The use of Radiation Grafted LDPE for the Removal of Malachite Green Dye from Wastewater

Kamal, H.[1]; Hegazy, E.A.[1]; Soliman, E.A.[2]; Shawky, H.A.[3], Kotp, Y.H.[3] and Farag, M.H.[1]

ABSTRACT

Removal of malachite green dye (MG) from industrial wastewater has been investigated using low density polyethylene (LDPE)-grafted–glycidylmethacrylate (GMA) then chemically modified with diethylamine (DEA), hydroxylamine (HA) or phosphoric acid (H_3PO_4). The effects of various factors; initial dye concentration, pH, contact time, temperature …etc on the adsorption process were studied and optimal experimental conditions were ascertained. The adsorption of MG on the prepared adsorbents were confirmed by Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). The contact time at equilibrium was found to be 120 minutes at pH=5.8 and temperature 40°C. Langmuir and Freundlich isotherms were applied to the data obtained at equilibrium. The maximum removal of dye was found to be 98% for the grafted film treated with phosphoric acid indicating that the prepared films would be a good alternative for the removal of MG dye from wastewater with high efficiency and good tool economically.

1. National Centre for Radiation Research and Technology, Atomic Energy Authority, Egypt, Cairo.

2. Department of Chemistry, Faculty of Science, Ain Shams University, Egypt, Cairo.

3. Desert Research Center.

INTRODUCTION

Wastewater pollution gives adverse effects on the world population of water which may cause health problems such as diarrhea (**Gupta *et al.*, 2004**) . Dyes have long been used in many industries like: painting, paper and pulp, textiles, plastics, leather, cosmetics, pharmaceuticals and food to color their products ((**Sartape *et al.*, 2017**) and (**Pallavi *et al.*, 2018**). Dyes have various conventional methods of removing from wastewaters like: coagulation, electrochemical process, adsorption, membrane separation process, chemical oxidation, reverse osmosis and anaerobic microbial degradation.

Adsorption is a surface phenomenon which results out of binding forces between atoms, molecules and ions of adsorbate and the surface of adsorbent (**Parashar, 2012**). Among these methods, adsorption is preferred over these treatments and is widely used due to low cost and high efficiency and ease of operation (**Min-Yu *et al.*, 2006**) and (**Malik, 2003**). Moreover as the adsorptions of the various adsorbents are not very large, and the new adsorbents which are more economical, easily available and highly effective are still needed so the work is still going on.

The purpose of this work is to determine effectiveness of removing malachite green dye as an example of cationic dye from wastewater using LDPE-g-GMA and treated with diethyl amine (DEA), hydroxyl amine (HA) or phosphoric acid (H_3PO_4). Kinetics and isotherm were also studied in this study.

The MG dye has molecular formula [$C_{23}H_{25}N_2Cl$] and the chemical structure of MG is shown in(Fig.1) by (**Ashis *et al.*, 2017**).
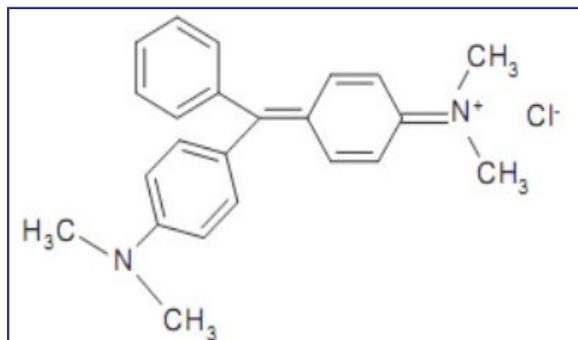
Fig. (1): Chemical Structure of Malachite Green.

MATERIALS AND METHODS

Malachite green (MG) dye content 90% from (Alpha-India) were utilized as received, glycidyl methacrylate (GMA) of purity 99% from (Merck). Diethylamine (DEA); 99% from (Sigma-Aldrich), hydroxyl amine (HA); 96% from (Shinyo-Japan), or phosphoric acid (H_3PO_4); 85% from (Aldrich). Other chemicals as solvents used, HCl, NaOH were provided from (Sigma-Aldrich) and utilized without extra purifications.

Preparation of LDPE Grafted Films

Strips of Low density polyethylene (LDPE) films with thickness 70 μm, were provided by (El–Nasr Co. for Medical Supplies, Egypt). LDPE films were cut to the dimension of (5cm×5cm), weighted and then immersed in (GMA/solvent: 15/85%) of GMA as a monomer and 1,4-Dioxane as a solvent, then subjected to gamma irradiation from ⁶⁰Co gamma cell 4000A, produced by the Atomic Energy of India installed at NCRRT, Egypt at a dose rate 2.5 kGy/h and different doses from 5 to 20 kGy. After the irradiation, the grafted films were removed, washed and soaked overnight in acetone to remove the residual monomer and homopolymers. After that were dried in oven at 50ºC for 24 h then weighted to a constant weight. The degree of grafting was determined as the

percentage increase of weight of LDPE films using the following equation:

$$\text{Degree of Grafting (\%)} = \frac{W_g - W_o}{W_0} \times 100 \quad (1)$$

Where W_g and W_o are the weights of LDPE-grafted and ungrafted films, respectively.

Chemical Modification of Grafted Films

Improvement of the hydrophilic and ion exchange properties of the grafted films was carried out by treating them with DEA, HA or H_3PO_4.

Treatment of Grafted Films with Functional Groups

LDPE-g-GMA films were treated with DEA, HA or H_3PO_4 as adsorbents for removal of MG dye by three different experimentals.

