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Removal of methylene blue dye from aqueous solution by using orange peel treated with acid as an adsorbent

Noor Ainee Zainol[a,b,*], Asma Baharuddin[a], Nor Aida Yusoff[a,b], Khairunissa Syairah Ahmad Sohaimi[a,b], Nor Munirah Rohaizad[a,b], Azlinda Abdul Ghani[a,b], Edza Aria Wikurendra[c], Ary Andini[d], Achmad Syafiuddin[c]

[a]*Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, Kampus Uniciti Alam, 02100 Padang Besar, Perlis, Malaysia, emails: aineezainol@unimap.edu.my (N.A. Zainol), asmabaharuddin29@gmail.com (A. Baharuddin)*
[b]*Centre of Excellence, Water Research and Environmental Sustainability Growth (WAREG), Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia, emails: aidayusoff@unimap.edu.my (N.A. Yusoff), syairah@unimap.edu.my (K.S.A. Sohaimi), normunirah@unimap.edu.my (N.M. Rohaizad), azlindaghani@unimap.edu.my (A.A. Ghani)*
[c]*Department of Public Health, Universitas Nahdlatul Ulama Surabaya, 60237 Surabaya, Indonesia, emails: edzaaria@unusa.ac.id (E.A. Wikurendra), achmadsyafiuddin@unusa.ac.id (A. Syafiuddin)*
[d]*Department of Medical Technology Laboratory, Universitas Nahdlatul Ulama Surabaya, 60237 Surabaya, Indonesia, email: aryandini@unusa.ac.id (A. Andini)*

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ABSTRACT

A vast amount of dye effluent is continually released into the water, posing a significant hazard to the natural environment and human health. This study aims to investigate the adsorption of methylene blue from an aqueous solution using orange peel as activated carbon. To comprehend the adsorption behavior, the influences of adsorbent dose (0.1–0.8 g), starting dye concentration (10–80 mg/L), and contact duration (10–80 min) were investigated. Fourier-transform infrared spectroscopy was used to recognize the functional group in orange peel. A non-linear pseudo-first-order reaction could describe the adsorption process. The process was best fitted with the Langmuir isotherm than the Freundlich isotherm. The results obtained were a high level of color removal achieved within a short time which was 50 min, and orange peel held as a potential low-cost adsorbent for dye removal from industrial wastewater.

Keywords: Methylene blue; Dye removal; Adsorption; Activated carbon; Low-cost adsorbent

1. Introduction

Wastewater is water mixed with certain substances, resulting in changes to biological, physical, and chemical properties. The discharge of wastewater containing dyes is a major problem in the environment. Dye is a common organic compound generally used in industries, such as leather tanning, printing, textiles, pulp/paper, cosmetics, plastics, and rubber industries [1]. Out of all these various industries, the textile industry ranked first when it comes to using dyes for the coloration of fibre. The dye industry is expected to develop by around 2%–3% each year due to rising worldwide dye production and consumption [2]. Textile dyes are generally made from azo compounds and their derivatives which are benzene groups. Azo compounds if too long in the environment,

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[*] Corresponding author.

will be a source of disease because it is carcinogenic and mutagenic [3]. Without proper treatment, the release of these organic dyes effluents is worrying for environmental and health problems [4]. Thus, the appropriate treatment is crucial for the overall safety and benefit of humans, animals, and the environment.

Methylene blue, known as methylthioninium, is one of the most harmful basic/cation dyes. It is widely used for coloring products in paper, temporary hair colorants, dyeing of cotton, wood, and silk [5]. Methylene blue can cause harmful effects, such as cyanosis, methemoglobinemia, dyspnea, and tachycardia. If methylene blue comes in contact with skin, it may cause skin irritation and allergic reaction. The dye's effluent also disturbs the photosynthesis process of aquatic plants by preventing and cutting off sunlight penetration into the water [6].

According to Crini and Lichtfouse [7] in the textile industry, nearly 200,000 tons of these dyes are lost to effluents every year, and most of these dyes escape conventional wastewater treatment processes and persist in the environment. For this reason, the removal of dyes from effluent has been extensively studied for many years, and lots of technologies have been developed. Among them, some popular techniques are oxidative degradation [8], biochemical degradation [9], photodegradation [10], electrocoagulation [11] and electrochemical degradation [12]. Comparatively, adsorption appears to be a significant method due to its extensive uses, such as ease of operation, low cost, wide availability, and recyclability [13,14].

