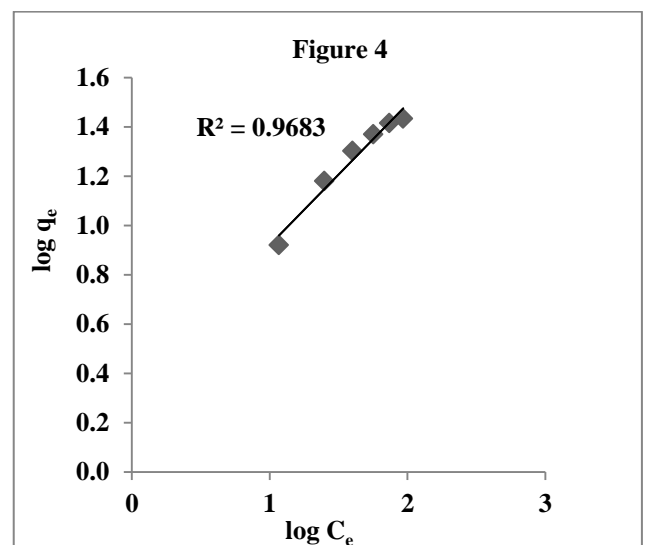


Fig.4 Freundlich Isotherm

The essential characteristics of the Langmuir isotherm can be described by a separation factor, R_L , which is defined by the following equation[9].

$$R_L = 1/1+bC_i$$

Where

C_i -optimum initial concentration of dye (mg/l)

b –Langmuir constant (l/mg)

The values of separation factor, R_L , indicate the nature of the adsorption process as given below :

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

In the present study, the values of R_L are observed to be fraction i.e., in the range of zero to one (0.2642 – 0.7602) which indicate that the adsorption process is favourable for these adsorbent.

Kinetics of adsorption

The kinetics and dynamics of adsorption of MG on RFW and TFW have been studied by applying the first order [10], [11] second order [12] Elovich kinetic models [13].

Pseudo first order equation

Lagergren equation: $\log (q_e - q_t) = \log q_e - k t/2.303$

where

q_e and q_t = amount of MG adsorbed at equilibrium time and at time ‘t’ respectively (mg/g)

k = first order adsorption rate constant (min^{-1})

$\log (q_e - q_t)$ was linearly correlated with time (t).

Pseudo second order equation: $t/q_t = 1/k_2q_e^2 + t/q_e$

k_2 – rate constant of second order adsorption (g/mg/min)

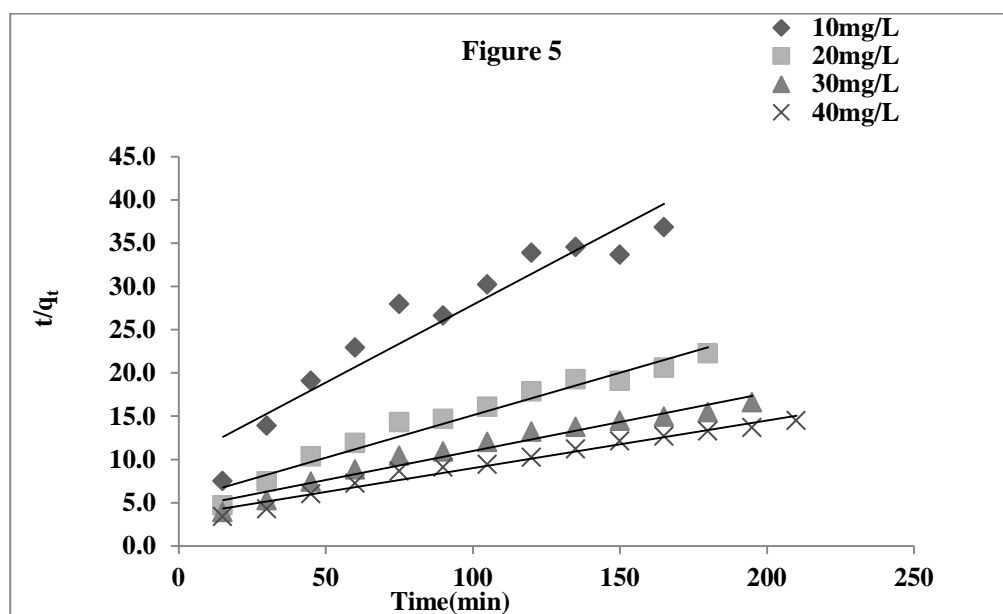


Fig.5 Pseudo second order kinetics

Elovich equation: $dq_t/dt = a \exp(-bq_t)$

a,b are constants

a – initial adsorption rate(mg/g/min)

b – extent of surface coverage and activation energy for adsorption (g/mg).