(1). A mixture of 1,4-dioxane and dimethylformamide (DMF) (1:4 v/v), and then 1 ml of DEA was added, **(2).** LDPE-g-GMA films were soaked in a mixture of alcoholic solution (water/methanol; 50/50 v/v) containing 6(%) of HA and **(3).** Phosphonation of LDPE-g-GMA was carried out by immersing the grafted films in 85% of H_3PO_4 aqueous solution. Grafted- treated films were soaked in different reaction mixtures at room temperature in a reflux system. The reactions were carried out at 80°C at different time intervals (2, 4, 6 and 8h) at pH 7. Then the treated films were washed repeatedly with distilled water to remove the excess reagents and dried in a vacuum oven at 50°C for 24 h.
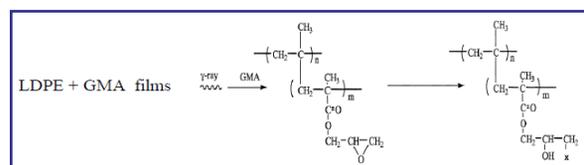
Scheme 1: Preparation of LDPE-g-GMA films treated with DEA, HA or H_3PO_4, where: X= –N(C_2H_5)2, –NH.OH or – PO_3H.

CHARACTERIZATION OF THE PREPARED ADSORBENTS

FTIR-Spectrophotometric Measurements

Mattson 1000 FTIR-spectrophotometer product of Unicom Ltd, England was used to detect the functional groups introduced by grafting and chemical treatment and also to confirm the MG dye adsorption at wavenumber^{-1} range from 4000 to 400 cm^{-1}.

Scanning Electron Microscope Measurements

The surface topography of the grafted and grafted treated films before and after dye adsorption was studied using JEOL SEM-25 Scanning electron microscope. Prior to, examination, the films were dried under sputter coated gold.

Adsorption Studies

Batch adsorption was studied for removal of MG dye onto the adsorbents using UV-spectrophotometer at wavelength (λ_{max} = 618 nm).

 by varying parameters. The parameters studied include effect of initial dye concentration, effect of pH, effect of contact time and effect of temperature on adsorption of MG dye and maintained shaking at 40 rpm.

The amount adsorbed at equilibrium on the different adsorbents (q_e, mg/g) and percentage of removal was calculated by using equations (2) and (3):

$$q_e = [(C_o - C_e) \times V] / W \quad (2)$$

$$\text{Removal (\%)} = [(C_o - C_e)/C_o] \times 100 \quad (3)$$

Where, **V** is the volume of dye solution (L), **W** is the weight of dried adsorbent (g), C_o and C_e are the dye concentrations at initial and equilibrium (mg/L), respectively.

RESULTS AND DISCUSSION

Effect of Solvent

The choice of solvent is essential to the success of radiation grafting experiments and also on the grafting yield. The solvent added to the monomer will be subjected to radiolysis and thus can contribute to chain initiation. Different solvents are chosen for the grafting of GMA onto LDPE to identify a suitable solvent and the results are shown in Table 1:

Table (1) : *Effect of different solvents on the degree of grafting (%) of GMA onto LDPE.*

Solvents	Degree of Grafting (%)	Remarks
Benzene	28.69	No homopolymer
D.M.F	79.60	Moderate homopolymer
Methanol	103.21	Moderate homopolymer
1,4-Dioxane	138.22	No homopolymer
Acetone	184.23	High homopolymer

As can be seen from Table 1, solvent is observed that the percentage of grafting of GMA onto LDPE is higher in acetone and dioxane than other solvents used. However, the high grafting yield obtained in acetone is due to formation of some homopolymer within the grafted samples leading to non-homogeneous grafting. It is observed that, the grafting proceeds homogeneously and appropriate degrees of grafting obtained in the presence of dioxane as a solvent. So that dioxane is chosen as solvent for the grafting of GMA onto LDPE.

Effect of Irradiation Dose

The effect of irradiation dose on the percentage grafting of GMA onto LDPE films in the presence of dioxane as a solvent are shown in (Fig.2). It is obvious that degree of grafting increases relatively rapidly with increasing irradiation dose while propagation is the main reaction, then slightly decrease after 20 kGy, as the termination of graft chains becomes more predominant.

Effect of Monomer Concentration

The grafting of GMA monomer onto LDPE was investigated at different monomer concentrations in (Fig.3). It is obvious that the percentage degree of grafting increases with increasing GMA concentration until reaches its maximum value at 15wt% due to increasing in free radical and active sites on the polymer/monomer pair, while above 15wt%, the percentage degree of grafting ~ reaches constant value. So that 15wt% was chosen as an optimum monomer concentration.
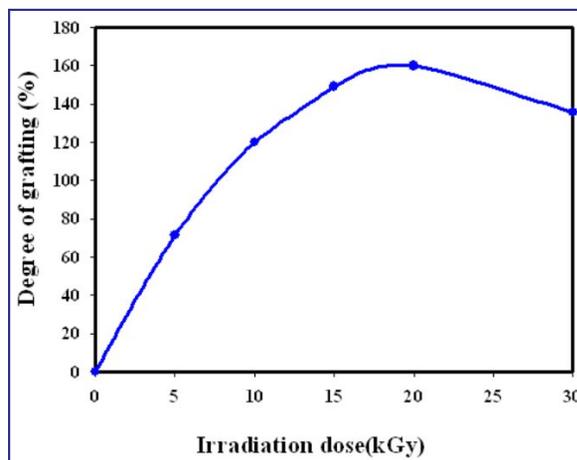
Fig. (2): Effect of irradiation dose on the grafting of GMA onto LDPE films using dioxane as a diluent, monomer concentration; 20wt (%).
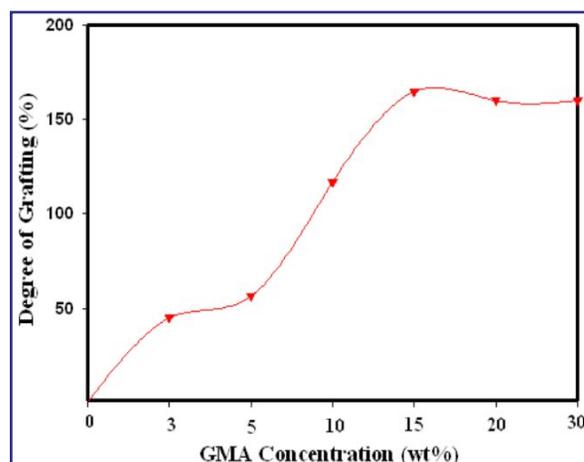
Fig. (3): Effect of monomer concentration on the grafting of GMA onto LDPE films using dioxane as a diluent and irradiation dose; 20 kGy.

