Removal of Dyes by Using Pumpkin Seeds as Adsorbent

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Abstract—**Adsorption method was commonly applied in wastewater treatment to remove dyes due to its simplicity of design and ease of operation. However, the cost of conventional adsorbent such as activated carbon is too high and required additives to improve it efficiency. Because of that, many agriculture waste had been studied as potential adsorbent to replace the current conventional adsorbent. Thus the aimed of this research is to prepared eight types of adsorbent from pumpkin seeds, and used it in adsorption process to determine the effectiveness of the adsorbents to remove basic dye methylene blue (MB) and acidic dye methyl orange (MO) from simulated wastewater. The pumpkin seeds were subjected into two type of treatments which are physical and chemical treatments. After the adsorbent preparation was completed, Fourier transform infrared spectroscopy (FTIR) was used to determine the number and positions of the functional groups available on adsorbent surface. In this research, the effect of adsorbent dosage, contact time and initial dyes concentration were studied toward percentage removal of dyes. The results showed that, as the adsorbents dosage, contact time and dyes initial concentration were increased, the percentage removal of dyes also increased. This research can be further used to design adsorption columns for dyes removal.**

Keywords— **Adsorption, Dyes removal, Methylene blue, Methyl orange, Pumpkin seeds**

I. Introduction

Dyes are simply defined as chemicals which on binding with a material will give distinct colour to them [1]. Based on their structure, dyes are divided into two parts which are anionic or cationic. The example of commonly used cationic and anionic dyes are methylene blue and methyl orange respectively. Usually these dyes are used in dyeing process. The unwanted by products from the dyeing process are basically release as wastewaters and have high colour content. Besides, having the higher chemical content, this wastewater also can change the physical and chemical properties of the water in the environment such as the biochemical oxygen demand (BOD), and chemical oxygen demand (COD), pH, temperature, and turbidity [2]. Lack of proper treatment will cause the dyes to maintain their own colour and structural integrity even being expose towards bacteria, soil and sunlight. Thus, the dyes loaded waste water need to be treated first before release to the environment.

There are a few treatment approaches covering from physical process, chemical process, and biological process or appropriate mixes of the process are available to treat dyes loaded wastewater before it can be harmlessly release into the surroundings [3]. Overall, each of the method has its benefits and drawback as shown in Table 1. Among them, adsorption is the best technique since it can remove organic and inorganic contaminants from wastewater. Besides, the adsorption process is preferable due to its simplicity in design and ease of operation. Furthermore, adsorption process has the capability to remove a various type of mixtures.

Presently, the current adsorbent used in the wastewater treatment to treat the effluent from industries is the conventional adsorbent such as activated carbon. However, the usage of activated carbon in the industries has been restricted due to the high cost of the adsorbent [4] and it usually required additives to improves its efficiency. Thus, low cost and effective substances to replace the activated carbon as conventional adsorbent have been a great concern. Therefore, the purposes of this study were to prepare low cost adsorbent using pumpkin seeds and to investigate it effectiveness to remove methylene blue and methyl orange that commonly found in waste water.

Table 1: Advantages and disadvantages of the available treatments process

Type of treatment	Advantages	Disadvantages	References
		Physical	
Adsorption	Suitable for all type of dyes	High cost of adsorbents. Problem with disposal.	[5] [6]
Ion exchange	Zero loss of sorbents	Cannot treat disperse dyes	[7] [8] [9]
Membrane filtration	Only for dyes with high quality effluent	Production of sludge. Not suitable for large volume	[10] [3]
Coagulation	Cost effective	Production of sludge. Need further treatment such as flocculation.	[11] [2]
		Chemical	
Fenton reagent	Low cost reagent	Problem with disposal	[12] [13] [14]
Ozonation	Does not generate sludge.	Short half-life and high operational cost.	[15] [16] [17]
Photocatalyst	Low operational cost	Produce toxic by product	[18] [19]
		Biological	
Aerobic	Only	Required a	[20]

degradation	effective to remove azo dyes. Low operational cost.	longer time for the treatment process.	[21]
Anaerobic degradation	By-products can be used as energy sources	Required further treatment under aerobic conditions.	[20] [22]

II. METHODOLOGY

A. Materials

Pumpkin seeds were collected from a local market in Shah Alam Selangor, Malaysia. The vinegar that used to treat the pumpkin seeds also obtained from the local market in Shah Alam. The methylene blue and methyl orange dyes used in this work were the analytical grade (Merck, Germany). All other chemicals used in this work were of analytical grade and used without further purification.

