

Removal of Cationic Dye from Aqueous Solutions by Modified Acid - Treated Pomegranate Peels (PUNICA GRANATUM): Equilibrium and Kinetic Studies

Mona A. Shouman^{*}, Soheir Abdel Aaty Khedr

¹National Research Center,
Laboratory of Surface Chemistry and Catalysis, Cairo, Egypt

^{*}Corresponding author's email: monashouman [AT] yahoo.com

ABSTRACT--- *In present research, a novel attempt was undertaken to evaluate the effect of various acid – treatments on the adsorption performance of pomegranate peels towards methyl green (MG) dye. The prepared adsorbents were characterized using FTIR, SEM, and BET measurements. A series of experiments were conducted in a batch system to assess the effect of the system variables, i.e. solution pH, temperature, ionic strength and contact time on the adsorption capacity. Maximum adsorption was taken place at pH 5.5 while equilibrium was achieved in 75 min. Equilibrium isotherms were analysed by using Langmuir, Freundlich, Temkin, and Dubinin – Radushkevich isotherm equations. The equilibrium data fitted very well to the Langmuir Isotherm and the maximum capacity reached 29 mg g⁻¹ at 303K. The adsorption kinetics was found to follow pseudo – second – order rate kinetic model. Thermodynamic parameters were also evaluated and revealed that the adsorption process is spontaneous and endothermic in nature.*

Keywords – Pomegranate Peel, Acid – treatment, Adsorption, Thermodynamics

1. INTRODUCTION

Many industries, such as dyestuffs, textile paper and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored waste water. The disposal of dye wastewater without proper treatment is a big challenge and cause serious hazards for the aquatic environment [1]. Discharging dyes into the hydrosphere give water undesirable color [2] and reduce sunlight penetration, with some dyes also being toxic/carcinogenic [3]. Dyes can be classified according to their structure as anionic and cationic [4]. In aqueous solution, anionic dyes carry a net negative charge due to the presence of sulphonate (SO₃⁻) groups, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulphur containing groups [5].

Biological, chemical and physical methods are three categories of dye removal technologies which have not been applied widely at large scale due to the high cost and disposal problems [6]. Various physical techniques including coagulation, precipitation, ion – exchange treatment, adsorption and co – precipitation have been used for the removal of dyes from wastewater [7, 8, 9, 10]. Among the physical technologies of dye removal, adsorption is one of the predominant methods used in wastewater treatment for dye removal due to its simplicity in operation and availability of a wide range of adsorbents. The increasing demand of efficient and economical treatment technology has given rise to a search of alternative low – cost adsorbents to substitute the use of commercial activated carbon that are expensive and difficult to be regenerated. The utilization of agro-wastes as adsorbent is currently receiving wide attention because of their abundant availability and low - cost owing to relatively high fixed carbon content and presence of porous structures. Many researchers in recent years have focused on the use of agro – wastes as adsorbents instead of activated carbon: banana stalk [11], groundnut hull [12], mango peels [13], rice husk [14], papaya seeds [15] and yellow passion fruit waste [16]. Recently, comparative studies of cationic and anionic dye adsorption by agricultural solid wastes and some other low-cost adsorbents were reported [17].

The proper selection of additives for modification of the adsorbents play crucial role in ensuring better efficiency and more cycles of usability. Physical modification involves suitable sizing of the adsorbents by chopping and grinding, thermal treatment (steam and microwave), ultrasonic irradiation, stirring, freezing, drying and high pressure (autoclaving). While, chemical modifications involve treatment of the adsorbents with an array of chemicals for washing, enhancement of binding groups, elimination of inhibiting groups and graft copolymerization. The chemicals that can be

used are mineral (hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid), organic acids (oxalic acid, citric acid, tartaric acid, salicylic acid), salts, alkanes, aldehydes, ketones, oxidizing agents, and chelating agents [18].

Punica Granatum, commonly called pomegranate, is one of the most popular fruits in the world due to its pleasant taste, high nutritional value, and many medical features. It is a by – product of the pomegranate juice industry and therefore is inexpensive. It consists of edible part, seeds, and peel. The pomegranate peel constitutes 5% to 15% of its total weight [19]. Recently, some studies have been done using pomegranate peel to remove Cr (VI) [20], Ni (II) [21], Fe(II) [19], Congo Red [22], and Amaranth Dye [23] from aqueous solutions.

In our research, acid modification was carried out using different activating agents such as phosphoric, nitric, sulphuric and citric acid onto the pomegranate peels for methyl green dye removal. The effect of different parameters such as, contact time, pH, ionic strength and temperature was studied. The data from the experiments were fitted with different models to identify the adsorption mechanism.

2. EXPERIMENTALS

2.1 Dye solution preparation

Methyl Green is a divalent cationic dye (C.I name Basic Blue 20) that is chosen in this study as an adsorbate. It has chemical formula $C_{26}H_{33}N_3Cl_2$, molecular weight 458.5 g/mol, and λ_{max} 631 nm. The chemical structure of Methyl Green is shown in Fig.1. Stock solutions were prepared by dissolving 0.1g of MG in 1 L distilled water. The desired concentrations were obtained by successive dilutions of the stock solution (100 ppm) with distilled water to the required concentrations.

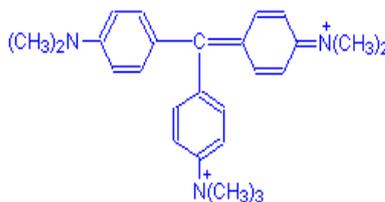


Figure 1: Chemical structure of methyl green dye

2.2 Preparation of the acid – modified adsorbents

The waste peels of pomegranate were first washed with distilled water and dried in sunlight until the moisture was partially evaporated. Complete evaporation was accompanied by placing the pomegranate in an oven at 70°C for overnight to remove moisture before use. The dried pomegranate peels were grounded in a ball mill. The sieved raw material was then divided into five portions. The first portion was used as it is for sorption (designated as RPP). The second portion was mixed with H_2SO_4 (ratio 1:1) and kept at room temperature for overnight (designated as MPPS). The third and fourth portions were soaked for 24h in a solution of phosphoric acid and nitric acid, (30 wt%, ratio 1:1) for overnight, respectively, (designated as MPPP and MPPN). The fifth portion was soaked in a solution containing citric acid (20 wt%, ratio 1:1, designated as MPPC). All the samples were washed with double distilled water to remove the excess acid several times then dried in an oven at 100 °C.

2.3 Batch adsorption studies

Batch adsorption experiments were carried out to study the effect of different parameters such as pH, contact time, and temperature. For each experiment run, 50 ml of dye solution with various concentration (20 – 100 mg/L), slurry pH = 5.5 and a known amount of adsorbate (0.1 gm) was taken in a 100 ml conical flask and agitated in a mechanical shaker at 120 rpm for a given time. The concentration of the dye was determined at 631 nm using UV – 2401 PC spectrophotometer (Shimadzu). The amount of dye adsorbed q_e (mgg^{-1}) was calculated using the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e (mgL^{-1}) are the initial and equilibrium concentration of dye in solution, V (L) is the volume of solution and W (g) is the weight of adsorbent. The percentage removal of dye was also calculated using the following relationship:

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Characterization of samples

The characteristics of the modified pomegranate peel had been subjected to various characterization parameters. Scanning electron microscope (SEM) was used to study the surface morphology of the samples. Fig.2 shows the SEM images for the raw and different acid – treated samples. Comparing all the figures, the surface was found to be rough and present a high density of pores of different size and shapes especially for the modified samples treated with phosphoric and nitric acid [24].