CHARACTERIZATION OF GRAFTED TREATED FILMS

FTIR-Spectra Measurements

FTIR spectra of LDPE-ungrafted, LDPE-g-GMA untreated and the grafted films that treated with DEA, HA or H_3PO_4 are shown in (Fig. 4). From (Fig. 4b), the strong peak observed at 1733cm^{-1} is due to C=O group stretching vibration and the band at 908 cm^{-1} is due to asymmetric stretching of the epoxy ring. These results clearly indicate that the introduction of LDPE-g-GMA onto LDPE films is clearly achieved. In the FTIR spectrum of the grafted-treated films (Fig. 4c, d and e), it is obvious that the intensity of the absorption band corresponding to C=O groups of grafted-untreated chains was decreased and shifted to 1732.3 cm^{-1}, 1729 cm^{-1}, 1725 cm^{-1} after treatment with DEA, HA, or H_3PO_4, respectively due to neighboring interaction of functional groups. The band at 908 cm^{-1} related to epoxy ring is decreased after the treatment with DEA and HA due to ring opining and residual epoxy groups clearly remained (**Kimmins et al., 2014**). This was proved by the disappearance of epoxy during phosphoric acid treatment. FTIR shows the change in properties and the interactions of functional groups between adsor-

bent and adsorbate. It can be seen that C=O group of the grafted-treated films with DEA, HA or H_3PO_4 shifted to 1731.7 cm^{-1}, 1727 cm^{-1}, 1736.3 cm^{-1}, respectively, after MG dye adsorption in (Fig.5). The broad band which assigned to overlapping of OH and NH stretching in the grafted-DEA-treated film was shifted to 3008 cm^{-1} after dye adsorption. The broad band shifting at 3350.10 cm^{-1} due to the reaction between adsorbent treated with HA and the board band shifting into 3016 cm^{-1} due to P-O in phosphoric acid after dye adsorption. Generally, the shift observed in the characteristic band of the adsorbents after MG dye adsorption is due to introduced new functional groups of MG dye on the sites of adsorbents. The characteristic peaks indicated that the functional group of MG can be adsorbed successfully. This shift in peak values may be due to the formation of chemical bond between functional groups present on the prepared film and MG.
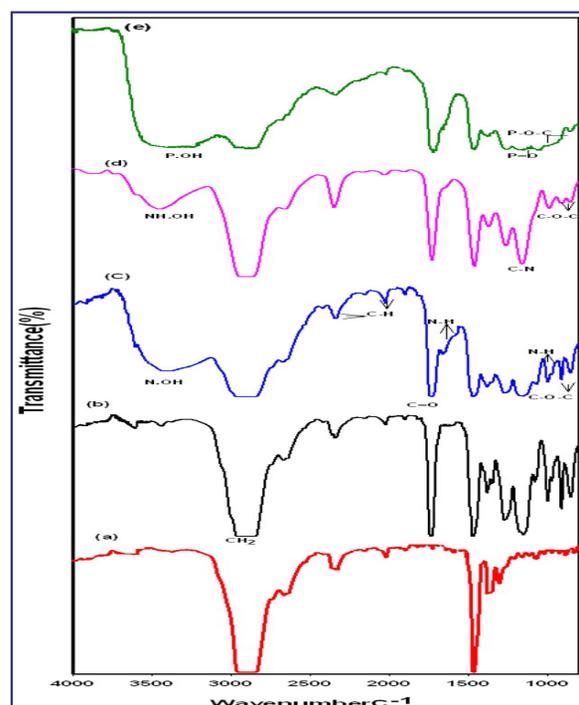
Fig. (4): FTIR spectra of (a)-LDPE ungrafted, (b)-LDPE-g-GMA-untreated and LDPE-g-GMA-treated films with (c)-DEA, (d)-HA or (e)-H_3PO_4 before dye adsorption.

SEM Microscope

The surface morphology of the grafted-treated films was investigated by SEM before and after dye adsorption in (Fig.6). This figure showed complete change in surface morphology. Before adsorption there was rough surface morphology as observed (Fig.6.a, b and c). The rough surface of the grafted-treated films can provide a high adsorption capacity, while smoother morphology was observed after adsorption of dye on the surface of adsorbent in (Fig. 6d, e and f). It can be also noted that the MG dye molecules occupied the pores of the grafted–treated films indicating the adsorption of MG dye by the polymeric adsorbents.

