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Research Article

Kinetics, thermodynamics and isotherm studies of malachite green adsorption by modified orange peel

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ABSTRACT

Kinetics, thermodynamics and isotherm studies of malachite green (MG) adsorption by orange peel (OP) modified with ethanol, calcium chloride and sodium hydroxide were performed. Adsorption kinetics was best fit the pseudo-second order model with correlation coefficients of 0.99 and 1 for the concentrations studied. Thermodynamic results indicated a spontaneous adsorption. Adsorption isotherm obeyed the Langmuir model. The Langmuir adsorption capacity was determined as 14.55 mg g^{-1}. Moreover, effects of initial dye concentration, temperature and pH on the adsorption were studied at the different contact times. The amounts of MG adsorbed onto OP increased with increasing contact time, initial dye concentration, solution temperature, and pH. Maximum dye adsorption was about 92.90% under all the experimental conditions. Percent desorption of MG from the surface of OP was lower in the alkali and HCl solutions and higher in an acetone-water mixture of 50%. FT-IR and SEM analyses were also recorded before and after the adsorption.

Keywords: Adsorption kinetics, thermodynamics, malachite green, orange peel

Modifiye portakal kabuğu tarafından malaşit yeşili adsorpsiyonunun kinetik, termodinamik ve izoterm incelemeleri

ÖZ

Etanol, kalsiyum klorür ve sodyum hidroksit ile modifiye edilen portakal kabukları (PK) tarafından malaşit yeşili (MY) adsorpsiyonunun kinetik, termodinamik ve izoterm incelemeleri gerçekleştirildi. Adsorpsiyon kinetiği incelenen konsantrasyonlar için 0.99 ve 1' lik korelasyon katsayıları ile yalancı ikinci dereceden modele en iyi uyum gösterdi. Termodinamik sonuçlar, adsorpsiyonun kendiliğinden olma eğiliminde olduğuna işaret etti. Adsorpsiyon izotermi ise Langmuir modeline uyum gösterdi. Langmuir adsorpsiyon kapasitesi 14.55 mg g^{-1} olarak belirlendi. Ayrıca, adsorpsiyon üzerine başlangıç boyar madde konsantrasyonu, sıcaklık ve pH' nın etkileri farklı temas sürelerinde incelendi. PK üzerine adsorplanan MY' nin miktarları, artan temas süresi, başlangıç boyar madde konsantrasyonu, çözelti sıcaklığı ve pH ile arttı. Maksimum boyar madde adsorpsiyonu tüm deneysel şartlar altında yaklaşık % 92 idi. PK yüzeyinden MY' nin yüzde desorpsiyonu alkali ve HCl çözeltilerinde daha düşük ve % 50' lik aseton-su karışımında daha yüksekti. Adsorpsiyondan önce ve sonra FT-IR ve SEM analizleri de kaydedildi.

Anahtar Kelimeler: Adsorpsiyon kinetiği, termodinamik, malaşit yeşili, portakal kabuğu,

1. INTRODUCTION

Many synthetic dyes have been used in various industries such as paper, textile, plastics, rubber, leather, cosmetics, pharmaceutical, and food industries.[1] The fact that these synthetic dyes mixture into water resources give greatly harm human's health and animals. Because, in the contact with organic body, these kinds of colored dyes cause harmful effects such as carcinogic, mutagenic, allergic dermatitis, and skin irritation.[2] Therefore, it is highly important to remove these kinds of the dyes from wastewaters. For this aim, a lot of methods such as activated carbon adsorption, coagulation, flocculation, membrane flotation, ion exchange, biosorption, etc. have been developed in treating the wastewaters which has various dyes.[3,4] Of these, activated carbon adsorption is an effective method to remove undesired dye or metal pollutants. However, its use is expensive and not suitable for developing countries. For this reason, the use of the cheapest adsorbents such as clay[5,6], fly ash[2,7], peat[8,9], perlite[4,10], fungi[11-13], yeast[14,15], alge[16] has been preferred by the researchers, recently. On the other hand, some researchers have extensively investigated the removal of dyes using as adsorbent the lignocellulose based materials such as rice husk[17], banana peel and orange peel[18], apple shell[19], lemon peel[20], jackfruit peel[21], pumpkin seed hull[22], olive pomace[23,24], walnut and poplar woods[25], recently. Of these low-cost adsorbents, orange peel (OP) is an agricultural waste and highly plenty. In orange production in the world, Brazil, America, Mexico, India, China, Spain, Indonesia come ahead, respectively.[26] Following these countries, the production of orange in Turkey is too much. Its amount is approximately 1 million 730 thousand tons according to the reports of year 2011.[26] OP is a lingo-cellulosic waste material which consists of cellulose, pectin, hemicellulose and lignin.[27] According to the literature investigation, the adsorption of some dyes using OP has been studied. For example, Annadurai and co-workers[18] have used orange peel for the adsorption of amido black 10B, congo red, methylene blue, rhodamine B, methyl violet and methyl orange. Arami and co-workers[28] have utilized orange peel as an adsorbent in removing the Direct red 80 and Direct red 23 from colored textile wastewater. In another study, Kumar and Porkodi [29] have studied only batch adsorber design and isotherm for malachite green adsorption onto orange peel.