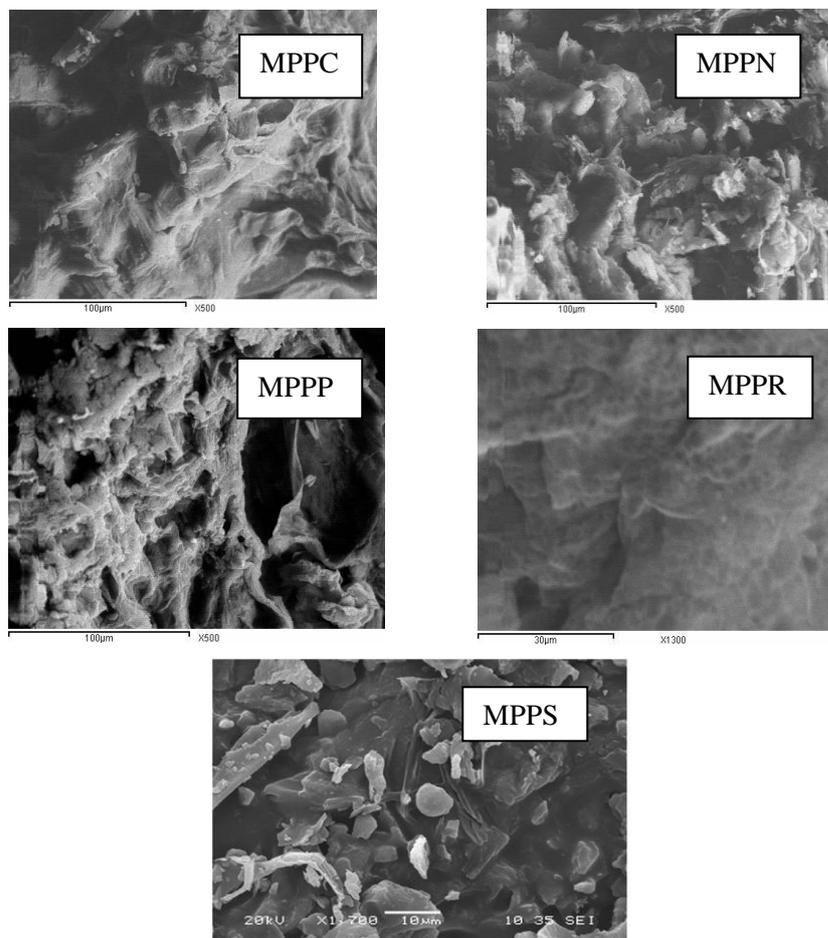


Figure 2: SEM images of acid – treated pomegranate peels using different activating agents

Surface area analysis of the modified samples was performed using Quantachrome NOVA Automated Gas Sorption System by nitrogen gas adsorption at 77K. The modification treatment with the different acids led to a change in the surface area. The specific surface areas were 252.4 m²/g ; 244.6 m²/g; 232.7 m²/g; 179.7 m²/g and 177.8 m²/g for the MPPP, MPPN, RPP, MPPS and MPPC samples, respectively. It has been reported that phosphoric acid is an especially preferred modifying agent because it tends to promote the structural integrity of the molecular sieve framework [25].

Fourier Transform Infrared Spectroscopy (FTIR) analysis was used to identify some characteristic functional groups of the untreated and acid – modified samples. The spectra were measured from 4000 to 400 cm⁻¹. Table 1 shows the tabulated data for FTIR spectra band assignments for the raw and different modified treated samples obtained from Fig.(3) .The peaks at 3430 cm⁻¹ indicate O – H stretching vibration and spectra bands observed at 2920 cm⁻¹ represent C – H stretching vibration of aliphatic C – H especially due to C – CH and C – CH₂ bonds. The peaks observed at 1730 cm⁻¹ corresponds to C = O stretching vibrations of aldehydes, ketones, lactones or carboxyl groups while peaks observed at 1620 cm⁻¹ corresponds to C = C – stretching of alkenes. The peaks at 1230 cm⁻¹ and 1030 cm⁻¹ correspond to – O – H bending vibration and C – O stretching vibration of carboxylic acid. Girgis et al., reported that for the FTIR spectrum of

carbon prepared by phosphoric acid activation, the band in the region of $1300 - 900 \text{ cm}^{-1}$ could be caused by phosphorous – oxy – containing functional groups. Therefore, the broad band observed at 1096 cm^{-1} could be attributed to P=O in organic phosphates, O – C bond in P – O – C linkage or P = OOH bond [26].

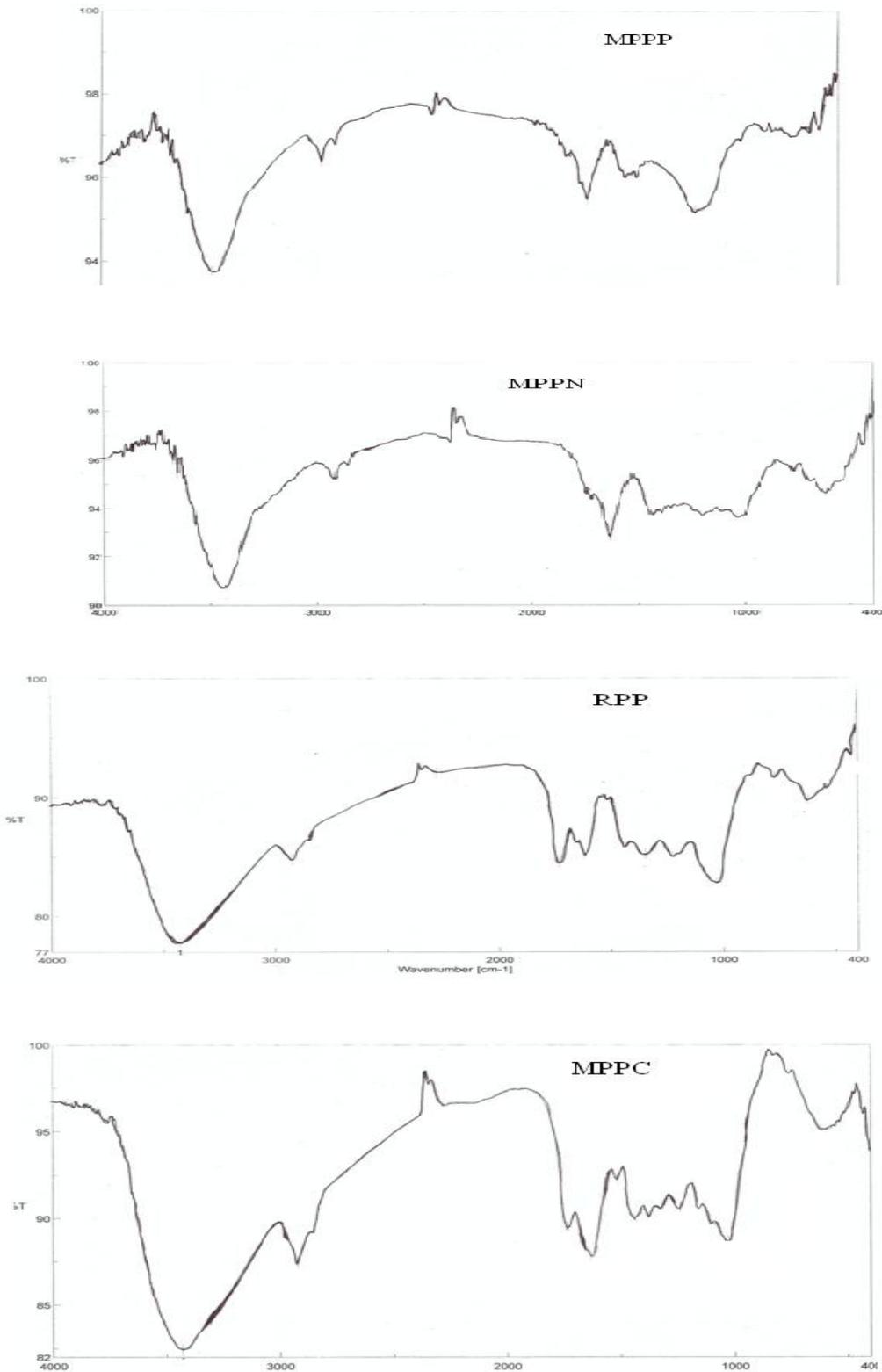


Figure 3: FTIR spectra of raw and different pomegranate peels using different activating agents