Fig. (5): FTIR spectra of LDPE-g-GMA treated films with (a)-DEA, (b)-HA or (c)-H_3PO_4 after dye adsorption.
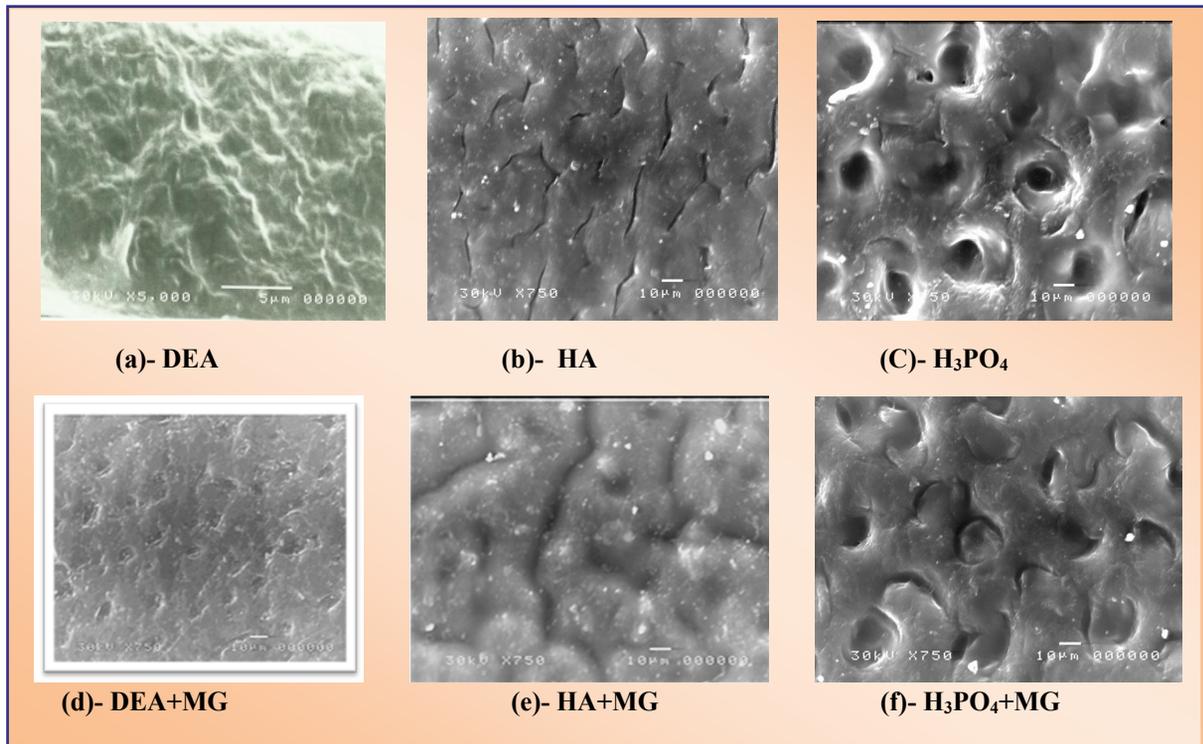
Fig. (6): SEM of LDPE-g-GMA treated films before and after adsorption MG dye.

Adsorption of Malachite Green Dye:

The adsorption of MG dye onto the grafted-treated films was investigated spectrophotometrically and the absorbance data obtained were converted into concentration data (Fig.7), showed the standard calibration curve of MG dye.
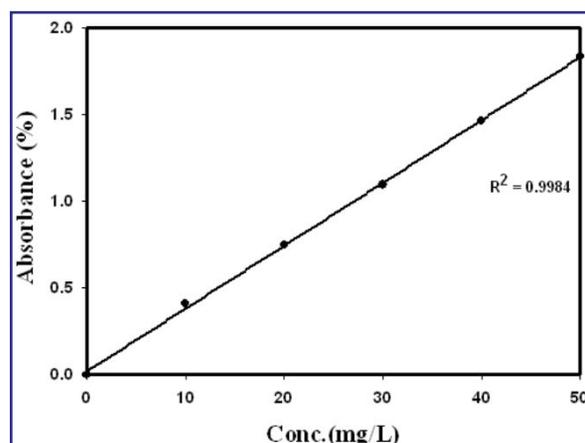
Fig. (7): Calibration curve of MG dye.

Effect of Initial Dye Concentration

The removal percentage increases with increasing the initial dye concentration of different prepared adsorbents in 50 ml of dye solution with different initial concentrations that ranged from10-50 mg/L that shown in (Fig.8). After that, the removal percentage remained constant at dye concentration higher than 40ppm as the active sites become saturated. The increase of the sorption capacity with increasing dye concentration confirmed strong interaction between MG dye and polymer. Increasing the initial concentration enhances the interaction between the dye and adsorbents from providing necessary driving force to overcome the resistances to mass transfer of dye **(Sartape *et al*., 2017).**