Adsorption is a physical process in which a solute (dye) is transferred from a solvent (effluent) to an adsorbent (solid matrix surface). This occurs when a liquid mixture comes into contact with a solid (adsorbent), and a mixture component (adsorbate) clings to the solid's surface. Adsorbents with high specific surface areas (m surface/g solid), such as activated carbon, enable little amounts of adsorbent to extract significant volumes of adsorbate from fluid mixes.

Among adsorbents, activated carbon is the most used adsorbent in various purification processes, including gas purification, sewage treatment, and purification. However, commercial activated carbon is costly and its regeneration is very difficult, especially for powdery activated carbon [15,16]. For the sake of reducing the treatment cost for methylene blue dye removal from wastewater, the researcher came out with the idea of developing low-cost adsorbents prepared from agricultural waste like grape waste [17], *Oryza sativa* L. [18], *Apium graveolens* [19], Mucuna beans [20], *Salacca zalacca* skin [21], spent coffee ground [22] and dragon fruit peel [23] and pomegranate fruit peel [24].

Orange peel comprises cellulose pectin, hemicellulose, lignin, and other low molecular weight compounds like limestone. Since the 1980s, orange production has continued to grow across the world, and in 2014, orange production clocked in at 68,925,200 tons, with much of that figure being used to make products like jams, marmalades, and juices–all of which result in the waste of orange peels at a massive scale (around 3.8 million tons of waste a year) [25]. This waste has little to no economic value, leading to serious disposal problems [26]. Furthermore, orange peel is an option as a low-cost adsorbent due to its abundance in nature, non-toxicity, and biodegradability. Articles on the removal of methylene blue dye from aqueous solutions are numerous but using acid-treated orange peel as an adsorbent is still not widely available. Therefore, this study was carried out to investigate the effect of adsorption of orange peel with a different parameter, such as dye concentration, adsorbent dosage, and contact time using methylene blue.

2. Materials and methods

2.1. Sample preparation

The orange, *Citrus sinensis* peel (mesocarp and exocarp) was collected from a local fruit stall. The orange peel was washed several times to remove other impurities attached to the surface and cut into small pieces (i.e., 3 cm × 3 cm). The orange peel was then dried in an oven for 24 h at 106°C.

2.2. Preparation of adsorbent

The 25-g of dried orange peel was ground into small pieces using a grinder. Then, the crushed orange peel was sieved using a Sieve shaker AS 200 control-RETSCH with 125 and 250 μm. The powder was then mixed with 100 mL concentrated phosphoric acid in a beaker. Then, it was stirred until the orange peel powder had fully absorbed the phosphoric acid [27]. It was then dried at room temperature for 24 h. Finally, it was burned in the Chamber Furnace Carbolite Gero CWF-1200 at 400° for 30 min to activate the carbon.

2.3. Methylene blue dye stock solution

The methylene blue stock solution was made by dissolving 0.1 g methylene blue dye powder in 1,000 mL of distilled water. The stock solution was diluted with distilled water [28]. Distilled water was used to dilute methylene blue concentrations of 10, 20, 30, 40, 50, 60, 70, and 80 mg/L from the produced stock solution. Before the adsorption procedure, the absorbance of the stock solution was measured with a UV-Vis spectrophotometer to create the calibration curve graph. The calibration curve was created by plotting the collected observation data against concentration.

2.4. Batch equilibrium study

The adsorption process has experimented with in the batch system under 30° temperature with initial methylene blue (10–80 mg/L) and varying shaking speed (300 rpm), contact times (10–80 min), and adsorbent dosages (0.1–0.8 g). The conical flask was then placed in a shaker at a shaking speed (350 rpm). A control sample was prepared. After the desired contact time, the flask was withdrawn from the shaker, and the mixture of dye and adsorbent was filtered. A UV-Vis Spectrophotometer was used to measure the dye concentration after the treatment.