Table 1: FTIR spectra band assignments for modified pomegranate peel

Assignment	Band position (cm ⁻¹)				
	RPP	MPPP	MPPC	MPPN	MPPS
O – H stretching vibration of alcohols and phenols	3430	3450	3430	3430	3440
C – H stretching of aliphatic groups	2925	2923	2923	2925	2920
- C ≡ C- stretching of alkynes	2280	2295	2278	2275	2270
C = O – stretching of aldehydes , ketones, lactones or carboxyl groups	1730	--	1730	--	--
- C = C – stretching of alkenes	1620	1624	1630	1624	1628
- C – N stretching of aliphatic amine	1228	1096	1240	1029	1030
Phosphorous – oxy containing functional groups	622	---	619	621	620

3.2 Effect of pH

The magnitude of electrostatic charges imparted by ionized dye molecules is primarily controlled by the pH of medium. The amount of dye adsorbed or rate of adsorption tends to vary with pH of aqueous medium [27]. Two possible mechanisms of adsorption of dye on the adsorbent may be considered; (a) electrostatic interaction between the adsorbent and the dye molecule, (b) a chemical reaction between the dye and the adsorbent. The effect of pH on the removal of methyl green is shown in Fig.(4). From this figure it is observed that at low pH values, the percentage removal decreased. However, when solution pH increased from 4.0 to 10, the percentage removal increased. The maximum percentage removal for methyl green adsorption was observed at pH 10 for all the modified samples under investigation.

At lower pH values, the surface of the samples under investigation becomes positively charged and a strong repulsive force occurs between methyl green (dicationic triarylmethane dye) and positive surface adsorbents. This leads to a decrease in adsorption percentage of methyl green on the adsorbent. On the contrary, when the pH of dye solution is increased, the surface tends to acquire negative charge, thereby resulting in an increased adsorption of dyes due to increasing electrostatic attraction between positively charged sorbate and negatively charged sorbent [28]. However, increasing the pH solution above 10 resulted in an increase in negatively charged OH⁻ which led to further decrease in percentage removal values. These results indicate that the protonation of MG occur in acidic medium.

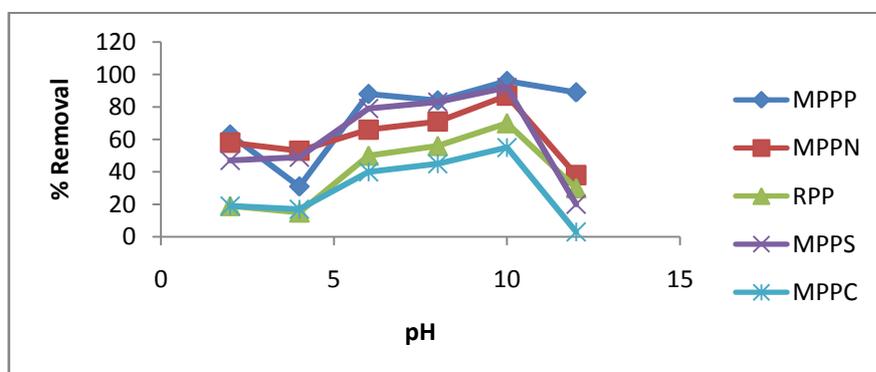


Figure 4: Effect of pH on the removal of methyl green prepared from different acid – treated pomegranate peel

3.3 Effect of ionic strength

Wastewater containing dye commonly has higher salt concentration and the effects of ionic strength are of some importance in the study of dye adsorption onto different adsorbents [29]. The effect of external ionic strength on the percentage removal of methyl green adsorption onto various modified samples was investigated in NaCl solutions with concentration range from 0.01 – 0.15M at 30°C and pH = 4 (Fig.5). Theoretically, when the electrostatic forces between the adsorbent surface and adsorbate ions are attractive, an increase in ionic strength will decrease the adsorption capacity. This result was confirmed in this study. Conversely, when the electrostatic attraction is repulsive, an increase in ionic strength will increase the adsorption [29, 30]. The experimental data from this study did not follow this convention. At high ionic strength, (0.08 – 0.15M NaCl), a notable decrease in percentage removal of methyl green was observed. The reduction in uptake of the dye is probably due to the excess Na⁺ ions which inhibit the approach of adsorbed ions to the active sites of the sorbent.

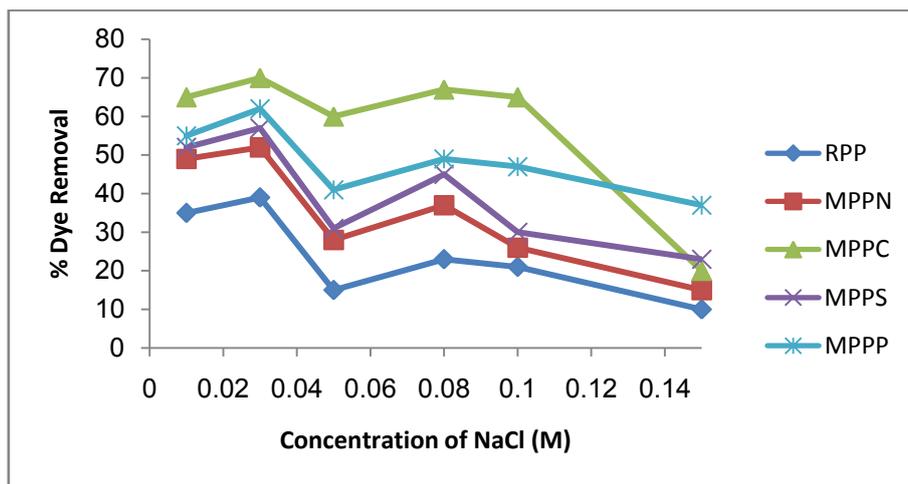


Figure 5: Effect of various NaCl concentrations on methyl green dye removal by various acid – treated modified pomegranate peels

3.4 Sorption Isotherm Studies

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [31]. The type of an adsorption isotherm model is very important in order to understand the adsorptive behavior for solid – liquid adsorption systems. Various isotherm equations have been used to discover the adsorption capacity of the acid modified samples prepared from pomegranate peel. Some of these equations are Langmuir, Freundlich, Tempkin and Dubinin – Radushkevich equations.

The Langmuir isotherm [32] is based on three assumptions, namely, sorption is limited to monolayer coverage, all surface sites are alike and only can accommodate one adsorbed atom and the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy. Based upon these assumptions, the Langmuir equation is expressed as:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \quad (10)$$

where C_e is the equilibrium concentration of adsorbate (mgL^{-1}), q_e is the amount of dye adsorbed at equilibrium, Q_o is the Langmuir constant related to maximum monolayer coverage capacity (mgg^{-1}) and K_L is the Langmuir constant related to energy of adsorption capacity (Lmg^{-1}). The linear plot of $1/q_e$ Vs $1/C_e$ is shown in Fig. (6). The constants Q_o and K_L can be calculated from the slope and intercept of the plot and the values are tabulated in Table 2.