B. Methods

Preparation of adsorbents using physical treatment

The pumpkin seeds were washed several time with distilled water to eliminate unwanted impurities, then it was spread in the aluminium foil and placed in the oven (Froilabo) for the drying process at temperature of 70˚C for 24 h. The dried pumpkin seeds were ground in a waring blender (04241-11 series) and were sieved into 500 µm size to get a fine powder. Then it was divided into four parts of adsorbents. The first part was uncalcined and labeled as PTUC while the other three adsorbents were calcined in the muffle furnace at 350 °C, 450°C and 500°C and labeled as P-350, P-450 and P-550 respectively. The adsorbents then were stored in airtight plastic containers. Figure 1 show the summarization of physical treatment process.

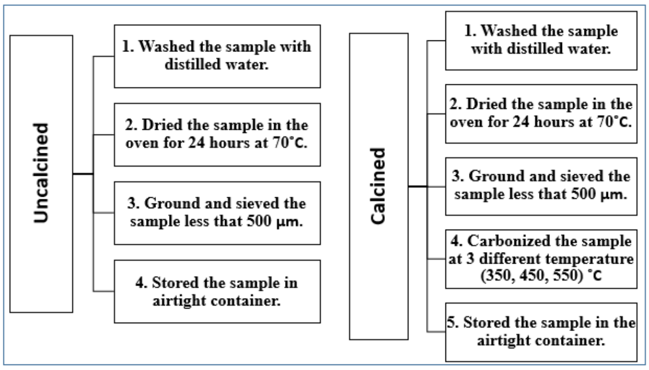


Fig. 1: Summarization of physical treatment

Preparation of adsorbents using chemical treatment

The pumpkin seeds were washed several time with distilled water to eliminate unwanted impurities then it was spread in the aluminium foil and placed in the oven (Froilabo) for the drying process at temperature of 70˚C for 24 h. Then it was soaked in the vinegar solution in a ratio 1:5 (100g pumpkin seeds = 500ml vinegar) for 24 h. After that, it was dried in the oven at temperature 70 ˚C for 24 h and then washed repeatedly with distilled water until pH range 6.5 to 7.5 is archived. Next, the pumpkin seeds were dried again for the third time at temperature 70°C for 24 hours. The dried pumpkin seeds were grinded in a waring blender (04241-11 series) to a fine powder and passed through the sieve of size 500 µm by using laboratory test sieve (Endecotts). Lastly, it was divided into four parts of adsorbents. The first part was uncalcined and labeled as CTUC while the other three adsorbents were calcined in the muffle furnace at 350 °C, 450°C and 500°C and labeled as C-350, C-450 and C-550 respectively. The adsorbents then were stored in airtight plastic containers. Figure 2 show the summarization of chemical treatment process.

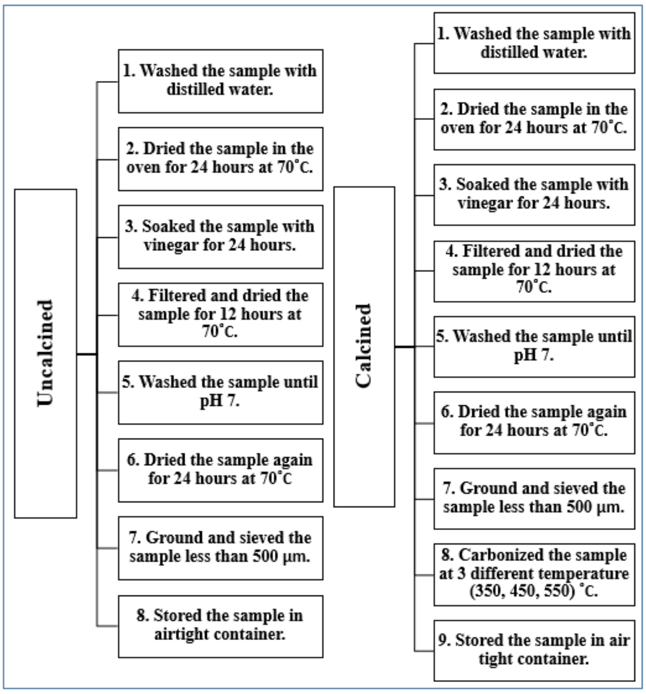


Fig. 2: Summarization of chemical treatment

Preparation of simulated dyes wastewater

Approximately 1.00g of methylene blue dye was added into 1000 ml distilled water to make 1000mg/L stock solution. The same procedure was applied to prepared the methyl orange stock solution. All other experimental solutions of desired concentrations were prepared from the stock solution by serial dilution.