Effect of pH

The surface charge depends on the pH of the solution. Effect of pH was studied by varying the pH of the dye solution from 2 to 6 and was adjusted by adding 0.1 M HCl or 0.1 M NaOH. LDPE-g-GMA treated films as adsorbents were studied in (Fig. 9). It has been observed that the removal percent increases with increasing the pH of dye solutions up to 5.8, then a saturation state was reached. These results indicated that at lower pH the dye cations become protonated and a competition may occur between the dye cations and H^+ for the active sites in the adsorbate by increasing the pH of the dye solution, the adsorbent become negatively charged and so the cationic dye molecule can be adsorbed and the removal percent increase. It is also obvious that the removal percent for the grafted films treated with phosphoric acid > hydroxyl amine > diethyl amine
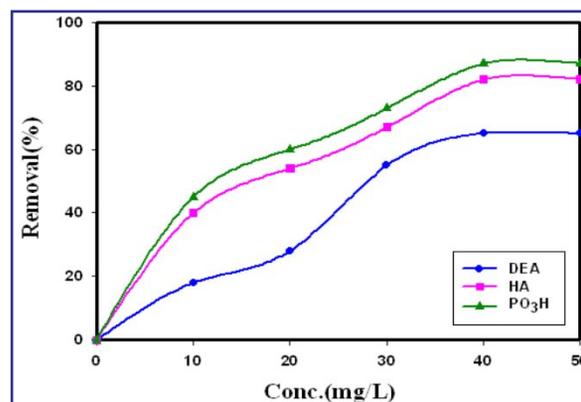
Fig. (8): Effect of initial conc. on the removal (%) of MG dye, temp. ~25°C, pH; 6 and time;24 h.
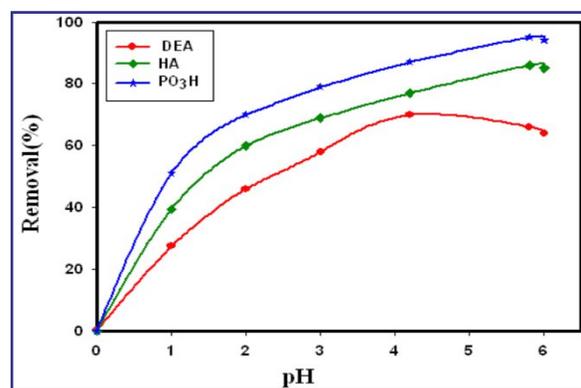
Fig. (9): Effect of pH on the removal (%) of MG dye; Conc.; 40 mg/L, temp.~25°C and time; (120 min.).

Effect of Contact Time

The effect of contact time on the removal of MG was carried out at various time intervals from 5 to 150 minutes. (Fig.10) showed the removal percent obtained using various time intervals at pH= 5.8 and temperature ~25°C. It is clear that the dye uptake is rapid in the earlier stages of adsorption process and hence the removal percent is high more than 70% of the initial dye concentration was removed within 20 minutes. These results may be due to that the active sites on the grafted treated films are vacant in the initial stages of the adsorption process. After a rapid initial dye uptake, there was transitional phase in which the rate of dye uptake was slow to reach equilibrium after 2h. The results showed that more than 90(%) of the initial dye concentration was removed by LDPE-g-GMA treated film with phosphoric acid at the equilibrium.
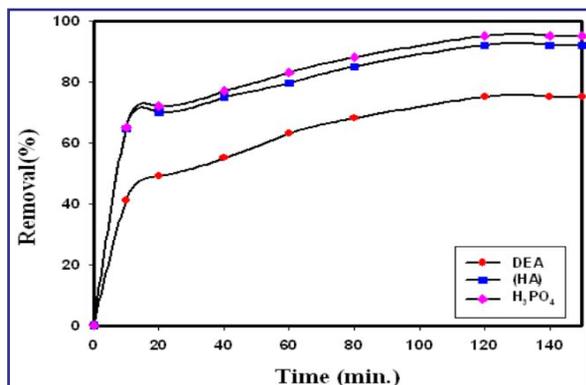
Fig. (10): Effect of contact time on the removal (%) of MG dye, conc.; 40 (mg/L), temp. ~25°C and pH; 5.8.

Effect of Temperature

The effect of temperature was studied by varying the temperature between 30 to 50°C and the results are shown in (Fig.11). It can be seen that the removal percentage increases with increasing the temperature from 30 to 40°C then level off. The results indicated the increase in kinetic energy and the dye molecules may also to undergo an interaction with active sites at the surface of adsorbents. In addition, increasing the temperature may allow the dye molecules to pen-

etrate into the grafted-treated film and react with the active sites. It is also obvious that the removal percent for the LDPE-g-GMA treated films with H_3PO_4 > HA > DEA.
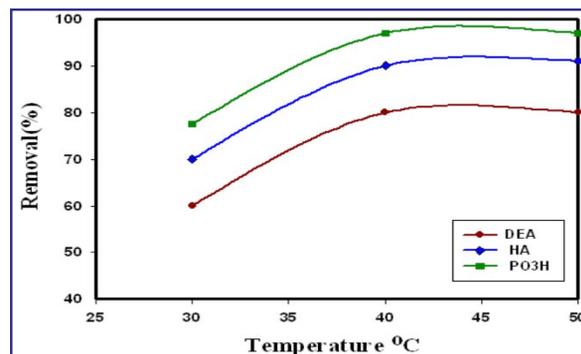
Fig. (11): Effect of temperature on the removal (%) of MG dye, conc.; 40 (mg/L), pH; 5.8 and time; (120 min.).

Kinetic Studies on Malachite Green Adsorption

The kinetics of basic MG dye on the prepared adsorbents was analyzed using the pseudo 1st order and pseudo 2nd order equations.

Pseudo-First-order Kinetic

Pseudo-1st–order model is given after integration by:

$$\ln(q_e-q_t)=\ln q_e-K_1 t \qquad (4)$$

Where, q_e and q_t are the amounts of dye adsorbed by the adsorbent (mg/g) at equilibrium and at time t and K_1(min^{-1}) is rate constant of the pseudo first order. In (Fig.12) represents the linear plot of $\ln[q_e-q_t]$ vs t (**Santhi et al., 2015**). The correlation coefficient (R^2), K_1, q_e (cal) were calculated and the results are shown in Table 2.
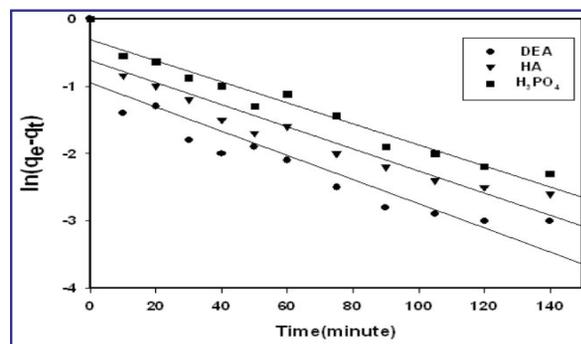
Fig. (12): Pseudo-first-order slope.

