

## Full Length Research Paper

# Adsorptive Removal of Methylene Blue and Malachite Green from Wastewater using Orange Peel as Adsorbent

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**ABSTRACT:** In the present study, the use of cheap and eco-friendly adsorbent (Orange Peel) has been studied as an alternative to commercial activated carbon for removal of dyes (methylene blue and malachite green) from wastewater by batch adsorption process. The parameters such as contact time, initial dye concentration, adsorbent dose, pH, particle size were investigated. From the results obtained; it was found that the adsorption increases with an increase in contact time, initial dye concentration, adsorbent dose and decreases with a decrease in the adsorbent particle sizes while the initial dye pH increases or

decreases depending on the pH. The kinetic models such as pseudo-first-order and pseudo-second-order were tested. It was found that the maximum adsorption capacities for methylene blue and malachite green on Orange peel were 5.286 mg/g and 4.121 mg/g respectively. The kinetic data fitted well with the pseudo-second-order model.

**Keywords:** Orange peel, adsorption dyes, industrial effluents, Kinetic studies and isotherm studies

## INTRODUCTION

Water is a valuable natural resource essential for the health of ecosystems. Water not only facilitates the movement of materials within various ecosystems but also links ecosystems with the atmosphere, lithosphere and biosphere. Water facilitates chemical reactions and the products of these chemical reactions to be carried either within the organism, ecosystems or across ecosystems (Kannan and Sundaram, 2013). About 97% of earth's water is held in oceans and therefore readily unavailable for human use, due to its dissolved salts. Humans mainly use underground or surface freshwater, which is less than 1% of the earth's supply. Increased environmental pollution as a result of industrialization is a major concern of the present world (Kaddan and Sundaram, 2013). Orange peel is largely composed of cellulose, hemicellulose, lignin, pectin and others. These components contain various functional groups such as hydroxyl and carboxyl which make orange peel to be

potential adsorbent material for removing many different pollutants like heavy metals and dyes from liquid media (Titi and Bello, 2015).

Dyes are widely used by several industries like plastics, textile, and paper, to color their final products (Chiou and Li 2002). The use and discharge of synthetic dyes from these industries is an environmental health concern especially to developing countries (Yang *et al.*, 2011). The textile industry alone consumes an excess of  $1.0 \times 10^7$  kilograms of dyes per year worldwide (Ahmad and Kumar, 2010) with almost 1 million kilograms of dyes per year being discharged into the aqueous environments (Cestari *et al.*, 2007). Most synthetic dyes are aromatic in nature which makes them to possess physical, chemical, thermal, biological and optical stability. Further, the presence of aromatic groups makes these dyes and their degraded products toxic, carcinogenic and mutagenic to life forms (Suteu and Bilba, 2009; Zaharia *et al.*, 2009).

Presence of dyes in industrial effluent poses serious threat to the environment. It interferes with the normal photosynthetic activities of aquatic life (Ponnusami *et al.*, 2010; Robinson *et al.*, 2002; Özer *et al.*, 2007), by decreasing light penetration for photosynthesis, and gas dissolution in lakes, rivers and other water bodies (Saratale *et al.*, 2011; Modi *et al.*, 2010). Most of these dyes have been shown to cause allergy, dermatitis, skin irritation and intestinal cancer to humans (Chatterjee *et al.*, 2007). The aim of this study is to determine the adsorption capacity of orange peel in removing the dyes from industrial effluents by using FTIR, SEM and UV-Vis spectroscopy analyses through equilibrium and kinetic studies.

## MATERIALS AND METHODS

### Preparation of orange peel

The orange was purchased from Katsina central market state. The peel was removed, washed thoroughly with tap water followed by distilled water. The washed orange peel was sundried followed by oven-drying at 105°C for 24 hours. The dried groundnut shell was pounded with a mortar and sieved to mesh sizes of 106µm, 250µm, 500µm and 800µm and stored in a plastic container labeled as OP (Orange Peel) for further analysis as our adsorbent.