2.5. Effect of contact time

The test was performed at eight different shaking periods of 10, 20, 30, 40, 50, 60, 70, and 80 min at the same beginning time for eight separate conical flasks with a 10 min interval. In each conical flask, 0.5 g of activated carbon dose was given to 10 mL of dye stock solutions with an initial dye concentration of 50 mg/L. The temperature was 30°C during the test, and the speed was 300 rpm. After the necessary time had passed, the absorbance of each conical flask was measured using a UV-Vis spectrophotometer.

2.6. Effect of initial dye concentration

The initial dye concentrations of 10, 20, 30, 40, 50, 60, 70, and 80 mg/L were used. The test was performed at 30°C for 50 min, and 0.5 g of activated carbon was added for each dye concentration range with 100 mL volume of solution. The absorbance for each concentration was measured using UV-Vis after 50 min.

2.7. Effect of adsorbent dosage

The test was performed at 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 g of activated carbon dosage. The test was carried out at 30°C for 50 min. The dosage was added to 100 mL of dye stock solutions with 50 mg/L of initial dye concentration in each conical flask. The absorbance for each conical flask was measured using UV-Vis after 50 min.

3. Results and discussion

3.1. Characterisation using Fourier-transform infrared spectroscopy

The temperature influenced the carbonization yield. The optimum condition was obtained at 400° and 30 min. The spectrum of orange peel was obtained from Fourier-transform infrared spectroscopy (FT-IR) in the 4,000–400 cm^{-1} wavelength range. Several identified functional groups from the spectra were listed in Tables 1 and 2.

According to Fig. 1, a –OH appears at the wide peak of 3,357.7 cm^{-1} due to the stretching vibration of hydrogen-bonded phenol and alcohol groups. Fig. 1 shows the FT-IR spectrum of orange peel as an absorbent, while Fig. 2 shows the FT-IR spectrum of activated carbon orange peel. Fig. 2 shows a reduction in the intensity of the peak detected at 3,357.7 cm^{-1} in Fig. 1. Due to the action of the acid on the orange peel, some of the alcohol groups were able to be transformed into ethers. The peak at 879.84 cm^{-1} in Fig. 2 was after that decreased and somewhat distorted, possibly due to a reduction in water content. The carbonization of the orange peel resulting from acid treatment was seen by the peak at 1,056.2 cm^{-1} in Fig. 1 and further decreased at 968 cm^{-1} in Fig. 2. This demonstrated that the functional group present in the orange peel was changed by acid-treated orange peel. As a result, acid-treated orange peel has a considerably higher capacity for methylene blue adsorption from an aqueous solution [28].

3.2. Effect of contact time, initial dye concentration, and adsorbent doses on adsorption

3.2.1. Effect of contact time

Contact time had a significant impact on the removal percentage since most of the adsorption process occurs in the first 30 min and then increases at a prolonged rate [29]. Fig. 3 depicts the quantity of methylene blue dye adsorbed during a period of 10–80 min. The procedure was carried out under stable conditions, with a 50 mL starting concentration of 50 mg/L of methylene blue, 0.5 g of adsorbents, and a temperature of 30°C.

The adsorption process increased along with contact time and reached an equilibrium in 60 min. There was no drastic uptake in the percentage of methylene blue removal. The graph showed that the highest percentage of methylene blue removed was 61% at 80 min. The methylene blue

Table 1
Functional group identified from spectra of orange peel

Peak wavelength (cm^{-1})	Functional group
1,056.2	Alcohol with primary structure C–O stretch
1,235.6	Ether, C–O–O stretch for cyclic ether
1,616.6	Nitromethane, N≡O stretch
1,739.4	Carboxylic acids C=O stretch
2,923.2	Alkanes H–C–H asymmetric and symmetric stretch
3,357.7	Phenols and alcohol O–H bond stretch

Table 2
Functional group identified from spectra of activated carbon orange peel

Peak wavelength (cm^{-1})	Functional group
2,803.6	Alkane H–C–H asymmetric and symmetric stretch
2,337.6	Nitrite C≡N stretch
1,106.5	Ether C–O–C stretch for cyclic ether
968	Alcohol with primary of CH_2OH for CO (stretch)
879.84	Aromatic compound with CH out-of-plane deformation