Table (2) : *Parameters of Pseudo 1ST order.*

LDPE-g-GMA treated films with	q_e, cal(mg/g)	K_1(1/min.)	q_e, exp.	R^2
DEA	3.6	0.015	8.6	0.823
HA	5.13	0.019	14.4	0.9005
H_3PO_4	10.73	0.020	21.8	0.9540

If the value of q_e cal. $\neq q_e$ exp. indicating that this model is inapplicable indicating that adsorption of malachite green (MG) onto grafted-treated films did not follow pseudo-first-order kinetics model as the same opinion (**Muinde *et al.*, 2017**).

***Pseudo-Second-order Kinetic*:**

The Pseudo-2nd order model proposed (**HO and McKay, 1999**) can be represented in the following linear form (R) by:

$$T/q_t = 1/K_2 * q_e^2 + t/q_e \qquad (5)$$

Where, q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at time t, respectively. k_2 is the Pseudo-2nd rate constant of the adsorption process. (Fig.13) represents the relationship between t/

qt vs t (**Sartape *et al.*, 2017**).

The correlation coefficient (R^2), K_2, q_e was calculated and the results are shown in Table 3 for Pseudo-2nd order.
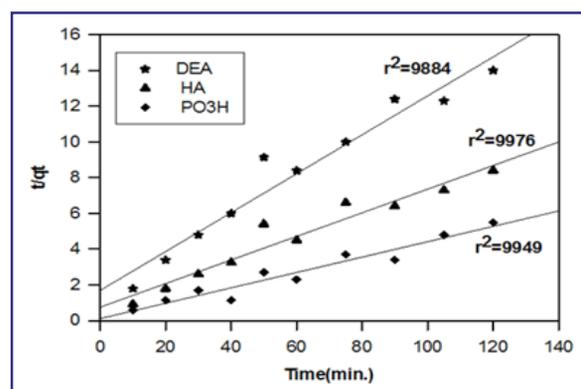
Fig. (13): Pseudo-second-order slope.

Table (3) : *Parameters of Pseudo 2nd order.*

LDPE-g-GMA treated films with	q_e, cal(mg/g)	K_2 (mg/g min.)	q_e, exp.	R^2
DEA	9.18	0.0323	8.6	0.9884
HA	15.15	0.0058	14.4	0.9976
H_3PO_4	23.25	0.016	21.8	0.9949

Table (3) showed that the pseudo-second order equation was applicable for all adsorbents and the correlation coefficient was (R^2=0.99). The calculated q_e values from the model were also in good agreement with the experimental values. The result indicates that the pseudo second order is better than pseudo-first order model for the adsorption of MG. These results are in good agreement with the previous studies as cyclodextrin-based adsorbent (**Crini *et al.*, 2007**), Pithophora spp. a fresh water algae

(**Kumar *et al.*, 2005**), carbon (**Zhang *et al.*, 2008**), NRH nitric acid treated rice husk), PRH (peroxide treated rice husk) (**Bendi *et al.*, 2013**), and Plumbago Zeylanica (PZ) (**Pallavi *et al.*, 2018**) were studied to follow the pseudo second-order model.

Adsorption Isotherms

Langmuir and Freundlich are the widely applied isotherm models. The linear equations are given:

Langmuir Isotherm

The Langmuir model is given by:

$$C_e /q_e = 1/K_L \times q_o + (1/q_o) C_e \qquad (6)$$

Where, C_e /q_e vs C_e is plotted, C_e(mg/L), q_e(mg/g) are the liquid phase concentration and amount adsorbed at equilibrium, respectively.

K_L(L /mg) and q_o(L /mg) are the Langmuir constants (**Sartape et al., 2017**) and can be calculated from the intercept and the slope.

The intercept gives $1/K_L$ value and the slope gives $1/q_o$ values are shown in (Fig.14). K_L can be calculated from the intercept and the value of q_o can be obtained from the slop are shown in Table 4.
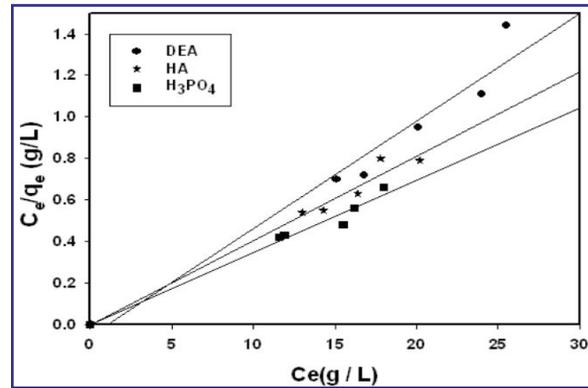
Fig. (14): Langmuir Isotherm Slope.