### Preparation of adsorbates

The analytical grade adsorbates (methylene blue and malachite green) were obtained from the laboratory without any further treatment. 50mg of each adsorbate was dissolved in 1L of distilled water as stock solution. The methylene blue solution was labeled as MB and malachite green as MG.

### Batch adsorption experiments

#### Effect of contact time

The experiment on the effect of contact time of the adsorbent was performed according to the previous works of Asiagwu *et al.* (2012). Orange peel mesh size 106µm (0.5g) was weighed into six different conical flasks containing MB dye solutions (50ml, 30mg/L) at pH 5.8. The flasks were then labeled for time intervals of 10, 20, 30, 40, 50 and 60 minutes and tightly covered and agitated at the appropriate time intervals. At the end of each time intervals, the suspensions were filtered and then centrifuged. The dye concentration was determined using UV-Visible Spectrophotometer (T60 PG instrument). The procedure was repeated using the

same amount of MG dye solution at pH 5.2.

#### Effect of initial dye concentration

This experiment was carried out by adding orange peel (mesh size 106µm) (0.5g) into five different conical flasks containing different concentrations of MB (50ml, 10, 20, 30, 40 and 50mg/L) at pH 5.8 at room temperature (25°C) and agitated for 20 minutes using flask shaker at 200rpm. The dye solutions were then separated from the adsorbent by filtration using filter paper and then centrifuged for 20 minutes. The residual dye concentrations were determined using UV Visible Spectrophotometer. The same procedure was repeated for MG solution at pH 5.2.

#### Effect of adsorbent dose

This experiment was conducted at initial dye concentration of MB solution (50ml, 30mg/L) at pH 5.8 and masses of Orange Peel (0.5, 1, 1.5, 2 and 2.5g) and agitation rate 200rpm at room temperature (25°C) for 20 minutes. The dye solutions were then separated from the adsorbent by filtration and then centrifuged for 20 minutes and filtered. The residual dye concentrations were determined using UV- Visible Spectrophotometer. The same procedure was repeated on MG solution at pH 5.2.

#### Effect of dye pH

The effect of dye pH was investigated at initial dye concentration of MB solution (50ml, 30mg/L) at room temperature (25°C) with Orange Peel (0.5g) at pH 2, 4, 6, 8, 10 and 12. The pH of the dye solutions were adjusted by the addition of NaOH (0.1M) or HCl (0.1M). The pH values were measured using pH meter. The mixture was agitated for 20 minutes. The dye solutions were then separated from the adsorbent by filtration and then centrifuged for 20 minutes and filtered. The same procedure was repeated on MG solution.

#### Effect of adsorbent particle sizes

The batch adsorption was carried out using MB solution (50ml, 30mg/L) at pH 5.8 and room temperature (25°C). The OP (0.5g) mesh sizes (106µm, 250µm, 500µm and 800µm) were agitated for 20 minutes at 200rpm using flask shaker. The dye solutions were then separated from the adsorbent by filtration using filter paper and then centrifuged for 20 minutes. The residual dye concentrations were determined using UV-Visible Spectrophotometer. The same procedure was repeated

on MG solution. In each case the percentage adsorption and equilibrium adsorption capacity,  $q_e$  (mg/g) were evaluated using equation 1 and 2 respectively.

$$\% \text{ adsorbed} = \frac{C_0 - C_e}{C_0} \times 100$$

$$q_e = \frac{C_0 - V}{w}$$

Where  $C_0$  (mg/L) initial dye concentration,  $C_e$  (mg/L) is the equilibrium concentration,  $t$  (min) is the time,  $V$  (L) is the volume of the dye solution used and  $w$  (g) is the mass of the adsorbent used (Yaneva and Georgieva 2014).