However, any work with regard to kinetic and thermodynamics of the adsorption of malachite green (MG) onto OP has been not reported so far. In this study, orange peel was considered to be used as an alternative and inexpensive adsorbent to the active carbon. Therefore, the kinetic and thermodynamics of the adsorption of MG onto OP was investigated by using batch adsorption technique. Moreover, the effects of contact time, initial concentration of MG, temperature, and pH on the adsorption were studied. Furthermore, desorption studies were also studied.

2. MATERIALS AND METHOTDS

2. 1. Materials

Firstly, orange was provided from orange fruit sold commercially from market. Then, peel of orange was stripped. Orange peel (OP) was washed for the removal of soil and dusts, and dried in an oven. The dried OP was crushed into powder. Then the powdered peels were sieved using a molecular sieve of 100-mesh. The component of OP is given in Table 1.

Table 1. The component of OP

Component	**Percentage**
Fleshy part of peel (crude fiber)	17.60
Extract without nitrogen	71.40
Protein	6.08
Oil	2.24
Ash	2.68

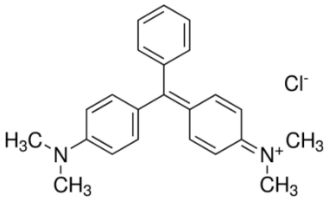
2. 1. 1. Modification of OP

OP was modified because it was determined that the adsorption capacity of OP was too low. Modification process was conducted as described in the literature.[30] Firstly, 10 g of OP was washed, dried and powdered. Then the powdered OP was treated with 50 ml of ethanol, 25 ml of 0.8 M NaOH solution and 25 ml of 0.8 M $CaCl_2$ solution for 20 h. After treatment for 20 h, the mixture obtained was filtered and washed well to pH 7. Then, it was dried to a constant weight at 60°C for 24 h.

2. 1. 2. Dye molecule as an adsorbate

Malachite green (MG), a cationic dye was provided by Merck. MG was utilized as received without any purification in adsorption process. Some physical properties and the molecular structure of MG are given in Table 2.[24,31]

Table 2. Some physical properties of MG

Common name	Malachite green
Other name	Aniline green; Basic green 4; Diamond green B; Victoria green B
IUPAC name	4-[(4-dimetilaminofenil)fenil-metil]-N,N dimetilanilin
Chemical formula	$C_{23}H_{25}ClN_2$
Class	Basic
Color index (C.I.)	42,000
Molecular weight (g mol^{-1})	364.91
Solubility in water (g l^{-1}) in 298 K	40
Solubility in ethanol	Good
Colors at different pH (indicator property)	Green-blue in water Yellow < pH 2 Green between pH 2-11.8 Colorless > pH 13.8
λmax (nm)	617
pKa	$pKa_1 = 6.90$, $pKa_2 = 10.3$
Molecular structure	

2. 2. Methods

2. 2. 1. Experiments for the adsorption of MG

Firstly, the 500 mg l^{-1} stock solutions of MG were prepared with pure water. Then the desired concentrations were prepared by diluting from these stock solutions. The pH values of dye solutions were adjusted by dropping diluted solutions of NaOH and HCl using a pH meter. The experiments were performed by shaking 0.20 g of OP with 100 ml-aqueous solutions of MG in 250 ml-Erlenmayers. In the experiments, a temperature-controlled shaking water bath was used. Adsorption process was performed at different concentrations, pHs and temperatures as for various contact times. After these contact times, the samples were taken from shaking bath and the centrifuged for 10 min at 4200 rpm. The supernatants were then analyzed to calculate the final concentration of MG at λ_{max} = 617 nm by an UV-Vis spectrophotometer. The adsorbed amounts of MG onto OP were calculated using Eq. (1).

$$q_t = \frac{(C_0 - C_0)\,V}{m} \qquad (1)$$

where, q_t represents the adsorbed amount of MG at time t (mg g^{-1}). C_0 indicates the initial MG concentration. C_t is concentrations of MG remained in solution at any time t (mg l^{-1}). V point to the dye solution volume used (l), and m indicates the adsorbent mass used (g). At the equilibrium time, q_t and C_t are expressed as q_e and C_e, respectively.