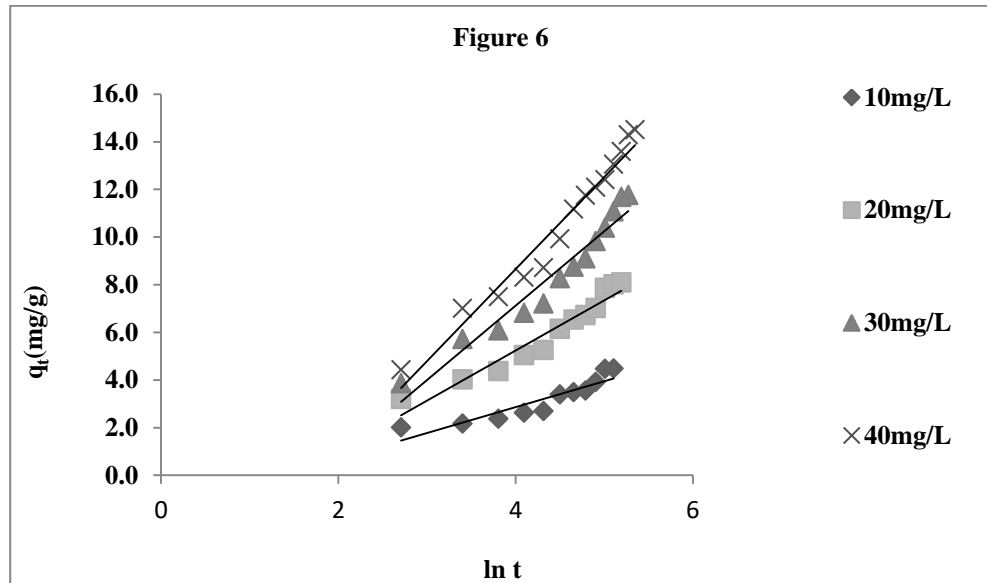


Fig.6 Elovich Kinetic model

The adsorption follows pseudo second order kinetic model (Fig.5) and Elovich model (Fig.6) very well than pseudo first order kinetic model.

Effect of Contact time

The effect of contact time on the amount of dye adsorbed was obtained at the optimum initial concentration of dye. The relevant data are also given in Table 1 and Table 2 .The extent of removal of MG by these adsorbents(RFW and TFW) is found to increase and reach a maximum value with increase in contact time .Similar results have been reported in literature for the removal of dyes[14].

Effect of adsorbent dose

The effect of dose of adsorbent on the amount of MG adsorbed was studied (Table - 3).The equilibrium value of amount adsorbed was observed to decrease with increase in dose of adsorbent. The percentage removal increases with increase in dose of adsorbent . This may be due to the increase in availability of surface active sites resulting from the increased dose of the adsorbent . Similar results have been noticed in literature[15].

Table 3: Effect of adsorbent dose on the removal of Malachite Green with PFR adsorbent

Adsorbent (PFR) Dose (mg)	%Removal	
	20mg/L	40mg/L
25	32.90	28.20
50	37.80	33.60
75	41.10	38.40
100	43.20	42.70
125	57.60	49.80
150	63.50	59.70
200	78.20	67.90
250	86.90	78.00
300	100.00	84.00
350		96.10
400		100.00

Conditions: Agitation time: 3.5 Hrs.; Initial pH: 7.2; Temp.: 302 K

Effect of Initial p^H

The effect of initial p^H of the dye solution on the amount of MG adsorbed was studied by varying the initial p^H, under constant conditions of other process parameters (Table-4). The p^H value changes slightly after adsorption and a decrease in p^H value is noted ($\Delta p^H = p^H \text{ final} - p^H \text{ initial}$) the optimum p^H, value is fixed as 7 to 10. The increase in initial p^H, after this optimum pH there is no change in adsorption, that is after optimum p^H value adsorption remains constant.

Table 4: Effect of solution pH on the removal of Malachite Green with PFR adsorbent

Initial pH	%Removal	
	20mg/L	40mg/L
3.0	53.80	46.50
3.5	63.10	52.00
4.0	69.90	59.10
4.5	72.60	64.50
5.0	78.00	68.60
6.0	85.20	70.10
7.0	87.10	71.00
8.0	87.80	71.70
9.0	89.60	72.30
10.0	90.10	72.90

Conditions: Agitation time: 3.25 Hrs.; Adsorbent dose: 100 mg/50 mL; Temp.: 302 K

Intra Particle Diffusion Study

The possibility of intra particle diffusion process was explored by using the Weber and Morris intra particle diffusion model [16] is,

$$q_t = k_i t^{0.5} + C$$

where

q_t - Amount of MG adsorbed at time t (mg/g)

C - intercept

k_i - intra particle diffusion rate constant (mg/g/min^{-1/2})

The value of C gives an insight into the thickness of the boundary layer. Large intercept suggests great boundary layer effect. Similar results were reported in literature [17].

Table 5: Intra particle diffusion of Malachite green with PFR adsorbent

$t^{1/2}$	q_t (mg/g)			
	10mg/L	20mg/L	30mg/L	40mg/L
5.5	1.785	3.030	3.600	3.040
7.7	2.105	3.840	4.590	5.940
9.5	2.270	4.310	5.160	6.440
11	2.530	4.760	5.970	7.020
12	2.710	5.130	6.720	8.000
12	3.105	5.640	7.230	8.900
13	3.130	5.880	7.785	9.520
14		5.910	7.860	10.040
				10.280

Conditions: Adsorbent dose: 100mg/50ml; Initial pH: 6.8; Temp.: 302 K

The values of q_t were found to be linearly correlated with values of $t^{1/2}$. The k_i values were calculated by using correlation analysis.

Effect of Temperature

Increase of temperature hardly increased q_e value. Gibbs free energy change (ΔG°) was found to be - 8.669 and - 13.509 kJ/mol at 34 °C, which indicates the spontaneous nature of adsorption.

Desorption studies

The poor desorption of dye malachite green with acetic acid indicates that the dye adsorbed onto the adsorbent through by chemisorption mechanism.

4. CONCLUSION

Malachite Green (MG) is found to adsorb strongly on the surface of TFW than RFW adsorbent. The percentage removal of MG increases with increase in contact time, adsorbent dose and initial p^H and increase with decrease in the initial dye concentration. Adsorption data were modeled with the Freundlich and Langmuir adsorption isotherms and various kinetic equations. The results suggest that pore diffusion is more important. The adsorption behaviour is described by a monolayer Langmuir type isotherm. The adsorption process is found to be second order and Elovich kinetic equations with intra particle diffusion as one of the rate determining steps. The present study concludes that RFW and TFW could be employed as low cost adsorbents as alternative to CAC for the removal of MG.

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