## RESULT AND DISCUSSION

### Effect of Contact Time

The results of the effect of contact time (10 - 60 minutes) on the percentage adsorption of Methylene blue and Malachite Green dyes onto OP adsorbent are presented in (Table 1). Generally, the rate of removal of dye increases with an increase in contact time to a certain extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material (Ansari and Mosayebzadeh, 2010). Figure 1 reveals that the adsorption is rapid in the initial stages and becomes slow in the later stages until equilibrium is achieved. It is clear that the amount of dye uptake was rapid within the first 10 – 20 minutes where it shows that the adsorption increases from 94.7% to 95.86% and 96.64% to 98.06% respectively on OP adsorbent. However, after 20 minutes, the amount adsorbed slowed down where the adsorption of MB and MG increases from 95.86% to 96% and 98.06% to 98.33% respectively on OP adsorbent. This continues to slow down until equilibrium is reached at 96.36% for MB on OP and 98.87% of MG on OP at 60 minutes.

### Effect of initial dye concentration

The results of the effect of initial dye concentration (10 – 50 mg/L) on the percentage adsorptions of Methylene blue and Malachite Green dyes onto Orange Peel adsorbent are presented on (Table 2). The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface (Salleh *et al.* 2011). At a low concentration there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active

sites required for adsorption of the dye molecules will be lacking (Kannan and Sundaram 2001). It can be observed from Figure 2 that the amount of MB adsorbed increases as the initial concentration increases. As the concentration of MB increased from 10 mg/L to 20 mg/L, there was a corresponding rapid increase in the amount adsorption from 90.14% to 94.31%. This percent removal was maximum at 50 mg/L which is in the region of 97.07%. On the other hand, the amount of MG adsorbed increases with increase in initial dye concentration. As the concentration of MG increases from 10 mg/L to 20 mg/L, there was a corresponding rapid increase in the amount of adsorption from 97.56% to 98.28%. The highest percentage removal was observed to be at 98.5%. This increase in MB and MG removal as the initial concentration of the solution is increased may be attributed to the effect of increasing concentration gradient which is the main driving force for the adsorption process. That is, the increase in initial concentrations of MB and MG has overcome the resistance to the mass transfer between the aqueous and solid phases which also enhanced the interaction between the dyes and adsorbents (Chang *et al.*, 2011).

### Effect of adsorbent dose

Adsorbent dose is an important parameter in adsorption studies as it gives the optimum dosage at which maximum adsorption occurs. The results of the effect of adsorbent dose (0.5 – 2.5 g) on the percentage adsorption of Methylene blue and Malachite Green dyes onto Orange Peel adsorbent are presented in Table 3 and compared on Figure 3. Generally, the percentage of dye removal increases with increasing adsorbent dosage. Figure 3 shows the percentage of removal of MB increases with increasing adsorbent from 96.2 % to 96.78 % as the dose increases from 0.5 to 2.5 g. On the other hand, it shows that the adsorption of MG increases from 97.39 % to 98.02 %. It is readily understood that the number of available adsorption sites and the surface area increase by increasing the adsorbent dose and it therefore, results in the increase in amount of adsorbed dyes (Malik *et al.*, 2007). Initially the rate of increase in the percent dye removal has been found to be rapid which slowed down as the dose increased. This phenomenon can be explained, based on the fact that at lower adsorbent dose the adsorbate (dye) is more easily accessible and because of this, removal per unit weight of adsorbent is higher. With rise in adsorbent dose, there is less commensurate increase in adsorption, resulting from many sites remaining unsaturated during the adsorption (Jain *et al.* 2003).

### Effect of initial dye pH

The results of the effect of initial dye pH (2 - 12) on the

Table 1. Effect of contact time of MB and MG on OP

	Orange Peel			
	MB		MG	
Contact time (min)	% adsorbed	q <sub>e</sub> (mg/g)	% adsorbed	q <sub>e</sub> (mg/g)
10	94.70	2.84	96.64	2.89
20	95.86	2.87	98.06	2.94
30	96.00	2.88	98.33	2.95
40	96.20	2.88	98.54	2.95
50	96.23	2.88	98.70	2.96
60	96.36	2.89	98.87	2.96