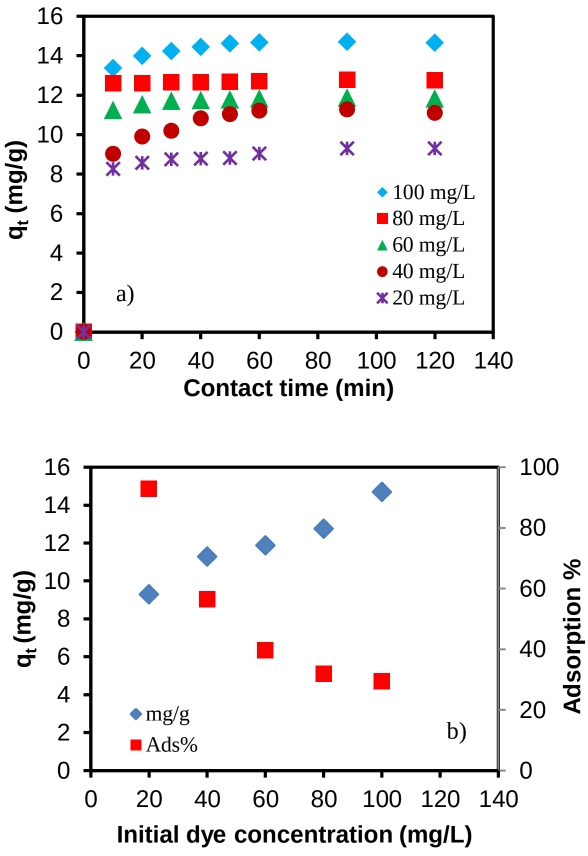


Figure 1. a) Effect of initial dye concentration on the adsorption of MG by OP as a function of contact time, b) The maximum adsorption and percent adsorption for individual concentration at the equilibrium time.

3. RESULTS AND DISCUSSION

3. 1. Determination of the equilibrium time

In order to determine the adsorption equilibrium time of MG onto OP, the experiments were conducted at various contact times, concentrations, pHs and temperatures. It was determined that a high adsorption taken place within the first 10 min. After this time, a gradual rise in the adsorption continued until 90 min. The maximum adsorption was reached at 90 min. Thus, the period of 90 min was adopted as an equilibrium time under all conditions studied.

3.2. Concentration effect on adsorption

The dye concentration effect on the adsorption of MG by OP was investigated for the concentrations between 20 and 100 mg l^{-1}. The results obtained are demonstrated in Figure 1.

From Figure 1a, it is clear that a rapid adsorption occurs within 10 min for all concentrations. After this time, a gradual increase in the adsorption continued to the equilibrium time of 90 min. The adsorption increased from 9.20 to 14.69 mg g^{-1} when the initial dye concentration increased from 20 to 100 mg l^{-1}. Percent adsorption was higher at the lower concentrations, lower at the higher concentrations (see Figure 1b). For example, the adsorption percent decreased from 92.90% to 29.39% when initial dye concentration increased from 20 to 100 mg l^{-1}. The fact that the adsorption percent decreases with a rise in the initial concentration indicates the saturation of adsorbent's surface. A similar trend has also been reported for MG biosorption by pineapple leaf powder.[32]

3. 3. pH effect on adsorption

The initial pH effect on MG adsorption by OP was investigated at pH values of 3, 5, 7 and 9. The results are demonstrated in Figure 2. It was seen that a high adsorption taken place 10 min for all the values, and thereafter a gradual rise in the adsorption of dye continued to 90 min. The adsorption was seen to be increased with an increase in pH from 3 to 9 (see Figure 2a). This situation can be explained as follows. Excess hydroxyl ions release into medium at the higher pH values, and the adsorbent surface becomes more negative. Therefore, more electrostatic interaction occurs between positively charged MG molecules and negatively charged OP. The adsorption percent also increased from 48.83% to 89.05% with a rise in pH from 3 to 9 (Figure 2b). A similar result has been found for MG adsorption by neem sawdust.[33]