Adsorption experiment.

This experiments were done in 250ml conical flasks. A known amount of adsorbent was added to 50ml dye solutions with an initial concentration of 20 ppm to 40 ppm. The solutions were placed in the shaker and agitate at 120 rpm at room temperature. After the set contact time, the solutions were withdrawn from the shaker. Then, the solutions were centrifuge at 1000 rpm for 15 minutes to separate the dyes and the adsorbent. After that, the residual dye concentration of the supernatant solution will be determine using UV/VIS spectrophotometer. There are three manipulated variables in this experiment which are adsorbent dosage, initial dyes concentration and contact time.

III. RESULTS AND DISCUSSION

A. Characterization of adsorbent

The Fourier transform infrared (FTIR) was done to determine the functional group that exist in the physical and chemical treated adsorbent.

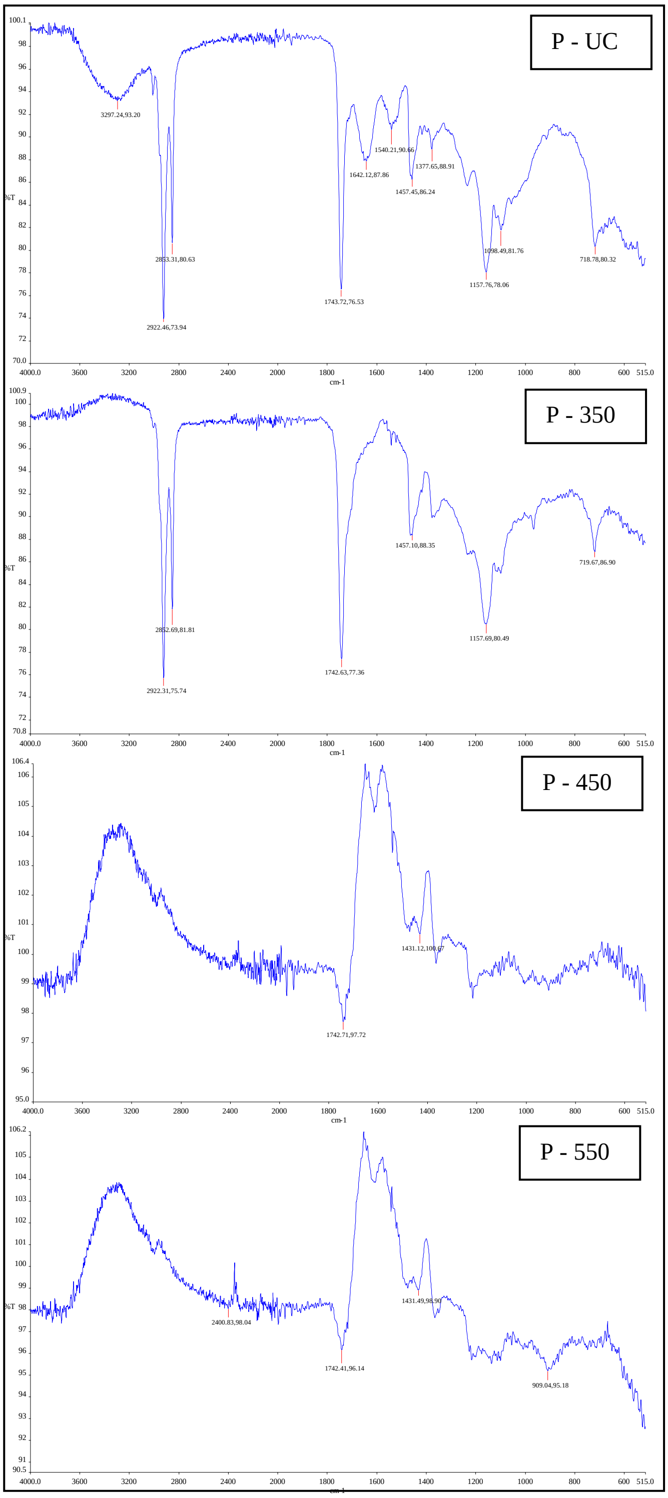


Fig. 1 : FTIR spectra of physical treatment adsorbent.(From the top P-UC, P-350, P-450, and P-550)