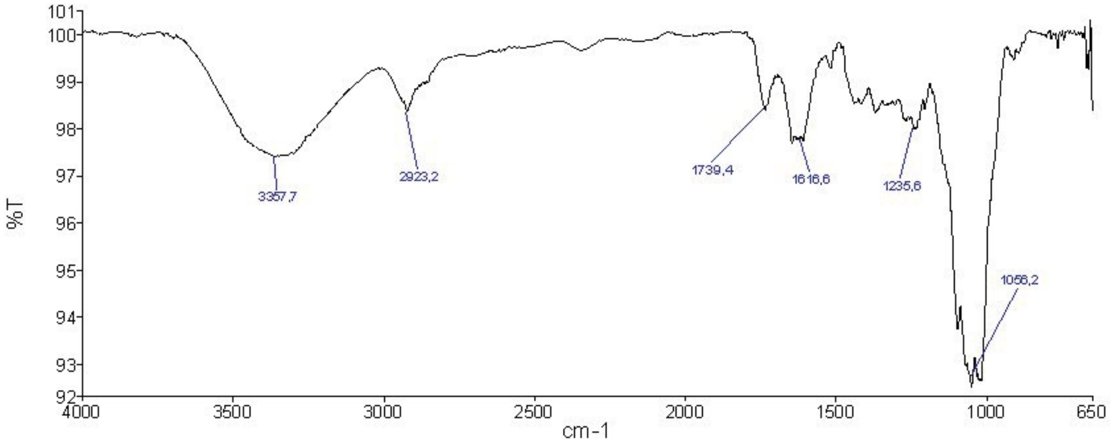


Fig. 1. FT-IR spectra of raw orange peel.

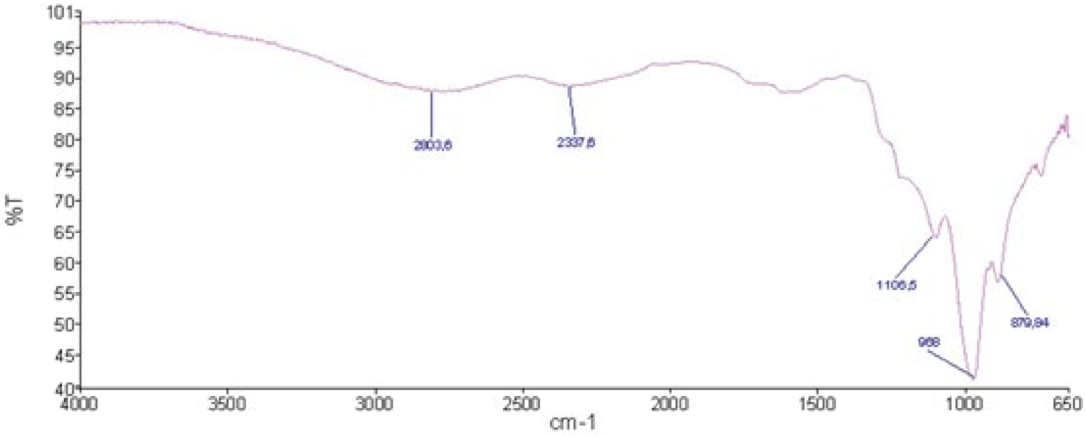


Fig. 2. FT-IR spectra of acid-treated orange peel.

molecules get to the boundary layer during the adsorption process, which then diffuses into the available activated carbon orange peel surfaces. The methylene blue will diffuse into the porous structure of the adsorbent. The percentage of methylene blue removal was high during the initial 50 min as the vacant binding sites on activated carbon orange peel surfaces were high.

However, as the contact time increased to 60 min, the percentage of methylene blue removal became slower. This shows that the binding sites on the adsorbents were already occupied with other methylene blue molecules. It reached a constant state at 60 min where there was little to no more adsorption process. The methylene blue molecules could not diffuse anymore because the binding sites were fully occupied.

Based on the percentage of methylene blue removal, the adsorbate was adsorbed in the chemisorption process. This is because the gap between the percentages from each time interval was not too big. Moreover, the adsorption rate was constantly increasing even at low temperatures. The adsorbate was bound to the surface of the adsorbent through a strong chemical bond.