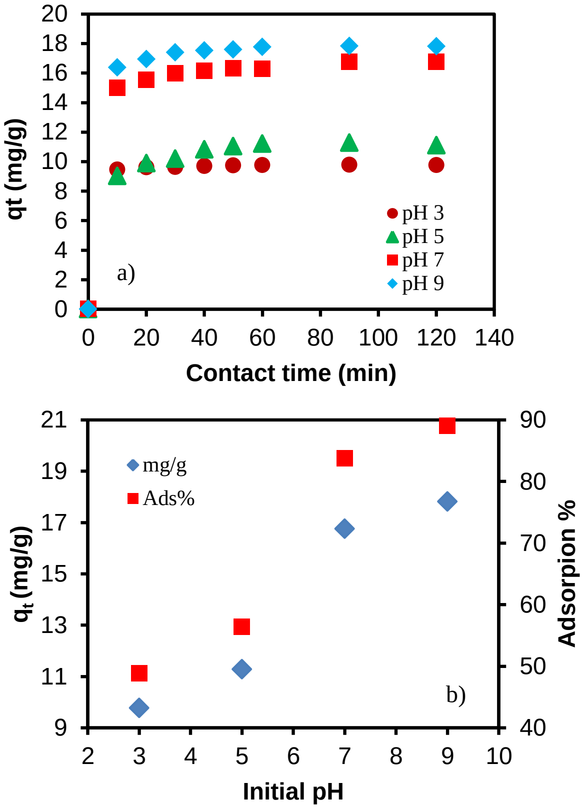


Figure 2. a) Effect of initial pH on the adsorption of MG by OP as a function of contact time, b) The maximum adsorption and percent adsorption for each pH at the equilibrium time.

3. 4. Temperature effect on adsorption

The temperature effect on MG adsorption by OP was studied at the temperatures of 293, 303, 313 and 323 K. The results are demonstrated in Figure 3. A high adsorption of MG was observed within 10 minutes for all temperatures as seen in concentration and pH effects, then small increments of adsorption continued to 90 min. The maximum adsorption of MG was determined as 11.28 and 12.50 mg g^{-1} at 293 K and 323 K, respectively (Figure 3a). As seen in pH effect, when the dye solution temperature increased up from 293 to 323 K, the adsorption percent also increased from 56.40% to 62.50% (Figure 3b). As seen from these data, the temperature effect on the adsorption is less. A similar result has been obtained for MG adsorption onto olive pomace.[24]

3. 5. Isotherm study

The equilibrium data obtained for MG adsorption by OP were fitted according to the Langmuir and the Freundlich isotherm models used commonly.

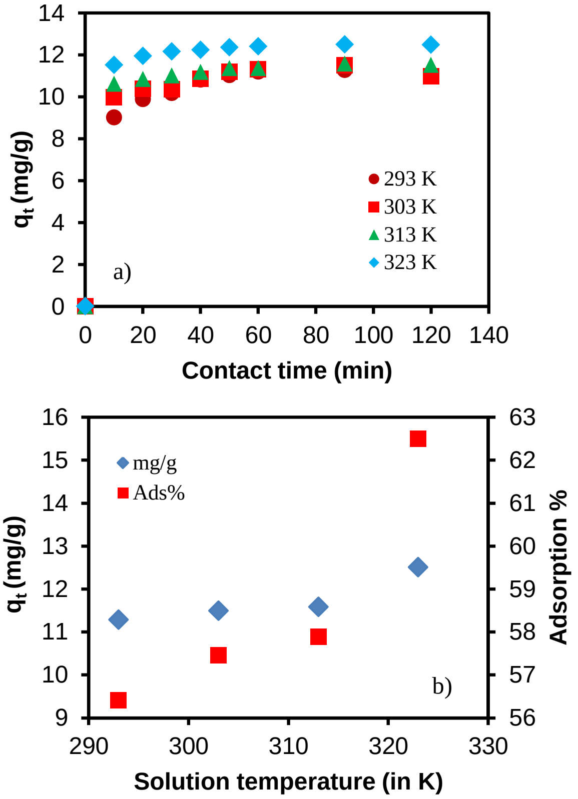


Figure 3. a) Effect of solution temperature on the adsorption of MG by OP as a function of contact time, b) The maximum adsorption and percent adsorption for each temperature at the equilibrium time.