The essential feature of the Langmuir isotherm to identify the feasibility and favorability of the adsorption process can be expressed by a dimensionless constant called separation factor (R_L) was calculated in each case using the following equation:

$$R_L = \frac{1}{1 + K_L C_o} \quad (11)$$

where K_L is the Langmuir constant and C_o is the initial dye concentration (mgL^{-1}). The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L > 1$ represent unfavorable adsorption, and $R_L = 1$ represent linear adsorption while adsorption is irreversible if $R_L = 0$ [33]. In the present investigation, the R_L values were less than one which indicates that the adsorption process was favorable.

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non – uniform distribution of heat of sorption over the surface. It can be expressed in the linear form as follows [34]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (12)$$

where q_e is the amount of dye adsorbed at equilibrium time (mgg^{-1}), C_e is the equilibrium concentration of the dye in solution (mgL^{-1}), K_F (Lg^{-1}) and n are isotherm constant which indicate the capacity and intensity of the adsorption, respectively. The values of K_F and $1/n$ were calculated from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$. (Table 3).

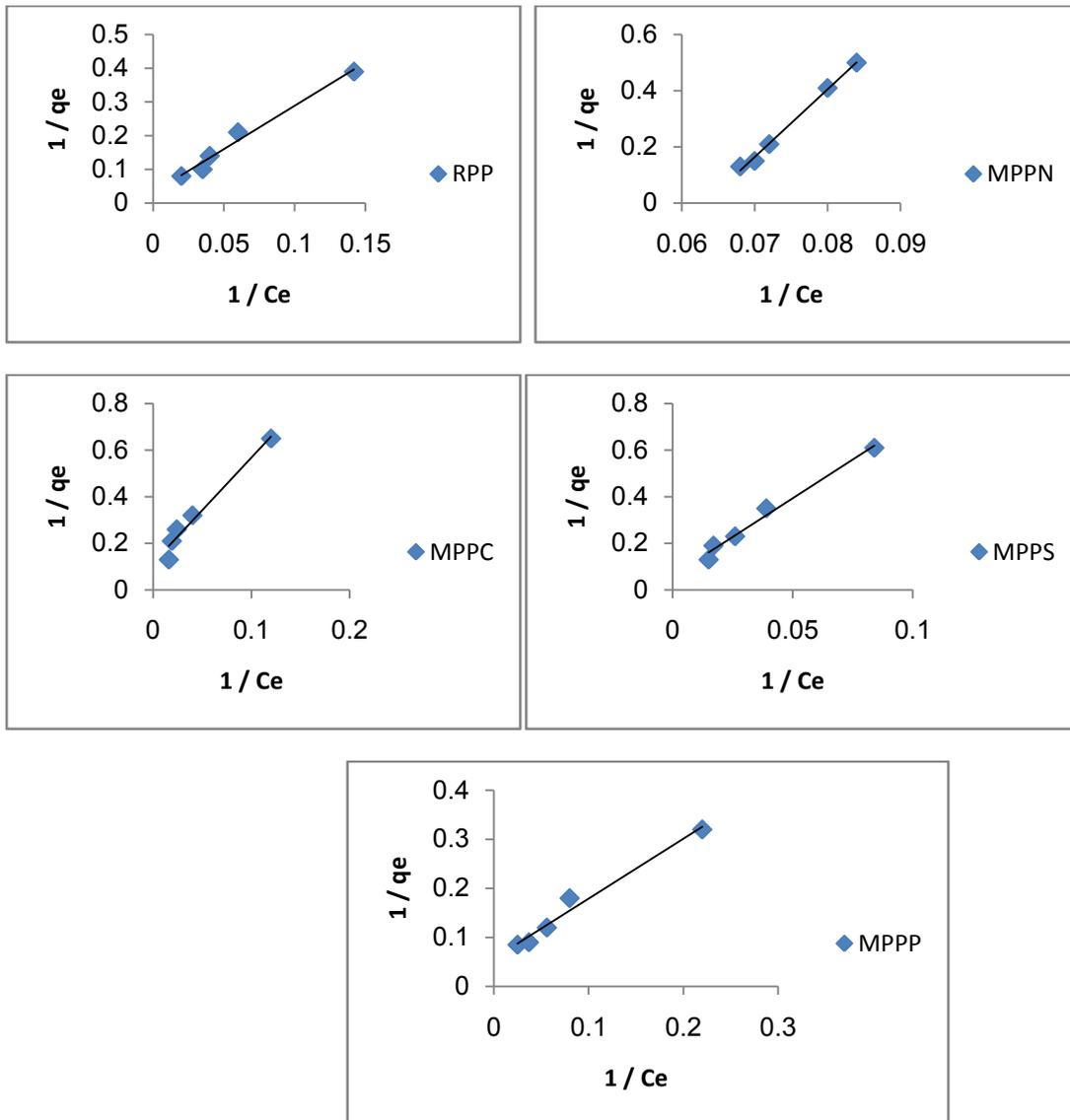


Figure 6: Langmuir isotherm plots for the removal of methyl green by modified pomegranate peels

The Temkin isotherm describes the behavior of adsorption systems on heterogeneous surfaces, and it has generally been applied in the following form [35] :

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (13)$$

Eq.(13) can be expressed in its linear form as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (14)$$

$$B_1 = RT/b \quad (15)$$

where B_1 is the Temkin constant related to heat of sorption (Jmol^{-1}), K_T is the Temkin isotherm constant (Lg^{-1}) corresponding to the maximum binding energy, R is the universal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and T is the absolute temperature (K). The adsorption data can be analyzed according to Eq.(14). Therefore, a plot of q_e Vs $\ln C_e$ enables the determination of the isotherm constants K_T and B_1 (Table 2).

The D – R isotherm [36] was used to determine the characteristic porosity and the apparent free energy of adsorption. The linear form can be represented as:

$$\ln q_e = \ln q_D - K_{DR} \varepsilon^2 \quad (16)$$

where K_{DR} is a constant related to the mean free energy of adsorption (mol^2J^2), q_D is the theoretical saturation capacity (molg^{-1}), ε is the polyani potential (Jmol^{-1}), which is related to the equilibrium concentration (C_e, gL^{-1}) as follows:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (17)$$

The slope of the plot of $\ln q_e$ Vs ε^2 gives K_{DR} as slope and $\ln q_D$ as the intercept. The isotherm parameters are represented in Table 2 (Fig. not shown). The mean free energy of the adsorption per molecule of adsorbate can be calculated using the following equation:

$$E = \frac{1}{\sqrt{2B}} \quad (18)$$

The magnitude of E is useful for estimating the mechanism of the adsorption reaction. In the case of $E < 8 \text{ kJ/mol}$, physical forces may affect the adsorption. If E is in the range of $8\text{--}16 \text{ kJ/mol}$, adsorption is governed by ion exchange mechanism, while for the values of $E > 16 \text{ kJ/mol}$, adsorption may be dominated by particle diffusion [37]. It can be observed from Table 3 that the mean free energy (E) is found to be in the range of $2.4\text{--}5.6 \text{ KJmol}^{-1}$ which is in the range of physical adsorption.