In figure 1, the peak at 3297 cm^{-1} in the wide-ranging absorption band at 3000–3600 cm^{-1} shown the present of O–H stretching vibrations of hydrogen bonded hydroxyl groups. This peak was clearly seen in the adsorbent P-UC and has disappear for the P-350, P-450, and P-550. Another peak at 2922 and 2853 cm^{-1}, shown the present of asymmetric C-H and symmetric C-H bands, respectively, exist in P-UC and P-350, but completely disappeared for the P-450 and P-550. This also be found by [23]. Stretching absorption band at 1743 cm^{-1} shown the present of carbonyl C=O in esters, aldehydes, ketone groups and acetyl derivatives. This band also present in adsorbent P-350, P-450 and P-550. The peak that at 1642 cm^{-1} may be due to olefinic C=C vibrations in aromatic region for the pumpkin seed shell [24]. Next, peak at 1157 and 1098 cm^{-1} indicated the C-O stretching vibrations in the raw material. The peak at approximately 1457 cm^{-1} is due to the present of C─H stretching. The peak at 1157 cm^{-1} indicated the existing of ester functional group. The absorption bands in the region 690–900 cm^{-1} was due to the C-H aromatics vibration.

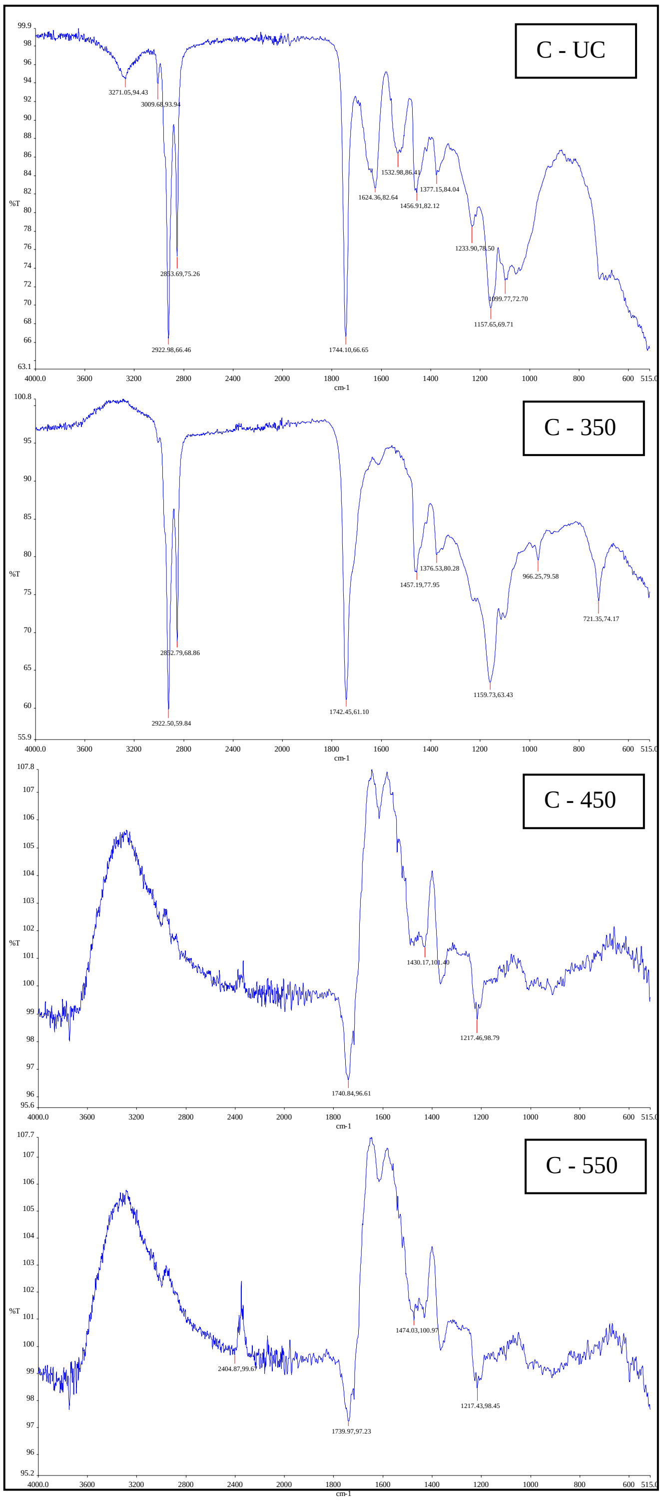


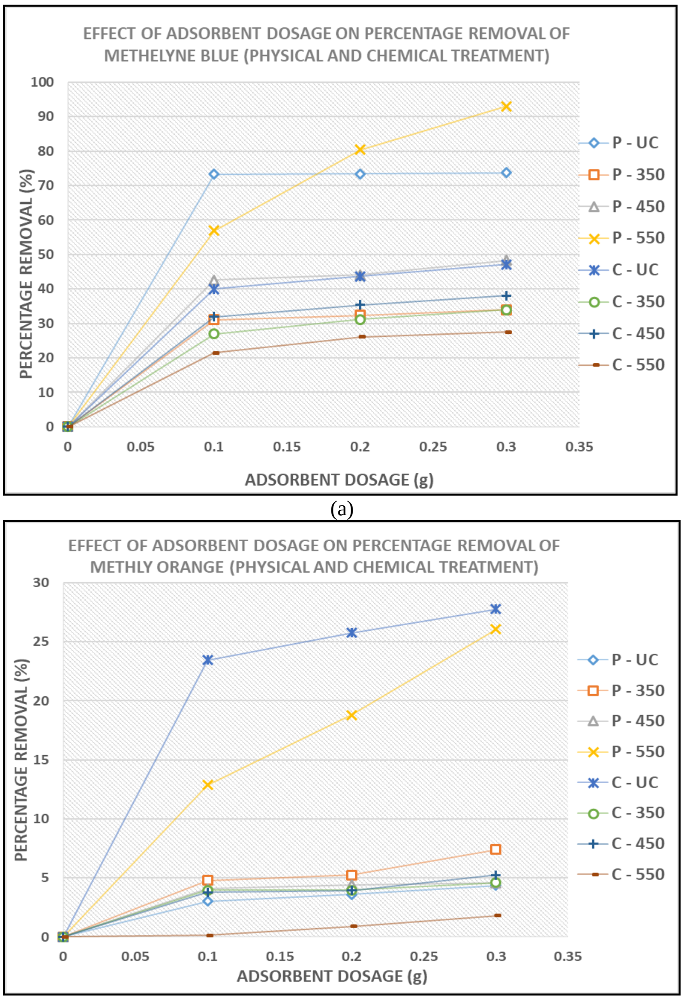