The linearized equations of these models are given in Equations (2) and (3).

$$C_e/q_e = 1/Q_o b + Ce/Q_o \quad \text{The Langmuir equation} \quad (2)$$

$$\ln q_e = \ln k + 1/n \ln C_e \quad \text{The Freundlich equation} \quad (3)$$

where, q_e indicates the adsorbed MG amount at equilibrium time (mg/g), C_e points to the MG concentration remained in solution at equilibrium time (mg l^{-1}). Q_0 is Langmuir adsorption capacity, and the *b* is the Langmuir constant indicating the adsorption energy. *k* and *n* are Freundlich isotherm constants, indicating the capacity and intensity of the adsorption, respectively. Isotherm studies were conducted for the initial concentrations of 20, 40, 60, 80, and 100 mg l^{-1}.

The Q_0 and b values were estimated from the slope and intercept of the plot of C_e/q_e versus C_e, respectively. Q_0 and *b* were estimated as 14.55 mg g^{-1} and 0.237 l mg^{-1} under concentration conditions studied, respectively. The value of the r^2 for the Langmuir isotherm was determined to be 0.98.

The *k* and *n* values were found from the intercept and slope of the plot of ln q_e against *ln* C_e, respectively. *k* and *n* were estimated as 5.71 mg g^{-1} and 5.19 g l^{-1}, respectively. The value of r^2 for the Freundlich isotherm was obtained as 0.88. From these results, the adsorption can be said to follow best the Langmuir model. The compatibility to the Langmuir isotherm points to monolayer coverage of MG on OP surface. A similar result has been found for MG adsorption by neem sawdust.[33]

3. 6. Desorption study

The experiments for desorption of MG from OP surface were conducted in 50% acetone-water mixture, 0.1 N HCl solution, and various alkali waters with various pH values. For this aim, 0.125 g dye-adsorbed OP was stirred well with each of 100 mL solutions for 120 min. After this time, samples withdrawn from the mixture were analyzed as described before. The results obtained are shown in Figure 4.

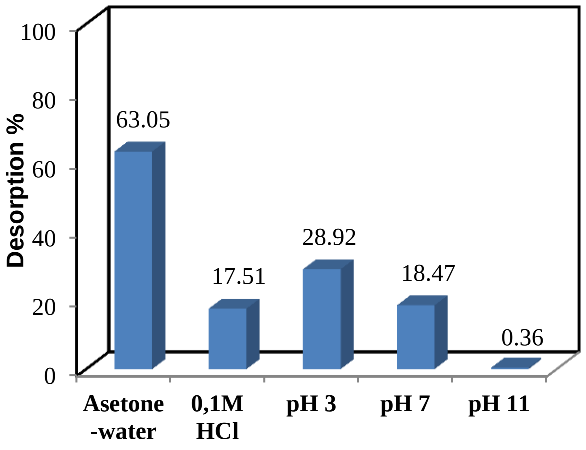


Figure 4. Desorption of MG from the surface of OP.

It was determined that percent desorption was lower in alkali and HCl solutions, and higher in 50% acetone-water mixture. For example, desorption percent was found to be 28.92, 18.47 and 0.36 in pH values of 3, 7 and 11, respectively. Percent desorption was 17.51 in 0.1 N HCl solution. Percent desorption was determined as 63.05 in 50% acetone-water mixture. The fact that desorption is low in alkali and HCl medium and higher in 50% acetone-water mixture indicates probably a chemical activation between OP and MG molecules. A similar result has been obtained for MG adsorption by olive pomace (pirina).[24] This situation has also been confirmed by kinetic study.

3. 7. Kinetics study

Kinetics of MG adsorption by OP was investigated according to three models used commonly. These kinetic models are given in linearized forms in Equations (4-6), respectively.

(a) The pseudo-first order kinetic model proposed by Lagergren[34] is given in Eq. (4)

$$\log(q_e - q_1) = \log q_1 - \frac{k_1}{2.303} t \qquad (4)$$

(b) The pseudo-second order kinetic model proposed by Ho and McKay[35] can be expressed as in Eq. (5)

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_2} t \qquad (5)$$

(c) The intra-particle diffusion model prosed by Weber and Morris[36] is expressed in Eq. (6).

$$q_t = k_i t^{1/2} + C \qquad (6)$$

where, k_1 indicates the rate constant for the pseudo-first order model, k_2 shows the rate constant for the pseudo-second order model, and k_i indicates the intra-particle diffusion rate constant. q_e indicates the adsorbed MG amounts per unit mass of OP at equilibrium. q_t is the adsorbed MG amounts as mg g^{-1} at any time. In Eq. (5), the initial adsorption rate (*h*) is equal to $k_2q_2^{\,2}$. Kinetic studies were performed for the initial concentrations of 20, 40, 60, 80, and 100 mg l^{-1}. All of the kinetic data obtained are presented in Table 3.