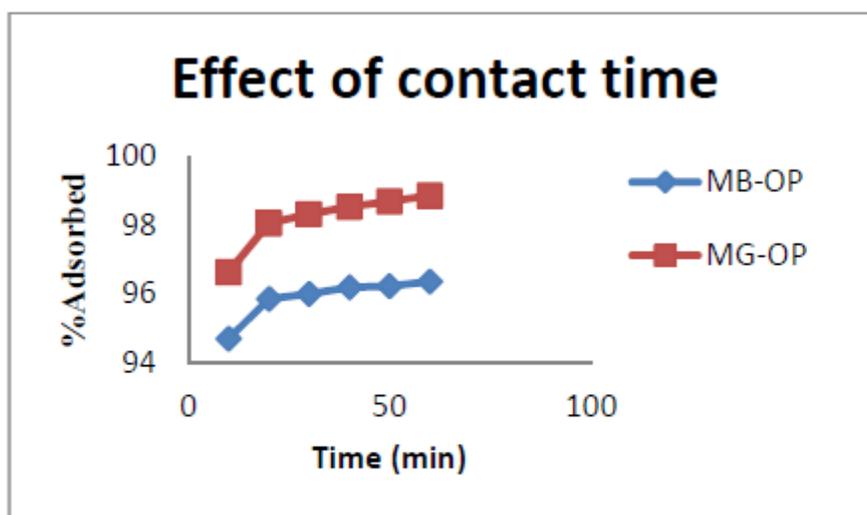


Figure 1 Effect of contact time

percentage adsorption of Methylene blue and Malachite Green dyes onto Orange Peel adsorbent are presented in (Table 4) and compared on (Figure 4). Generally, at low pH solution, the percentage of dye removal will decrease for cationic dye adsorption, while at a high pH solution the percentage of dye removal will increase for cationic dye adsorption (Salleh *et al.* 2011). For cationic dyes (MB and MG), lower adsorption of dye at acidic pH is probably

due to the presence of excess H<sup>+</sup> ions competing with the cation groups on the dye for adsorption sites. With an increase in the solution pH, the electrostatic repulsion between the positively charged cationic dyes and the surface of adsorbent is lowered and consequently the removal efficiency is increased (Ansari and Mosayebzadeh, 2010). Figure 4 reveals that the adsorption of MB on OP increases from 95.22% at pH 2

Table 2. Effect of initial dye concentration of MB and MG on OP

Initial dye conc. (mg/L)	Orange peel			
	MB		MG	
	% adsorbed	qe (mg/g)	% adsorbed	qe (mg/g)
10	90.14	2.85	97.56	2.91
20	94.31	2.88	98.28	2.96
30	96.11	2.88	98.29	2.97
40	96.99	2.87	98.5	2.96
50	96.07	2.87	98.5	2.94