Fig. 2 : FTIR spectra of chemical treatment adsorbent.(From the top C-UC, C-350, C-450, and C-550)

In figure 2, the peak at 3271 cm^{-1} in the wide-ranging absorption band at 3000–3600 cm^{-1} shown the present of O–H stretching vibrations of hydrogen bonded hydroxyl groups. This peak was clearly seen in the C-UC and has disappear for the C-350, C-450, and C-550. Another peak at 2922 and 2853 cm^{-1}, shown the present of asymmetric C-H and symmetric C-H bands, respectively, exist in C-UC and C-350, but completely disappeared for the P-450 and P-550. This also be found by [23]. Stretching absorption band at 1744 cm^{-1} shown the present of carbonyl C=O in esters, aldehydes, ketone groups and acetyl derivatives. This band also present in adsorbent C-350, C-450 and C-550. The peak that at 1624 cm^{-1} [1] may be due to olefinic C=C vibrations in aromatic region for the pumpkin seed shell

[24]. Next, peak at 1157 and 1099 cm^{-} indicated the C-O stretching vibrations in the raw material. The peak at approximately 1456 cm^{-1} is due to the present of C─H stretching. The peak at 1157 cm^{-1} indicated the existing of ester functional group. The absorption bands in the region 690–900 cm^{-1} was due to the C-H aromatics vibration.