As seen from [previous results](#) that the Langmuir isotherm provides the best correlation for the experimental data, whereas the Freundlich, Temkin and Dubinin–Radushkevich isotherms were not fitted with the experimental data. This suggests that MG adsorption is limited with monolayer coverage and the surface is relatively homogenous in terms of active sites and there is significant interaction among the MG molecules. Since the Langmuir equation assumes that the surface is homogenous. The surface modification on the pomegranate peel using H_3PO_4 was shown to be able to increase its adsorption capacity on MG, from 10 to 29 mgg^{-1} . Our findings showed that the treatments with sulphuric acid and citric acid resulted in reduced uptakes of MG. This was due to the removal of the hydroxide groups by the acidic treatment which produced acidic oxygen functional groups on the modified surface. However, the higher adsorption of MG on the H_3PO_4 – treated pomegranate peel was due to the adsorption of negative ions PO_4^{3-} on the positive sites on the carbon surface, thus making the surface becomes more negatively charged, thus facilitating adsorption of the positive charged molecules of MG. This result shows that acid treatments might have different effects on the different acid – modified pomegranate peels [29]. (Table 2)

3.5 Effect of contact time

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period of time signifies the efficiency of the adsorbent for its use in wastewater treatment. In physical adsorption, most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. The effect of contact time for the removal of methyl green by various adsorbents is shown in Fig. (7). The dye was rapidly adsorbed in the first 30 min, and then the adsorption rate decreased gradually and reached equilibrium in about 75 min. In the beginning, the adsorption rate was fast as the dye ions were adsorbed by the exterior surface of the modified samples. When the adsorption of the exterior surface reached saturation, the dye ions entered onto the pores of the adsorbent particles and was adsorbed by the interior surface of the particle [38].

Table 2: Isotherm parameters for the adsorption of methyl green on different modified pomegranate peels

Isotherms	Parameters	RPP	MPPP	MPPC	MPPN	MPPS
Langmuir	$Q_m(\text{mg g}^{-1})$	20	29	10	25	12
	$K_L(\text{Lmg}^{-1})$	0.021	0.02	0.021	0.024	0.013
	R_L	0.4	0.3	0.27	0.34	0.46
	R^2	0.99	0.99	0.98	0.99	0.98
Freundlich	$K_F(\text{mg g}^{-1})(\text{Lmg}^{-1})$	1.99	2.51	1.26	1.25	1.25
	$1/n$	0.89	0.9	0.7	0.9	0.86
	R^2	0.97	0.96	0.96	0.95	0.97
Temkin	$K_T(\text{L mg}^{-1})$	0.54	0.93	0.26	0.49	0.61
	B	3.2	3.8	3.8	8.3	1.9
	R^2	0.92	0.95	0.94	0.94	0.95
Dubinin Radushkevich	$q_D(\text{mgg}^{-1})$	12.81	20	7.0	33.1	49.4
	$E(\text{KJ mol}^{-1})$	3.3	2.5	5.6	2.6	2.4
	R^2	0.92	0.93	0.93	0.95	0.94

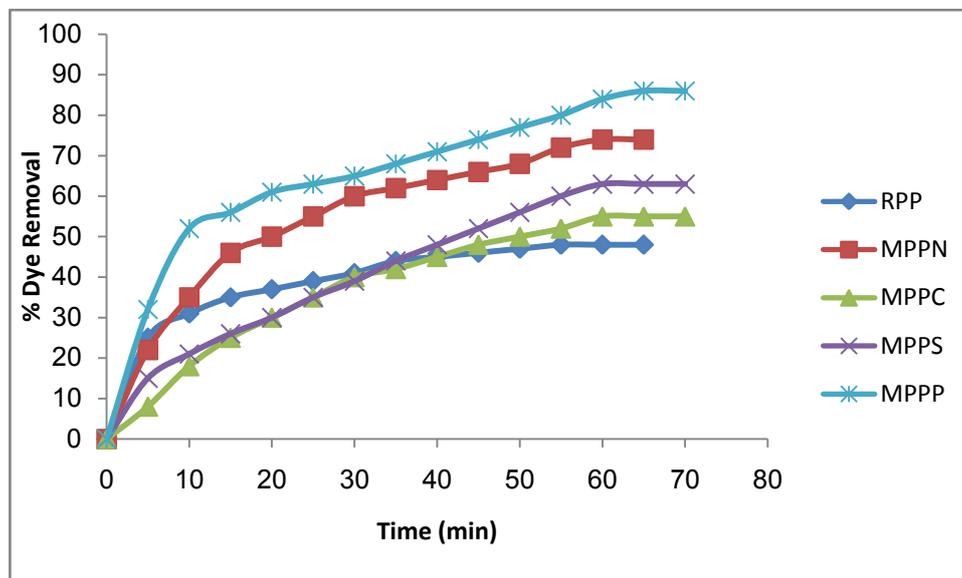


Figure 7: Effect of contact time on the removal of methyl green dye (Temp=30°C, initial dye concentration 100mgL⁻¹, adsorbent dosage=0.5 gm) using modified pomegranate peels

3.6 Adsorption Kinetic Study

Sorption kinetic mechanics can be based on diffusion mass transfer processes or chemical reaction kinetics. The sorption kinetics of a sorbent depends on the property of the adsorbate, experimental conditions, temperature and pH value. In this study, four kinetic models were studied, namely, pseudo – first – order, pseudo – second – order, Bangham and Elovich models.

The Lagergren's rate equation [39] is one of the most widely used rate equation to describe the adsorption of an adsorbate from the liquid phase. The linear form of the pseudo – first – order equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (19)$$

where q_e and q_t (mgg^{-1}) refer to the amount of dye adsorbed at equilibrium and at any time t (min), respectively, and K_1 is the equilibrium rate constant of pseudo – first – order adsorption (min^{-1}). The slopes and intercept of $\log(q_e - q_t)$ Vs t plot were used to determine K_1 and q_e . The values of K_1 , q_e , along with the correlation coefficients (R^2) are tabulated in Table 3. It is seen from Table 3 that the R^2 values is less than 0.99 suggesting that the present adsorption system does not follow pseudo – first – order process.

The pseudo – second – order kinetic model (40) is represented by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (20)$$

where q_e and q_t refer to the amount of dye adsorbed (mgg^{-1}) at equilibrium and at any time t (min), respectively. K_2 is the pseudo – second – order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The plots between t / q_t versus t were drawn and shown in Fig.(8). The K_2 and q_e values were determined from the slope and intercept of the plot, and R^2 values are represented in Table 3. The correlation coefficients for the linear plots of t/q_t against t for the second-order equation were observed to be close to 1 indicating the applicability of the pseudo – second – order model.

The Elovich equation is one of the most useful models for describing chemisorptions which is expressed as follows:[41]

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t \quad (21)$$

where a is the initial adsorption rate ($\text{mgg}^{-1} \text{min}^{-1}$) and b is the adsorption constant related to the extent of surface coverage and activation energy for chemisorption and q_t is the amount of dye adsorbed at time t (min). The values of a and b can be obtained from the slope and intercept of the linear plots of q_t versus $\ln t$. The parameter a , b and R^2 are given in Table 3. In the case of using the Elovich equation, the correlation coefficients are lower than those of the pseudo second-order equation. The Elovich equation does not predict any definite mechanism.

Kinetic data were further used to know about the slow step occurring in the present adsorption system using Bangham's equation [42]

$$\log \log \left(\frac{C_0}{C_0 - q_t m} \right) = \log \left(\frac{K_0 m}{2.303 V} \right) + \infty \log t \quad (22)$$

where C_0 is the initial concentration of adsorbate in solution (mgL^{-1}), V is the volume of solution (ml), m is the weight of adsorbent per liter of solution (gL^{-1}), q_t (mgg^{-1}) is the amount adsorbed at time t , and ∞ (<1) and K_0 are constants. Linear plot of $\log \log (C_0 / C_0 - q_t m)$ versus $\log t$ did not yield perfect linear curves ($R^2 < 0.99$) showing that the diffusion of adsorbate into pores of the adsorbent is not the only rate controlling step [43].