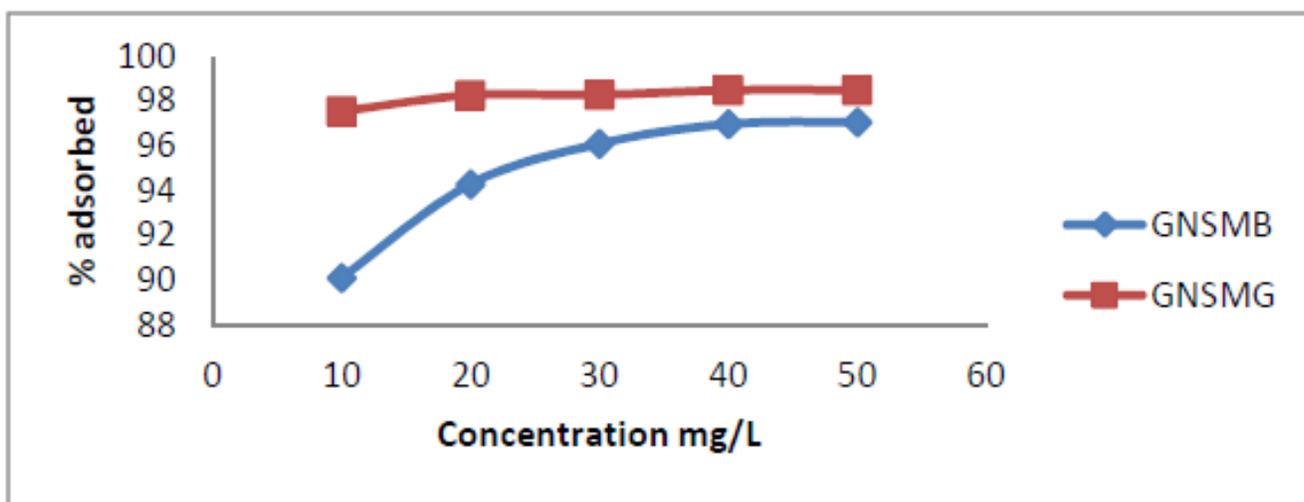


Figure 2 Effect of initial dye concentration

to the highest point of adsorption at 96.29% at pH 8. From there it slows down to 95.01% at pH 12. On the other hand, the adsorption of MG on OP increases from 97.02% at pH 2 to the highest point of adsorption at 99.22% at pH 8. From there it slows down to 97.81% at pH 12.

#### Effect of adsorbent particle size

The results of the effect of adsorbent particle sizes (106 $\mu$ m, 250 $\mu$ m, 500 $\mu$ m, 800 $\mu$ m) on the percentage

adsorption of Methylene blue and Malachite Green dyes onto Orange Peel adsorbent were presented in (Table 5), and compared on (Figure 5). Smaller particle sizes provide large surface area hence a higher number of surface active sites. The dyes adsorbed increased as the sorbent particle size decreased. It was suggested that the increase in adsorption depended on the large external surface area for small particles; this removes more dye in the initial stages of the adsorption process than the large particles. Figure 5 shows that the adsorption of MB and MG decreases from 95.71% to 94.75% and 97.31% to 93.35% respectively on OP as the particle sizes

Table 3. Effect adsorbent dose of MB and MG on OP

Adsorbent dose (g)	Orange peel			
	MB		MG	
	% adsorbed	qe (mg/g)	% adsorbed	qe (mg/g)
0.5	96.20	2.88	97.39	2.92
1.0	96.35	1.44	97.47	1.46
1.5	96.48	0.96	97.66	0.97
2.0	96.51	0.72	97.91	0.73
2.5	96.76	0.58	98.02	0.58

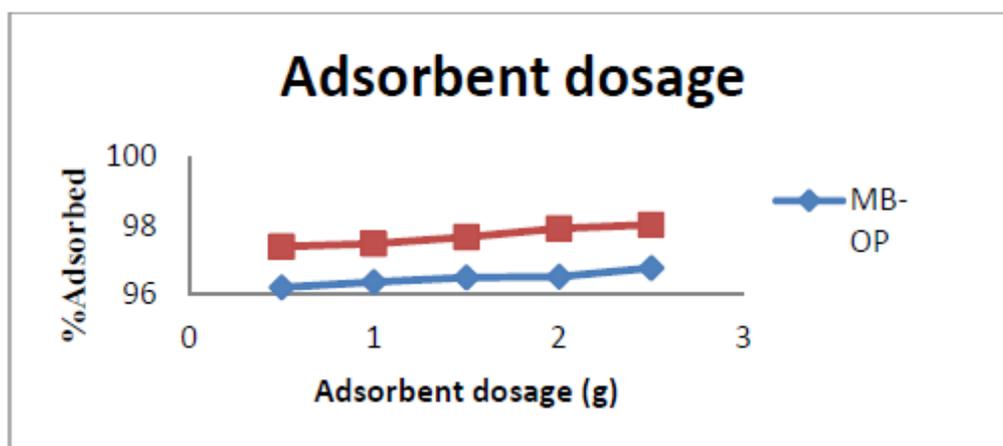


Figure 3 Effect of adsorbent dosage

increases from 106 $\mu$ m to 800 $\mu$ m. This is due to decrease in the surface area of the adsorbent particle sizes and hence, the decrease in the surface active sites.