Firstly, the plots of log (q_e - q_1) versus *t* for the pseudo-first order model were drawn for all the initial concentrations at 293 K and natural pH. Correlation coefficients of the plots (i.e. r^2 values) obtained by means of linear regression analysis were between 0.896 and 0.987 for all concentrations between 20 and 100 mg l^{-1}. The values of q_e from the pseudo-first order kinetics model are not in agreement with experimental q_e values ($q_{e(exp)}$). This situation indicates that the adsorption does not follow this model. Therefore, these plots are not given.

Table 3. Kinetic parameters of adsorption of MG onto OP at different concentrations

		Pseudo-first order model			**Pseudo-second order model**			**Intra-particle diffusion**		
C_0 (mg l^{-1})	$q_{e(exp)}$	k_1 (min^{-1})	q_e (mg l^{-1})	r^2	k_2 (g mg^{-1}min^{-1})	q_e (mg l^{-1})	r^2	k_1 (mg/g.min^2)	r^2	C
20	9.29	0.023	1.236	0.896	0.0459	9.425	0.999	0.1525	0.961	7.826
40	11.28	0.065	5.494	0.958	0.0236	11.765	0.999	0.3730	0.892	8.157
60	11.88	0.046	1.150	0.964	0.1197	11.961	1	0.0944	0.828	11.08
80	12.76	0.016	4.822	0.987	0.2550	12.771	1	0.0258	0.952	12.49
100	14.69	0.076	3.602	0.964	0.0538	14.925	1	0.2091	0.842	12.97

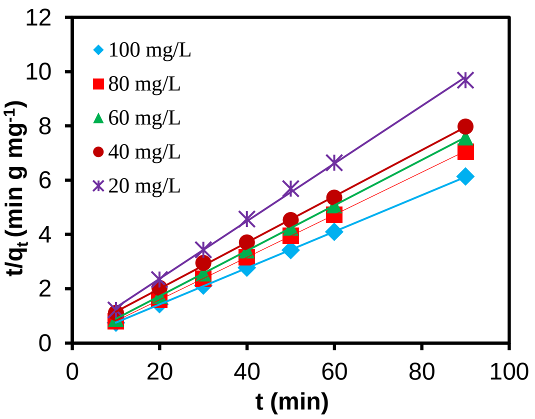


Figure 5. Pseudo-second order plots of the adsorption of MG by OP.

Secondly, the linear plots of *t/qt* versus *t* for the pseudo-second order model were drawn for all concentrations at 293 K and natural pH. The plots obtained are shown in Figure 5. The r^2 values were between 0.994 and 1 for all concentrations studied. The r^2 from these plots have high values. The values of q_e from these model were in consistent with experimental q_e values ($q_{e(exp)}$), and thus the adsorption obeys the pseudo-second order kinetics. This situation may probably indicate a chemical activation of MG molecules with the functional groups on OP surface. Similar results have been reported for the adsorption of MG by clinoptilolite[31] and biosorption of MG by pineapple leaf powder.[32]

Finally, due to mass transfer effect, the plots of q_t against $t^{1/2}$ for the intra-particle diffusion model were drawn for all the concentrations at 293 K and natural pH. The obtained plots are illustrated in Figure 6. For these plots, the r^2 values were determined as 0.842 and 0.961 for all concentrations studied. It may be said that the adsorption obeys the intra-particle diffusion for only a low concentration of 20 mg l^{-1} with a high correlation coefficient of 0.961. Also, the *C* values increased with a rise in initial dye concentration, representing boundary layer thickness between adsorbent and adsorbate.

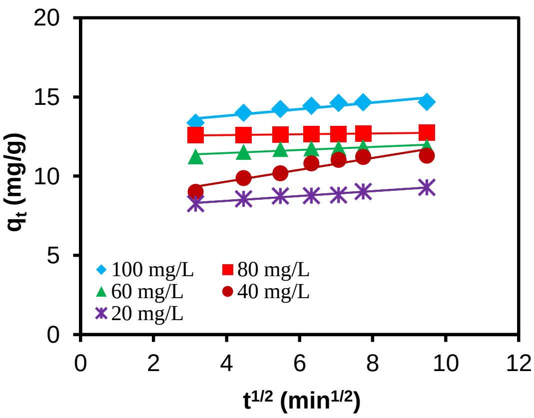


Figure 6. Intra-particle diffusion plots of the adsorption of MG by OP.