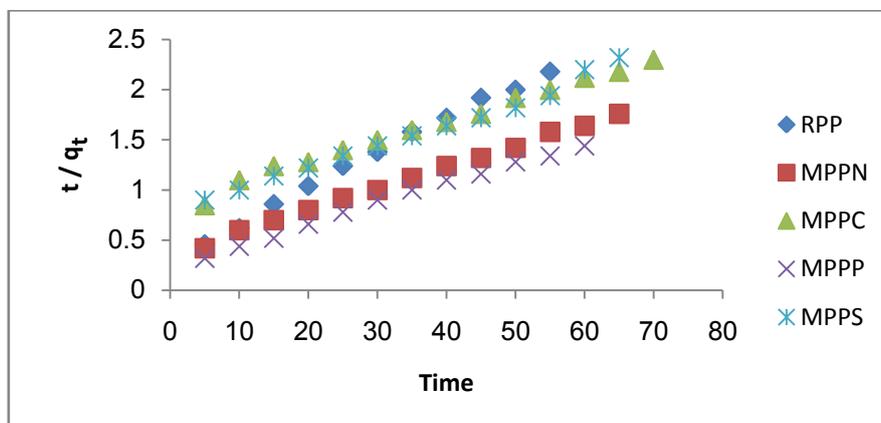


Figure 8: Langmuir isotherm plots for the removal of methyl green by modified pomegranate peels

Table 3: Kinetic parameters for the adsorption of methyl green on different modified pomegranate peels

Equations	Parameters	RPP	MPPP	MPPC	MPPN	MPPS
Pseudo – first - order	$K_1(\text{min}^{-1})$	0.004	0.041	0.02	0.05	0.03
	$q_e (\text{mg g}^{-1})$	15.8	30.2	36.3	27.5	28.8
	R^2	0.99	0.98	0.99	0.98	0.99
Pseudo – second - order	$K_2(\text{g mg}^{-1}\text{min}^{-1})$	0.005	0.002	5.01	0.001	0.001
	$q_e (\text{mg g}^{-1})$	25.0	43.4	32.7	36.8	34.6
	R^2	0.99	0.99	0.99	0.99	0.99
Elovich	$a(\text{mg g}^{-1}\text{min}^{-1})$	7.29	10.66	6.96	9.32	7.51
	$b (\text{g mg}^{-1})$	0.16	0.10	0.15	0.12	0.17
	R^2	0.96	0.97	0.97	0.96	0.95
Bangham	$K (\text{g})$	29.58	12.44	3.31	6.45	4.47
	A	0.31	0.31	0.57	0.25	0.53
	R^2	0.93	0.92	0.93	0.92	0.94

3.7 Effect of Temperature and adsorption thermodynamics

The effect of temperature on the adsorption of methyl green onto the various acid – treated samples was investigated by varying the adsorption temperature at 298, 313 and 333 K. Fig.(9) shows the plot of amount adsorbed versus various acid – modified treated samples at different temperatures. According to this figure it was found that the amount adsorbed increased with the increase in temperature of the system from 298 – 333 K. These results indicate the endothermic nature of the adsorption process. Increasing the temperature was known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbate and adsorbent, creating new adsorption sites hence increasing increasing the rate of intraparticle diffusion of adsorbate molecules into the pores of the acid – treated samples at higher temperatures [44, 45].

The determination of the thermodynamic parameters; enthalpy of adsorption (ΔH°), Gibb's free energy of adsorption (ΔG°) and entropy of adsorption (ΔS°), is important to evaluate the thermodynamic feasibility and the spontaneous nature of the process. An adsorption process is generally considered as physical if $\Delta H^\circ < 84 \text{ kJmol}^{-1}$ and chemical when ΔH° lies between 84 – 420 kJmol^{-1} [46]. Therefore, the thermodynamic constants can be obtained from the equations:

$$\Delta G^\circ = -RT \ln K_L \quad (23)$$

where ΔG° is the Gibb's free energy (kJmol^{-1}), R is the universal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$), K_L is the Langmuir constant and T is the absolute temperature (K). Values of K_L may be calculated from the relation $\ln q_e / C_e$ Vs q_e at different temperatures [47, 48]. The values of other parameters such as enthalpy change (ΔH°) and entropy change (ΔS°), may be determined from Van't Hoff Equation:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (24)$$

ΔH° and ΔS° can be determined from the slope and intercept of Van't Hoff plot of $\ln K$ Vs $1/T$. The data is tabulated in Table 4(Fig. not shown). The negative ΔG° values confirm the spontaneous nature and feasibility of the adsorption process. Furthermore, it is observed from Table 4, that the positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption [49, 50]. In case of physical adsorption, increasing the temperature of the system increases the extent of dye adsorption and this rule out the possibility of chemisorptions [51]. This observation is in good agreement with the results shown in Fig.(9). The positive value of ΔS° show the increased

disorder and randomness at the solid / solution interface during the adsorption of methyl green onto the acid – modified samples under investigation.

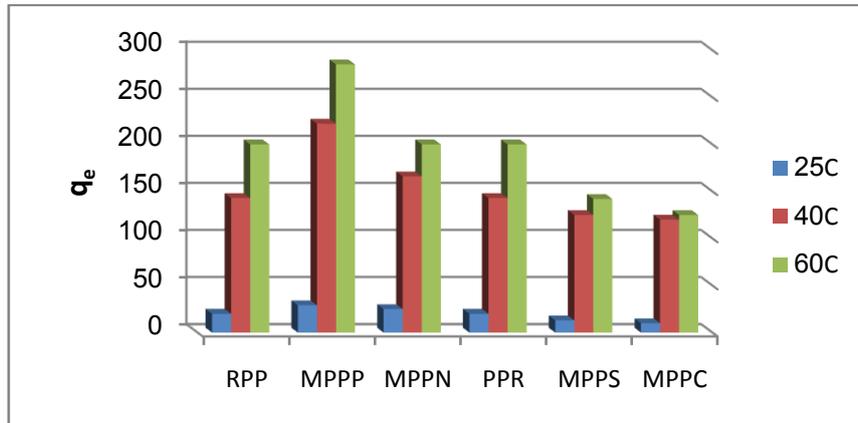


Figure 9: Effect of temperature for different acid – treated pomegranate peels on the removal of methyl green

In order to further support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows [52]:

$$\theta = 1 - \frac{C_e}{C_o} \quad (25)$$

$$S^* = (1 - \theta) e^{-E_a/RT} \quad (26)$$

$$\ln S^* = \ln(1 - \theta) - \frac{E_a}{RT} \quad (27)$$

$$\ln(1 - \theta) = \ln S^* + \frac{E_a}{RT} \quad (28)$$

The sticking probability S^* , is a function of the adsorbate / adsorbent system under investigation, its value lies in the range $0 < S^* < 1$ and is independent on the temperature of the system. The θ is the surface coverage, which can be calculated from equation 5. The values of E_a and S^* were estimated from the slope and intercept of the plot of $\ln(1 - \theta)$ Vs $1/T$ (Fig.10 and Table 4). The positive values of E_a indicate the endothermic nature of the adsorption process which are in agreement with the positive values of ΔH° and lie in the range of physisorption. The sticking probability values were less than 1, which indicates that the probability of methyl green dye to stick on the surface of the investigated samples is very high as $S^* \ll 1$. These values also confirm that the sorption process is physisorption.