Table (4) : *Parameters of Langmuir Isotherm.*

LDPE-g-GMA treated films with	q_o	K_L	R^2
DEA	0.094	11.4	0.957
HA	0.030	24.6	0.977
H_3PO_4	0.015	29.4	0.979

Freundlich Isotherm

The Freundlich isotherm model is given by:

$$\ln q_e = \ln K_f + 1/n_f \ln Ce \qquad (7)$$

Where: K_f is the Freundlich constant (L^{-1} gm) (**Pallaviand et al., 2018**), $1/n_f$ is the heterogeneity factor. (Fig.15) shows the relationship between $\ln C_e$ vs $\ln q_e$. The slope gives $1/n_f$ value and the intercept gives ln K_f value as shown in Table 5. The heterogeneity factor $1/n_f$ is a measure of the deviation from linearity of the adsorption and ranges between (0 and 1) which indicate the degree of non-linearity between solution concentration and adsorption. A higher value of K_f indicates a higher capacity for adsorption than a lower value (**Xiangliang and Zhang., 2009**).
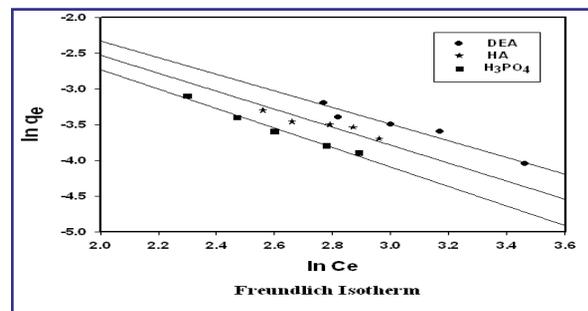
Fig. (15): Freundlich isotherm slope.

Table (5) : *Parameters of Langmuir Isotherm.*

LDPE-g-GMA, treated films with	K_f	$1/n_f$	R^2
DEA	0.134	1.39	0.996
HA	1.010	1.03	0.997
H_3PO_4	1.64	0.66	0.999

The values of linear R^2 coefficient were high of Freundlich isotherm indicating the suitable values of its constants. So, the adsorption isotherm for adsorption MG dye is better by Freundlich model than Langmuir model as the same opinion result (**Dhahir et al., 2013**).

Thermodynamic Studies

The thermodynamic studies play an important role in understanding the heat change in the adsorption process. The effect of temperature of the adsorbents on the adsorption of MG was investigated at 323, 313, 303 K. Thermodynamic parameters, such as change in enthalpy [ΔH°], entropy [ΔS°] and Gibb's free energy [ΔG°] were investigated using the equations (8) & (9):

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R}\frac{1}{T} \qquad (8)$$

$$\Delta G^\circ = -RT\ln K_C \qquad (9)$$

The negative values of ΔG° presenting in the Table 6, indicates that physisorption is dominating the weak chemical interactions as said by (**Pallavi et al., 2018**), and with increase in temperature, the negative values of ΔG° decreases indicated the spontaneous adsorption process.

Where, standard enthalpy (ΔH°), standard entropy (ΔS°) and Gibbs free energy (ΔG°), Kc is constant, (R=8.314 J/mol K) and T is the absolute temperature (K) were agreed by (**Sartape et al., 2017**) and (**Pallavi et al., 2018**). The ΔH° and ΔS° were calculated from the linear Van't Hoff plot i.e. ln Kc vs. 1/T showed in (Fig.16).
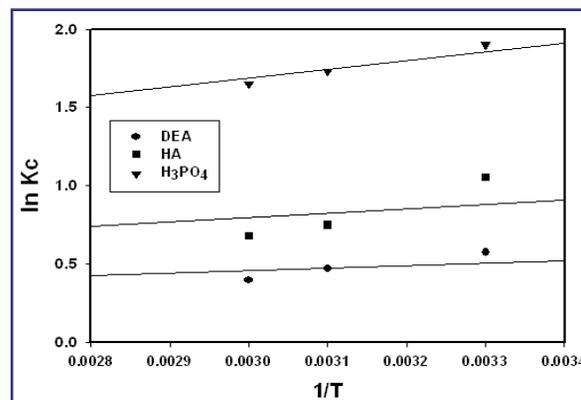
Fig. (16): Van't Hoff plots for adsorption of MG on LDPE g-GMA treated films with DEA, HA or H_3PO_4.

The values of ΔH° and ΔS° were calculated from the slope [-ΔH°/R] and the intercept [ΔS°/R] of the plots of ln Kc vs 1/T (**Santhi et al., 2015**). The ΔH° values of grafted-treated films are presented in Table 6 and the negative value of ΔH° indicated the exothermic process.

Table (6) : *Values of thermodynamic parameters.*

Temperature (K)	ΔG^O (kJ/mol) DEA	ΔG^O (kJ/mol) HA	ΔG^O (kJ/mol) H_3PO_4	ΔH^O (kJ/mol) at (313 K)
303	-4.089	-7.435	-15.346	DEA= -1.28
313	-3.841	-6.985	-14.416	HA= - 2.24
323	-3.71	-6.750	-13.951	H_3PO_4= - 4.65

CONCLUSION

Batch adsorption experiments show that the adsorption of MG dye onto LDPE-g-GMA and treated with DEA, HA or H_3PO_4 was dependent on many variables including contact time, pH, MG concentration, and temperature. Type of chemical treatment i.e. type of functional group, has an important role in the adsorption process. Freundlich model was best fit the isotherm data and Pseudo second order kinetics followed the kinetic values. Thermodynamic analysis indicated that the adsorption of MG dye onto grafted-treated films was exothermic and

spontaneous. The removal (%) at 40ºC is found to be 80 (%) for DEA, 89 (%) for HA and 98 (%) for H_3PO_4, respectively. It can be concluded that the LDPE-g-GMA that treated with H_3PO_4 is more efficient adsorbent for MG dye than other films since its removal dye efficiency reached 98(%).