#### Kinetic studies

The results for the adsorption kinetic studies for Methylene blue and Malachite Green on Orange Peel were presented on (Table 7), showing the values of all the kinetic models and their constants.

#### Adsorption isotherm studies

The results for the adsorption Isotherm Studies for

Orange Peel were presented on (Table 7), showing the values of all the adsorption isotherms constants corresponding to the adsorptions of Methylene blue and Malachite Green dyes.

#### Scanning electron microscopy (S.E.M)

The surface morphology of OP adsorbent was shown on (Figure 6).

The figure revealed that the surface of OP using S.E.M (Phenom /800-07334) has irregular macro pores. Its expanded cavities allow the diffusion of dye molecules through the macro pores.

Table 4. Effect of initial dye pH of MB and MG on OP

Initial dye pH	Orange Peel			
	MB		MG	
	% adsorbed	qe (mg/g)	% adsorbed	qe (mg/g)
2	95.22	2.85	97.02	2.91
4	96.17	2.88	98.87	2.96
6	96.29	2.88	99.00	2.97
8	95.73	2.87	99.22	2.97
10	95.70	2.87	98.04	2.94
12	95.01	2.85	97.81	2.93

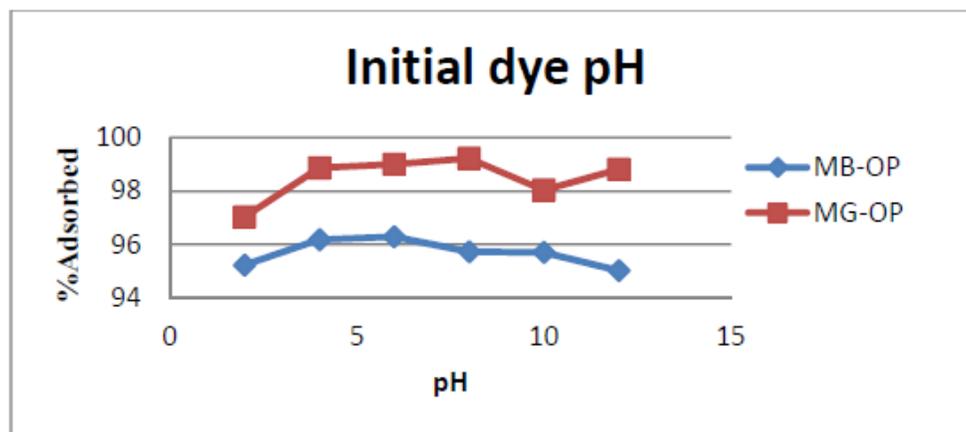


Figure 4 Effect of initial dye pH

Table 5. Effect of adsorbent particle size of MB and MG on OP

Adsorbent particle size $\mu m$	Orange Peel			
	MB		MG	
	% adsorbed	qe (mg/g)	% adsorbed	qe (mg/g)
106	95.71	2.87	97.31	2.91
250	95.11	2.85	97.79	2.93
500	94.96	2.84	97.68	2.03
800	94.75	2.84	93.35	2.80

Table 6. Kinetic Models

Kinetic Models	Constants	Orange	
		MB	MG
Pseudo first order	$q_{e(\text{exp})}$ mg/g	0.978	0.995
	$q_{e(\text{cal})}$ mg/g	3.801	0.028
	$K_1$ min <sup>-1</sup>	0.073	0.071
Pseudo second- order	$R^2$	0.973	0.974
	$q_{e(\text{exp})}$ mg/g	0.978	0.995
	$q_{e(\text{cal})}$ mg/g	0.980	0.998
	$K_2$ gmin <sup>-1</sup>	8.530	6.693
	$R^2$	1	1

Table 7. Isotherm model

Isotherm parameters	Constants	Orange Peel	
		MB	MG
Langmuir	$q_m$ (mg/g)	5.286	4.121
	$K_L$	0.897	0.186
	$R_L$	0.100	0.349
	$R^2$	0.999	0.995
Freundlich	$ n $	1.068	1.062
	$K_F$	0.194	1.030
	$R^2$	0.997	0.995