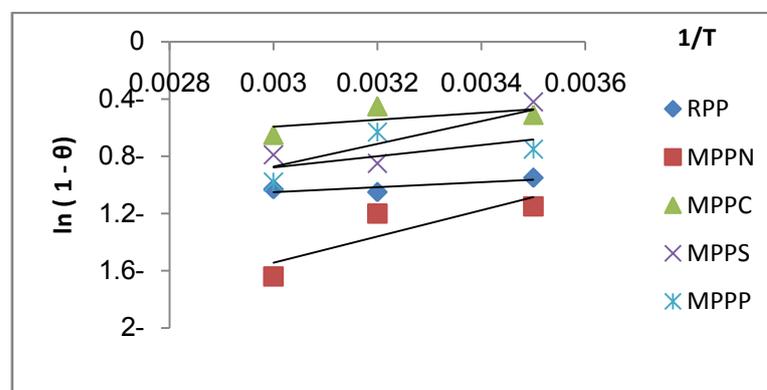


Figure 10: Plot of $\ln(1-\theta)$ Vs reciprocal temperature for the adsorption of methyl green dye

Table 4: Thermodynamic parameters for the adsorption of methyl green on different modified pomegranate peels

Adsorbents	Temp.(K)	$\Delta G^\circ(\text{KJ mol}^{-1})$	$\Delta H^\circ(\text{KJ mol}^{-1})$	$\Delta S^\circ(\text{J mol}^{-1}\text{K}^{-1})$	$E_a(\text{KJ mol}^{-1})$	S^*
RPP	298 313 333	- 23.0 - 24.8 - 28.1	13.66	84.6	2.49	0.31
MPPP	298 313 333	- 25.6 - 24.3 - 23.4	3.56	78.9	2.77	0.32
MPPC	298 313 333	- 23.0 - 24.4 - 26.2	4.57	78.7	2.37	0.37
MPPS	298 313 333	- 21.8 - 24.0 - 25.9	11.05	79.8	4.75	0.25
MPPN	298 313 333	- 23.4 - 24.8 - 26.7	3.94	80.5	2.23	0.18

4. CONCLUSION

The present investigation showed that untreated and acid – modified pomegranate peels show promising results as adsorbents for the removal of methyl green (MG) cationic dye from aqueous solution. Removal of methyl green is pH dependent and the maximum removal was attained at pH 10 for all adsorbents. Comparative study on the various acid – modified samples showed that the sample treated with phosphoric acid shows a maximum adsorption capacity, 29mgg^{-1} . The equilibrium adsorption is practically achieved in 65 min. The equilibrium data were well fitted to Langmuir isotherm model than the other models under investigation. Kinetic studies showed that the adsorption followed the pseudo – second – order model. The adsorption capacity of the dye decreased by increasing the ionic strength of the solution. The determination of the thermodynamic parameters (ΔG° , ΔH° and ΔS°) indicate the spontaneous and endothermic nature of the adsorption process.

REFERENCES

- [1] Garcia – Montano J, Torrades F, Perez – Estrada LA, Oller I, Malto S, Maldonado MI, Peral J, "Degredation Pathways of the Commercial Reactive Azodye Procion Red H-E7B under Solar – Assisted Photo – Phenton Reaction", *Environmental Science Technology*, vol.42, pp. 6663 – 6670, 2008.
- [2] Al – Degs YS, El – Barghouthi MI, .Khraisheh MA, Ahmad MN, Allen SJ, " Effect of surface area, micropores, secondary micropores and mesopore volumes of activated carbons on reactive dye adsorption from solution", *Seperation Science and Technology*, vol.39, pp. 97 – 111, 2004.
- [3] Wang S, Boyjoo Y, Choueib A, Zhu H, " Removal of dyes from solution using fly ash and red mud", *Water Research*, vol.39, pp. 129 – 138, 2005.

- [4] Robinson T, McMullan G, Marchant R, Nigam P, " Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative", *Bioresource Technology*, vol.77, pp. 247 – 255, 2001.
- [5] Netpradit S, Thiravetyan P, Towprayoon S, "Adsorption of three azo reactive dyes by metal hydroxide sludge; effect of temperature, pH and electrolytes", *Journal of Colloid and Interface Science*, vol.270, pp. 255 – 261, 2004.
- [6] Hesas RH, Niya AA, Wan Dand WA, Satiu JN, "Preparation and Characterization of Activated Carbon from Apple Waste by Microwave – Assisted Phosphoric acid activation: Application in Methylene Blue Adsorption", *Bioresources*, vol.8, no.2, pp. 2950 – 2966, 2013.
- [7] Aksu Z, "Application of biosorption for the removal of organic pollutants: A review." *Process Biochemistry*, vol.40, pp. 997 – 1026, 2005.
- [8] Crini G, "Non – conventional low – cost adsorbents for dye removal: A review", *Bioresource Technology*, vol.60 pp. 67 – 75, 2006.
- [9] Forgacs E, Cserhàti T, Oros G, "Removal of synthetic dyes from wastewaters. A Review", *Environmental International*, vol.30 pp. 953 – 971, 2004.
- [10] Qu JH, "Research progress of novel adsorption processes in water purification. A review." *J. of Environmental Sciences*, vol 20(1), (2008) 1 – 13.
- [11] Bello OS, Ahmad MA, Ahmad N, " Adsorptive features of banana (*Musa paradisiacal*) stalk – based activated carbon for malachite green dye removal, *Chem. Ecol.*, vol.28 ,pp. 153 – 167, 2012.
- [12] Bello OS, Fatona TA, Falaye FS, Oscuolale OM, Njoku VO, " Adsorption of eosin dye from aqueous solution using groundnut hull – based activated carbon: Kinetic, equilibrium and thermodynamic studies", *Environ. Eng. Sci.*, vol.29, pp. 186 – 194, 2012.
- [13] Bello OS, Ahmad MA, " Adsorption of dyes from aqueous solution using chemical activated mango peels, In: *Proceedings of the 2nd International Conference on Environmental Science and Technology (ICEST)*, vol.2, pp. 108 – 113, 2011.
- [14] Rahman IA, Saad B, Shaidan S, Sya ES, Riza EL, "Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical – thermal process", *Bioresource Technol.*, vol.14 ,pp. 1578 – 1583, 2005.
- [15] Hameed BH, "Evaluation of papaya seeds as a novel non – conventional low – cost adsorbent for removal of methylene blue", *J. of Hazard. Mater.*, vol. 162, pp. 939 – 944, 2009.
- [16] Pavan FA, Lima EC, Dias SP, Mazzocato AC, " Methylene blue biosorption from aqueous solution by yellow passion fruit waste", *J. of Hazard. Mater.*, vol.150, pp. 703 – 712, 2008.
- [17] Mohamed Salleh MA, Mahmoud DK, Abdul Karim WW, Idris A, " Cationic and Anionic dye adsorption by Agricultural Solid Wastes: A comprehensive review, *Desalination*, vol.280, pp. 1 – 13, 2011.
- [18] Patel S, "Potential of fruit and vegetable wastes as novel biosorbents: summarizing the recent studies", *Environ.Sci.Biotechnol.*, vol.11, pp. 365 – 380, 2012.
- [19] Moghadam MR, Nasirizadeh N, Dashti Z, Babanezhad E., "Removal of Fe (II) from aqueous solution using pomegranate peel carbon: equilibrium and kinetic studies", *International Journal of Industrial Chemistry*, vol.4 pp. 19, 2013.
- [20] El – Nembr A, "Potential of pomegranate peel carbon for Cr (VI) removal from wastewater: kinetic and isotherm studies, *J. of Hazard. Mater.*, vol.161, pp. 132 – 141, 2009.
- [21] Bhatnagar A, Minocha AK, "Biosorption optimization of nickel removal from water using *Punica Granatum* peel waste", *Colloid Surface B*, vol.76, pp. 544 – 548, 2010.
- [22] Ghaedi M, Tavallali H, Sharifi M, Nasiri SK, Asghari A, " Preparation of low cost activated carbon from *Myrtus Communis* and pomegranate and their efficient application for removal of Congo Red from aqueous solution", *Spectrochim. Acta Part A*, vol.86, pp.104 – 114, 2012.
- [23] Ali HA, Egzar HK, Kamal NM, Sahed NA, Mashkour MS, "Removal of Amaranth Dye from aqueous solution using pomegranate peel", *Int. Journal of Basic and Applied Science IJBAS – IJENS*, vol.13, pp. 57 – 64, 2013.
- [24] Wan Nik WB, Rahman MM, Yusof AM, An FNi, Che Adnan CM, " Production of activated carbon from Palm Oil Shell Waste and its Adsorption Characteristics, *Proceedings of the 1st International Conference on Natural Resources*", *Engineering and Technology*, 24 – 25th July, Putrajaya, Malaysia, pp. 646 – 654, 2006.
- [25] Girgis BS, Attia AA, Fathy NA, " Modification in adsorption characteristics of activated carbon produced by H₃PO₄ under flowing gases", *Colloid Surface A. Physicochem Eng. Aspect*, vol.299, pp. 79 – 87, 2007.
- [26] Girgis BS, Smith E, Louis MM, El – Hendawy ANA, "Pilot production of activated carbon from cotton stalks using H₃PO₄", *Journal of analytical and pyrolysis*, vol. 68(1), pp. 180 – 184, 2009.
- [27] Zvezdelina LY, Nedyalka VG, "Insights into Congo Red Adsorption on Agro – Industrial Materials – Spectral, Equilibrium, Kinetic, Thermodynamic, Dynamic and Desorption Studies. A Review", *International Review of Chemical Engineering (I.R.E.C.H.E.)*, vol.4 (2), pp. 127 – 146, 2012.
- [28] Pan X, Zhang D, "Removal of malachite green from water by *Firmiana simplex* wood fiber", *Electronic Journal of Biotechnology*, vol.12, pp. 1 – 10, 2009.