REFERENCES

- **Ashish, S.S.; Aniruddha, M.M.; Vikas, V.J.; Prakash, D.R.; Mansing, A.A. and Sanjay, S.K. (2017):** Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. *Arab J., Chem.*, 10: 3229.

- **Bendi, R.; Pathpireddy, M.; Reddy, K. and Challapalli, S. (2013):** Low cost adsorbents from agricultural waste for removal of dyes. *Environ. Prog. Sustain. J.,* 33(1):38**.**

- **Chetna, P. (2012):** Removal of Malachite Green dye by adsorption using char. *Rourkela NIT J.,* 108CH036.

- **Crini, G.; Peindy, H.N.; Gimbert, F. and Robert, F. (2007):** Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies. *Sep. Purif. Technol. J.*, 53 (1): 97.

- **Gupta, V.K.; Mittal, A.; Krishnan, L. and Gajbe, V. (2004):** Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. *Sep. Purif. Technol. J.*, 40: 87.

- **Ho, Y.S. and Mckay, G.A. (1999):** A kinetic study of dye sorption by biosorbent waste product pith. *Resour. Conserv. Recy. J.*, 25 (3): 171.

- **Kumar, K.V.; Sivanesan, S. and Ramamurthy, V. (2005):** Adsorption of malachite green onto *Pithophora* sp., a fresh water algae: Equilibrium and kinetic modeling. *Process Biochem. J.*, 40 (8), 2865.

- **Malik, P.K. (2003):** Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36. *Dyes Pigments J.,* 56:239.

- **Min-Yu, T. and Su-Hsia, L. (2006):** Removal of methyl orange dye from water onto raw and acid activated montmorillonite in fixed bed. *Desalin. J.*, 201: 71.

- **Muinde, V.M.; Onyari, J.M.; Wamalwa, B.; Wabomba, J. and Nthumbi, R.M. (2017)**: Adsorption of malachite green from aqueous solutions onto rice husks: Kinetic and equilibrium studies. *AJEP J.*, 8: 215.

- **Pallavi, P.; King, P. and Prasanna, Y. (2018):** Use of plant biomass for removal of malachite green from aqueous solution and optimization using Central Composite Design (CCD). *Rasayan J. chem.*, 11 (1): 203.

- **Saadiyah, A.D.; Enaas, A.H.; Sanaa, T.S. and Noor, F. (2013):** Adsorption of malachite green dye from aqueous solution onto iraqi raw al-hussainiyat deposit. *ECB J.*, 2 (11): 866.

- **Santhi, M.; Kumar, P.E. and Muralidharan, B. (2015):** Removal of malachite green dyes by adsorption onto activated carbon–Mno_2–Nanocomposite– Kinetic study and equilibrium isotherm analyses. *IOSR J. AC.*, 8: 33.

- **Scott, D.K.; Paul, W. and Neil, R.C. (2014):** Amine-functionalization of glycidyl methacrylate-containing emulsion-templated porous polymers and immobilization of proteinase K for biocatalysis. *Polymer J.*, 55 (1): 416.

- **Xiangliang, P. and Daoyong, Z. (2009):** Removal of malachite green from water by *Firmiana simplex* wood fiber. *Electron. J. Biotechn.*, 12 (4): 997.

- **Zhang, J.; Li Y.; Zhang, C. and Jing, Y. (2008):** Adsorption of malachite green from aqueous solution onto carbon prepared from Arundo donax root. *Hazard. Mater. J.*, 150 (3): 774.

استخدام البولى اثيلين المنخفض الكثافة المطعم باستخدام الاشعاع لإزالة صبغة المالكيت جرين من المياه الملوثة

هناء كمال محمد[1] ـ السيد احمد عبد العزيز حجازى[1] ـ السيد أحمد سليمان عبد العزيز[2] ـ حسام أحمد شوقى[2] ـ يسرا حافظ قطب[2] ـ ميرال حسنى عبد الجواد فرج[1]

تمت دراسه تحضير بعض الأغشيه الصناعيه ذات المجموعات الوظيفيه لإزالة صبغة الملاكيت جرين من مياه الصرف الصناعي وذلك بالتطعيم الأشعاعي لأفلام البولي إثيلين المنخفض الكثافة المطعم بمونمر الجليسيديل ميثاكريلات (GMA) ومعالجة هذه الأغشيه المطعمه بواسطة الداى اثيل أمين ، والهيدروكسيل أمين أوحمض الفوسفوريك ،و تم عمل توصيف للأغشيه المحضره بواسطة الأشعه تحت الحمراء (FTIR) والماسح المجهري الآلكتروني (SEM) قبل وبعد ادمصاص الصبغه. وتمت دراسة العوامل المؤثره على ادمصاص هذا النوع من الصبغات مثل تأثير التركيز الأولي وزمن التلامس ودرجة الحموضة ودرجة الحرارة للصبغه. وأسفرت هذه الدراسه على أن الزمن اللازم للوصول الى ازالة معظم الصبغه والتى تصل الى نسبة 98 (٪) بعد حوالي ساعتين من الزمن فى درجة حموضه مقدارها ٥٫٨ عند درجة حراره $40^{o}C$. ونستنتج من هذه الدراسه أن الأغشيه المحضره سوف تكون بديلا جيدا للممتزات الآخرى لآزالة صبغة الملاكيت جرين ومايشابهها من صبغات بمياه الصرف الصناعي بكفاءه عاليه وكأداه جيده اقتصاديا.

1.   المركز القومي لبحوث وتكنولوجيا الإشعاع – هيئة الطاقة الذرية – القاهرة – مصر.

2.   قسم الكيمياء – كلية العلوم – جامعة عين شمس – القاهرة – مصر.

3.   مركز بحوث الصحراء.