B. *The effects of adsorbents dosage*

The effect of adsorbent dosage on the percentage removal of dyes was investigated by varying adsorbent dosage from 0.1g, 0.2g and 0.3g while keeping initial dyes concentration and contact time constant at 20 ppm and 30 min respectively. Figures 3 (a) and (b) showed the effect of adsorbent dosage on percentage removal of MB and MO respectively. For MB, adsorbent P-550 achieved percentage removal of 56.94% at dosage of 0.1g which increased to 80.38% and 93.00% at dosage of 0.2g and 0.3g respectively. For MO, 12.87% percentage removal was achieved by using P-550 at dosage of 0.1g which increased to 18.79% and 26.05% at dosage 0.2g and 0.3g respectively. Based on the graph trend in figures 3 (a) and (b), the percentage removal of dyes increases when increasing the adsorbent dosage. This is because increasing the adsorbent dosage leads to the higher amount of available adsorption sites for adsorption process. According to [25] the percentage removal of dyes increase when the adsorbent dosage increase, can be attributed to the increases of surface area and availability of more binding sites for the adsorption process.



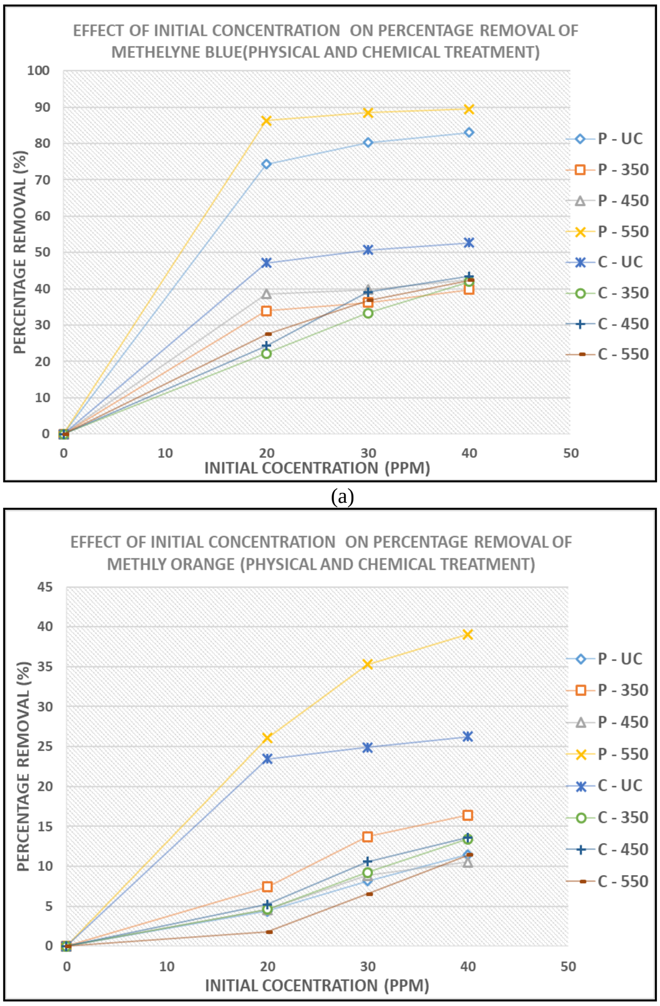
(a)

(b)

Fig. 3: Effect of adsorbent dosage on percentage removal of (a) MB and (b) MO using physical and chemical treatment adsorbents. (contact time = 30 minutes, initial dye concentration = 20 ppm, temperature = 35 °C, shaking speed = 150 rpm)

C. *The effect of initial dyes concentration*

To studied the effect of initial dyes concentration on the percentage removal of dyes, some experiments were conducted by changing the initial dyes concentration from 20 ppm, 30 ppm, and 40 ppm while maintaining the adsorbent dosage and contact time at 0.6g and 30 min respectively. Figures 4 (a) and (b) showed the effect of initial dyes concentration on percentage removal of MB and MO respectively. The percentage removal of MB was about 86.30% at initial concentration of 20 ppm and then slightly increased to 88.51% and 89.52% at initial concentration of 30 and 40 ppm respectively when using adsorbent P-550. For MO, adsorbent P-550 is able to remove about 26.05% of MB for initial concentration of 20 ppm and increase to 35.28% and 39.05% for initial concentration of 30 and 40 ppm respectively. Based on the graph trend in figures 4 (a) and (b), percentage removal of dyes increases when the initial dyes concentration increase. Typically, the initial dyes concentration creates the initial driving force to overcome all the mass transfer resistance between the aqueous and solid surfaces. The higher concentration of dyes creates higher driving force for dyes molecules to bind with the adsorption sites. This will result in the higher fractional adsorption ratio between the numbers of dye molecules to the number of available actives sites and hence an increase in adsorption process and the percentage removal of these dyes. This finding also supported by [26], as he stated that a higher initial dyes concentration enhances the adsorption process.