- [29] Alberghina G, Bianchini R, Fichera M, Fisichella S, “Dimerization of Cibacron Blue F3GA and other dyes: influence of salts and temperature, *Dyes and Pigments*, vol.46, pp. 129 – 137, 2000.
- [30] Germán – Heins J, Flurry M, “Sorption of Brilliant Blue FCF in soils as affected by pH and ionic strength”, *Geoderma*, vol.97, pp. 87 – 101, 2000.
- [31] Ghaedi M, Tavallali H, Sharifi M, Kokhdan SN, Asghari A, “Preparation of low cost activated carbon from *Myrtus Communis* and pomegranate and their efficient application for removal of Congo Red from aqueous solution”, *Spectrochimica Acta, Part A*, vol.86, pp. 107 – 114, 2012.
- [32] Langmuir I, “The adsorption of gases on plane surface of glass, mica, and platinum”, *J.Am.Chem.Soc.*, vol.40 pp. 1361, 1918..
- [33] Crini G, “Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer”, *Dyes and Pigments*, vol.77 (2), pp. 415 – 426, 2008.
- [34] Freundlich HMF, “Über die adsorption in lösungen, *Zeit, Phys.Chem.(Leipzig)*, vol.57 A, pp. 385 – 470, 1906.
- [35] Temkin MJ, Pyzhev V, “Recent modification to Langmuir isotherms”, *Acta Physiochim, USSR*, vol.12, pp. 217 – 222, 1940.
- [36] Dubinin MM, Radushkevich LV, “Equation of the characteristic curve of activated charcoal”, *Chem. Zentr.*, vol. 1 (1), pp. 875 – 890, 1947.
- [37] Vargas AM, Cazetta AL, Kunita MH, Silva TL, Almeida VC, “Adsorption of methylene blue onto activated carbon produced from flamboyant pods (*Delonix vegia*) : study of adsorption isotherms and kinetic models, *Chem. Eng .Journal*, vol.168, pp. 722 – 730, 2011.
- [38] Nidheesh PV, Gandhimathi R, Ramesh ST, Ananthasingh TS, “Kinetic analysis of crystal violet adsorption onto bottom ash, *Turkish J. Eng. Env. Sci.*, vol.36, pp. 249 – 262, 2012.
- [39] Lagergren S, “Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga, Svenska Ventenskademiens, Handlingar*, vol.24, pp. 1 – 39, 1898.
- [40] McKay G, Ho YS, “Pseudo – second – order model for sorption processes”, *Process Biochem.*, vol.34, pp. 451 – 465, 1999.
- [41] Chein SH, Clayton WR, “Application of Elovich equation to the kinetics of phosphate release and sorption on soils”, *Soil Sci. Am. J*, vol.44, pp. 265 – 268, 1980.
- [42] Aharoni C, Sideman S, Hoffer E, “Adsorption of phosphate ions by collodion – coated alumina”, *Journal of Chemical Technology and Biotechnology*, vol. 29 (7), pp. 404 – 412, 1979.
- [43] Tütem E., Apak R., Unal CF, “Adsorptive removal of chlorophenols from water by Bituminous Shale”, *Water Research*, vol. 32 (8), pp. 2315 – 2324, 1998.
- [44] Tan IAW, Ahmad AL, Hameed BH, “Enhancement of basic dye adsorption uptake from aqueous solutions using chemically modified oil palm shell activated carbons”, *Colloids and Surface A: Physicochem. Aspects*, vol.318, pp. 88 – 96, 2008.
- [45] Ahmad R, Kumar R, “Adsorptive removal of congo red dye from aqueous solution using bael shell carbon, *Appl.Surf.Sci*, vol.257, pp. 1628 – 1633, 2010.
- [46] Jnr MH, Spiff AI, “Effect of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by caladium bicolor (wild cocoyam) biomass”, *Electronic Journal Biotechnology*, vol. 8, pp. 162 – 169, 2005.
- [47] Amin NK, “Removal of direct blue – 106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics, *J. of Hazard. Mater.*, vol.165, pp. 52 – 62, 2009.
- [48] Kaur S, Rani S, Mahajan RK, “Adsorption kinetics for the removal of hazardous dye Congo Red by biowaste materials as adsorbents, *Journal of Chemistry*, Article ID 628582, pp. 1 – 12, 2012.
- [49] Arivoli S, Kalpana K, Sudha R, Rajachandrasekar T, “Comparative study on the adsorption kinetics and thermodynamics of metal ions onto acid activated low cost carbon”, *Electronic J.Chem.*, vol.4, pp. 238 – 254, 2007.
- [50] Amin NK, “Removal of direct blue – 106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics” *J. of Hazard. Mater.*, vol.165 (1 – 3) pp. 132 – 141, 2009.
- [51] Han R, Zou W, Yu W, Cheng S, Wang Y, Shi J, “Biosorption of methylene blue from aqueous solution by fallen phoenix tree’s leaves”, *J. of Hazard. Mater.*, vol.141, pp. 156 – 162, 2007.
- [52] Kannan K, Sundaram MM, “Kinetics and mechanism of removal of methylene blue by adsorption on various carbons – a comparative study”, *Dyes and Pigments*, vol.51, pp. 25 – 40, 2001.