3. 8. Thermodynamic study

The thermodynamic parameters of MG adsorption by OP were investigated using Equations (7-9) below.[24]

$$\Delta G° = -RT \ln K_c \quad (7)$$

$$Kc = C_{Ae}/C_{As} \quad (8)$$

$$\ln Kc = - \Delta H°/RT + \Delta S°/R \quad (9)$$

where, C_{Ae} denote the concentrations of MG adsorbed onto OP at the equilibrium time (mg l^{-1}). C_{Se} represents MG concentration unadsorbed in solution at the equilibrium (mg l^{-1}). K_c indicates the adsorption equilibrium constant. $\Delta G°$ shows standard Gibbs free energy change. $\Delta H°$ and $\Delta S°$ indicate standard enthalpy and entropy changes, respectively. R points to the ideal gas constant. The values of $\Delta G°$ and K_c were estimated using Equations (7) and (8), respectively. Eq. (9) indicates Van't Hoff equation. The $\Delta H°$ and $\Delta S°$ values were estimated from the slope and intercept of the plot of ln K_c against 1/T according to Van't Hoff equation, respectively. All thermodynamic parameters determined are given in Table 4. The $\Delta G°$ values were found as negative. These negative values indicate a spontaneous nature of the adsorption. The $\Delta H°$ and $\Delta S°$ values were determined as 6.04 kJ mol^{-1} and 22.52 J mol^{-1} K^{-1}, respectively. The $\Delta H°$ value indicates an endothermic adsorption process. The positive $\Delta S°$ indicates a randomness adsorption of MG molecules onto OP. A similar result has been determined for MG adsorption onto olive pomace.[24]

Table 4. Thermodynamic parameters of the adsorption of MG onto OP

Temperature (in K)	K_c	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
293	1.29	-6.27	6.04	22.52
303	1.35	-7.56		
313	1.37	-8.26		
323	1.66	-1.37		

3. 9. SEM analysis

The SEM analyses of raw OP, modified OP and the dye-adsorbed modified OP were recorded. The images obtained are shown in Figure 7. The SEM images in Figure 7a and b show the surface structures of OP and modified OP, respectively. After modification, as can be seen from Figure 7b, the surface of OP has become some homogeneous. After adsorption, OP surface is significantly coated with MG molecules, denoting a surface adsorption (Figure 7c).

3. 10. FT-IR analysis

In order to determine the functional groups on OP surface caused to the adsorption, FT-IR analyses were conducted. Before and after the adsorption, FT-IR spectra are illustrated in Figure 8. As seen in Figure 8a, the broad and strong band at 3,304 cm^{-1} indicates OH groups of cellulose and the stretching vibration of NH and NH_2 groups. After modification, this band shifted to 3,270 cm^{-1}. After adsorption, this band shifted to 3,294 cm^{-1}. The band at 2,902 cm^{-1} can be attributed to CH stretching vibration of CH, CH_2 and CH_3 groups.[37] After modification, this band shifted to 2,987 cm^{-1}. After adsorption, this band shifted to 2,918 cm^{-1}. The band at 1,606 cm^{-1} indicates the stretching of COO^- group.[24] After modification the intensity of this band increased slightly. After adsorption this band shifted to 1,599 cm^{-1}. The peak at 1408 cm^{-1} indicates the stretching of C=C groups in aromatic ring.[37] After modification, the intensity of this band increased slightly. After adsorption, the intensity of the band decreased markedly and shifted to 1,414 cm^{-1}. The band at 1,049 cm^{-1} may be assigned to stretching vibration of CO groups of carboxylic and alcohols.[30] After modification and adsorption, this band did not change. All these findings indicate that phenolic and carboxylic groups, characteristic bonds of proteins, and polymeric compounds in the structure of OP have an important role to adsorb MG molecules.