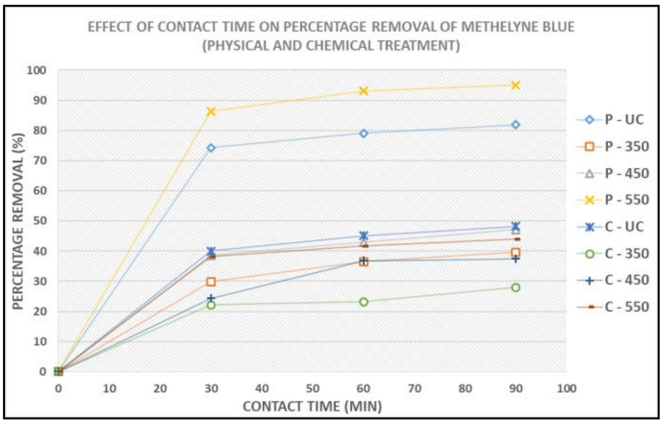
(a)

(b)

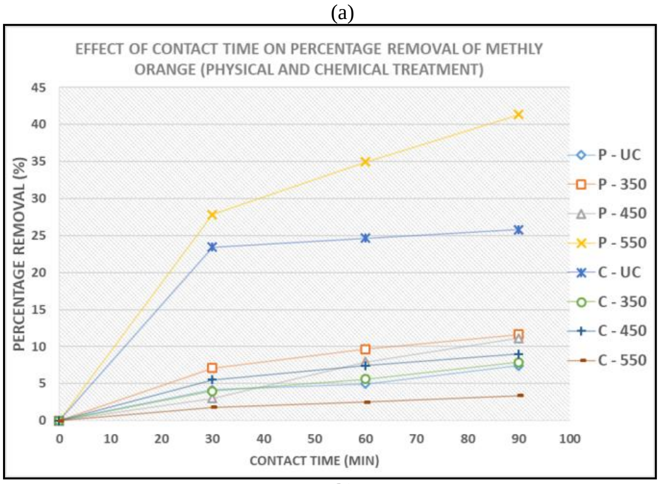
Fig. 4: Effect of initial concentration on percentage removal of (a) MB and (b) MO using physical and chemical treatment adsorbents. (adsorbent dose = 0.3g/50 ml, contact time 30 minutes, temperature = 35 C, shaking speed = 150 rpm)

D. *The effect of contact time between adsorbent and adsorbate*

The effect of contact time on percentage removal of dyes was investigated by varying the contact time from 30 min, 60 min and 90 min. Other parameter such as adsorbent dosage and initial concentration was maintained at 03.g and 20 ppm respectively. Figures 5 (a) and (b) showed the effect of contact time on percentage removal of MB and MO respectively. Increase in contact time increased the percentage removal of MB from 86.30 % within the first 30 minutes to 93.03 % and 95.08% at contact time 60 and 90 minutes respectively when using adsorbent P-550. For MO, the percentage removal changed from 27.85 % at a contact time of 20 minutes to 34.96 % and 41.36% at contact time of 60 and 90 minutes respectively when using adsorbent P-550. The rate of percentage removal of dyes is higher at the beginning is due to the large surface area of adsorbent being available for the adsorption of dyes molecules at the first 30 min [27]. After 30 minutes, there was only a slight increment in percentage removal. This happened due to the decrease in binding sites as time increases [28].



(a)



(b)

Fig. 5: Effect of contact time on percentage removal of (a) MB and (b) MO using physical and chemical treatment adsorbents. (adsorbent dose = 0.6g/100 ml, initial dye concentration = 20 ppm, temperature = 35 C, shaking speed = 150 rpm)

IV. Conclusion

The studies presented revealed that the adsorption of the two dyes increases when adsorbent dosage, initial dyes concentration and contact time increases. Pumpkin seeds an agriculture waste, has been successfully used to derive an effective low cost adsorbent. The generated data can be used as baseline data to design adsorption column for dyes removal.

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