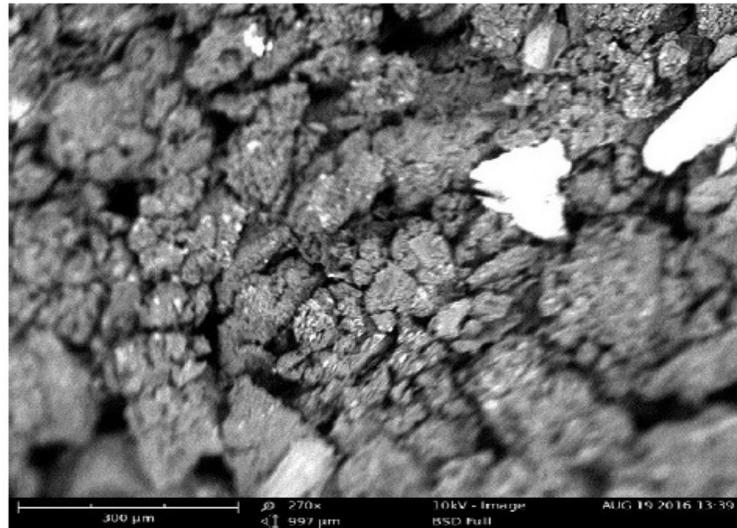


Figure 6 S.E.M image of Orange Peel

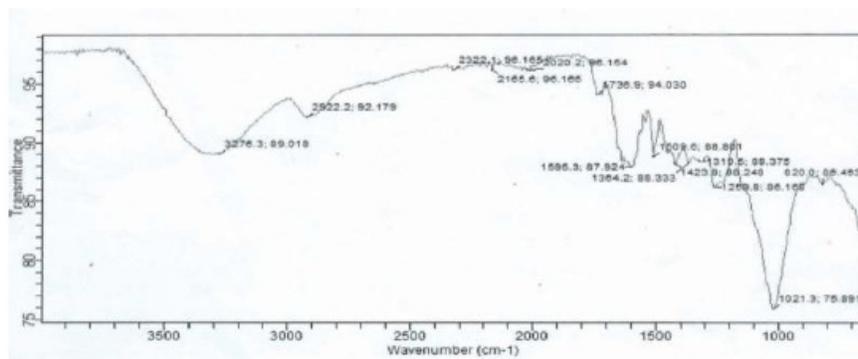


Figure 7 FTIR of Orange Peel before adsorption

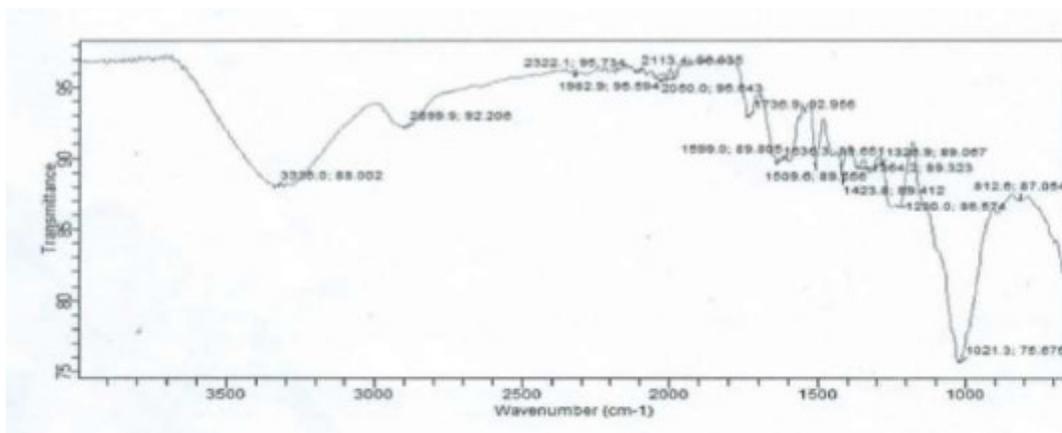


Figure 8 FTIR spectra of Orange Peel after adsorption with MB

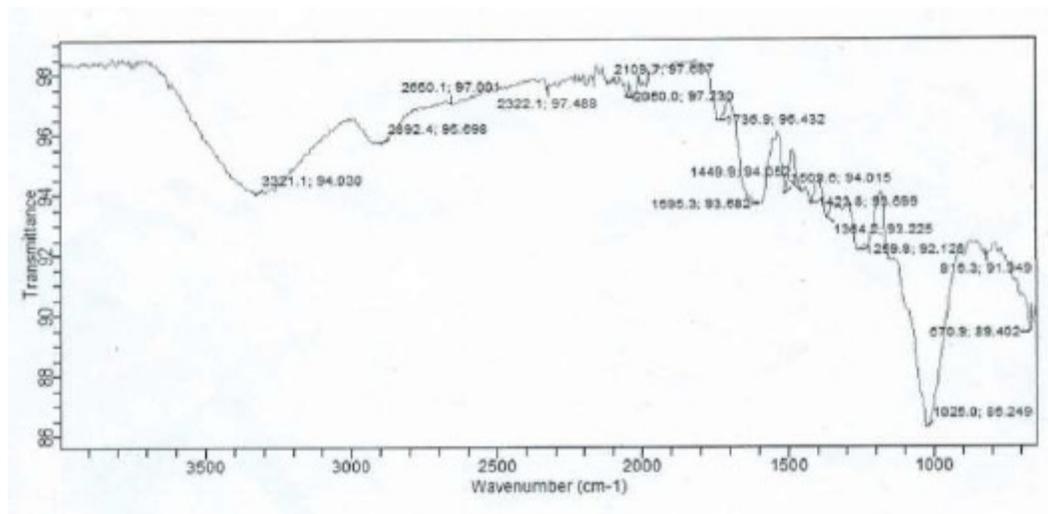


Figure 9 FTIR spectra of Orange Peel after adsorption with MG

## Conclusion

It can be concluded that the percentage adsorption of all the dyes tends to increase with increase in the contact time. At first the increase in adsorption is very rapid as there are lots of free sites for the adsorption to take place. Rate of adsorption decreases at later stages till saturation is reached due to saturation of active sites. The optimum contact time for equilibrium was found to be 20 minutes. There was increase in adsorption with the increase in the initial dye concentrations due to the high driving force for mass transfer at a high initial dye concentration. As the adsorbent dose increases, the % adsorption increases due to the availability of free sites. The % adsorption varied with the dye solution pH depending on whether the dye solution is acidic or basic. The % adsorption was found to decrease with an increase in the adsorbent particle size due to the decrease in the adsorbent surface area. Langmuir and Freundlich models were used for the description of the adsorption isotherm. The data fitted all the isotherm models. The monolayer maximum adsorption capacity for Methylene blue and Malachite Green dyes were 5.286 and 4.121 mg/g on Orange Peel respectively. The values of the Langmuir separation factor  $RL$  suggest that all the adsorption processes are favourable. The Freundlich isotherm constant  $nF$  for the adsorption of MB and MG on OP and indicates adsorptions on heterogeneous surfaces. Pseudo second order best fitted the adsorption. An intra-particle diffusion model was used to calculate the intra-particle diffusion coefficients. The FTIR spectra revealed the presence of functional groups such as C=O, COO<sup>-</sup>, OH, CN e.t.c and showed some changes in the surface properties of the adsorbent after adsorption as

compared to that of before adsorption. This facilitates the adsorption of adsorbent and dye molecules. The S.E.M image of Orange Peel showed rough surfaces and heterogeneous pore distributions through which adsorption takes place. Thus it could be concluded that Orange Peel, which is waste material and very abundant, can be used for the removal of Methylene blue and Malachite Green dyes from waste water.

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