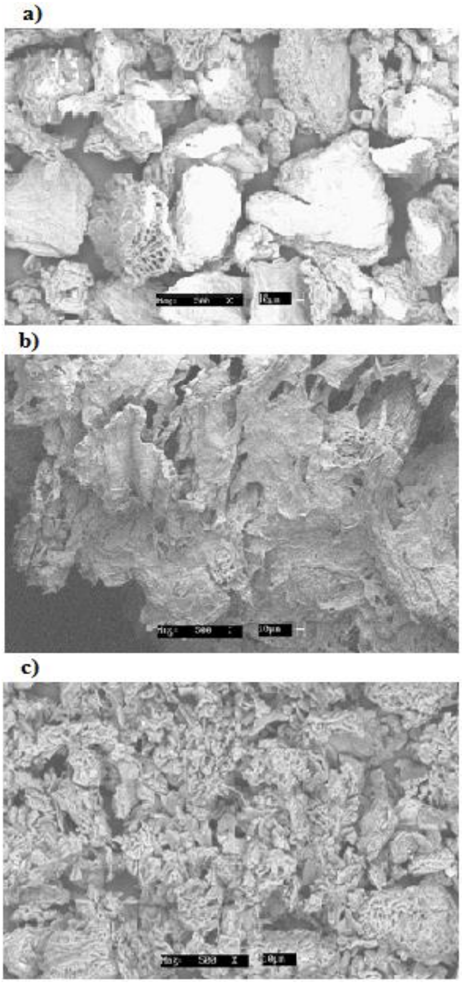


Figure 7. SEM image of orange peel: a) before adsorption, b) modified orange peel, c) after adsorption.

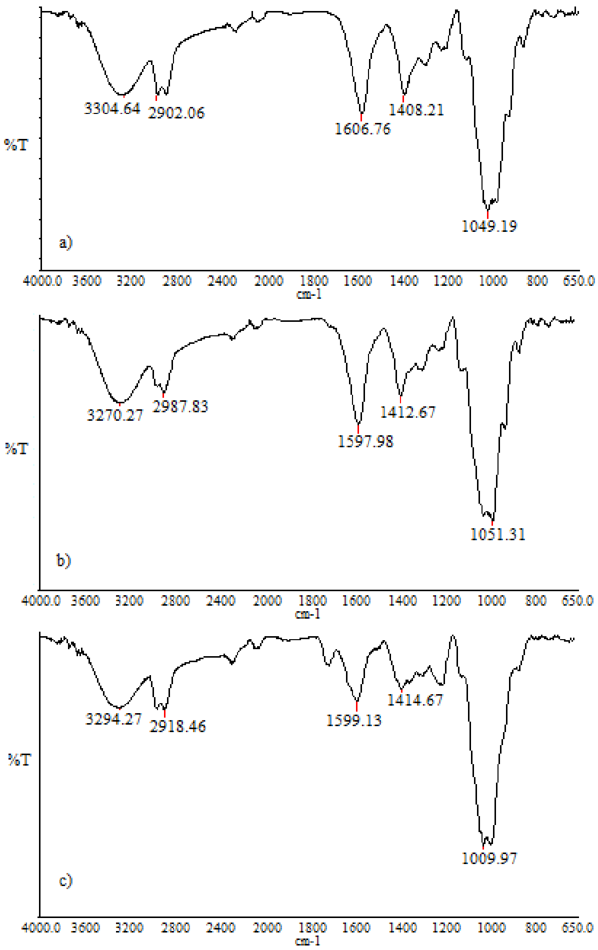


Figure 8. FT-IR spectra of orange peel: a) before adsorption, b) modified orange peel, c) after adsorption.

4. CONCLUSIONS

As an alternative to activated carbon, OP was utilized as an adsorbent for MG adsorption from solution by batch adsorption technique. The kinetics, thermodynamics, and isotherm studies of the adsorption process were performed. Adsorption kinetics was in the best consistent with the pseudo-second order model. Thermodynamic results indicated a spontaneous and endothermic adsorption. Adsorption isotherm obeyed best the Langmuir model. Moreover, the adsorption of MG onto OP was studied at various initial dye concentrations, pHs, and temperatures. The amounts of the dye adsorbed by OP increased with increasing contact time, initial dye concentration, solution temperature, and pH. The maximum dye adsorption was determined about 92.90% under all the experimental conditions studied. Desorption results showed that a chemical activation may be between OP particles and MG molecules. Consequently, it was concluded that OP would be also utilized as a potential, cheap and effective adsorbent for the removal of some other dyes as well as MG.

ACKNOWLEDGEMENTS

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Conflict of interest

We declare that there is no a conflict of interest with any person, institute, and company, etc.

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