3.2.2. Effect of initial dye concentration

The percentage of methylene blue removal for 50 mL of different ranges of initial concentration of methylene blue (10–80 mg/L) was studied. The experiment was run at 30° for 50 min. The maximum uptake for the adsorption process was when it reached the concentration range of 10–50 mg/L, where the percentage decreased from 80% to 35%. However, the adsorption rate gradually decreased when it reached a concentration of 60–80 mg/L. The percentage of removal stayed constant at 31% at 80 mg/L.

Based on Fig. 4, the adsorption capacity increased as the initial dye increased, and the percentage removal decreased with an increase in initial dye concentration. The adsorption depended on the initial concentration of methylene blue because, at low concentrations, the ratio of methylene blue molecules to the available binding sites at the adsorbate surface area was low, making it independent of initial concentration. However, when at high concentration, the unoccupied binding sites are reduced, so the percentage removal becomes dependent on initial concentration [29]. It can also be associated with the faster methylene blue saturated binding site on the adsorbent surface.

3.2.3. Effect of adsorbent doses

The effect of variation in adsorbent dosage from 0.1 to 0.8 g used to remove methylene blue. The experiment was run under constant parameters with 50 mL of 50 mg/L initial concentration of methylene blue at a temperature of 30°. Fig. 5 shows a rapid increase from 0.1 to 0.5 g adsorbent dosage with removal of 14%–38%. The adsorption process reached a constant state at dosage above 0.5 g. This may be due to the increase in the availability of the binding sites at the adsorbent surface. The increase in dosage provides more sites for dye saturation during the process [30].

The gap between the percentage of removal for each dosage showed a tremendous gap based on the graph. This shows that the adsorbate was adsorbed on the monolayer. This means that only one molecule can take over the sites. That was why the data obtained from each dosage interval showed a considerable gap percentage value. This was because of the high ability of the adsorbent to adsorb more than one methylene blue molecule.

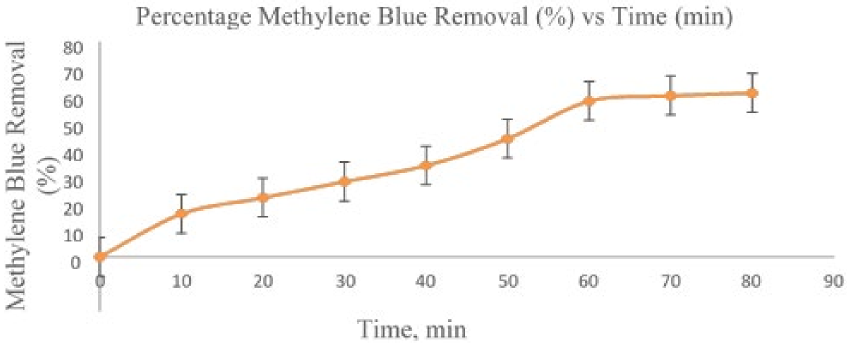


Fig. 3. Effect of contact time at the time range of 10–80 min.

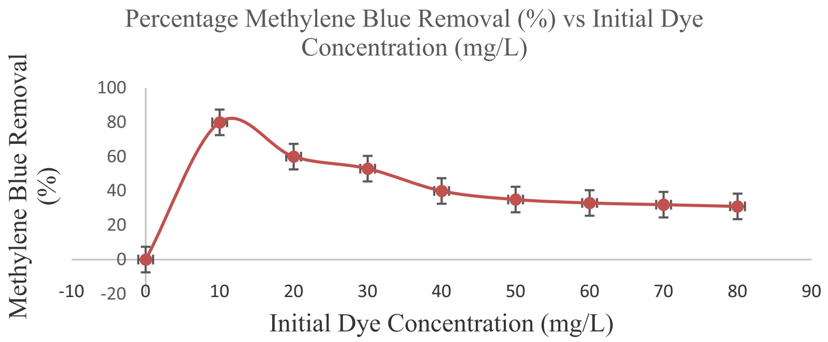


Fig. 4. Effect of initial dye concentration at the concentration range of 10 to 80 mg/L.

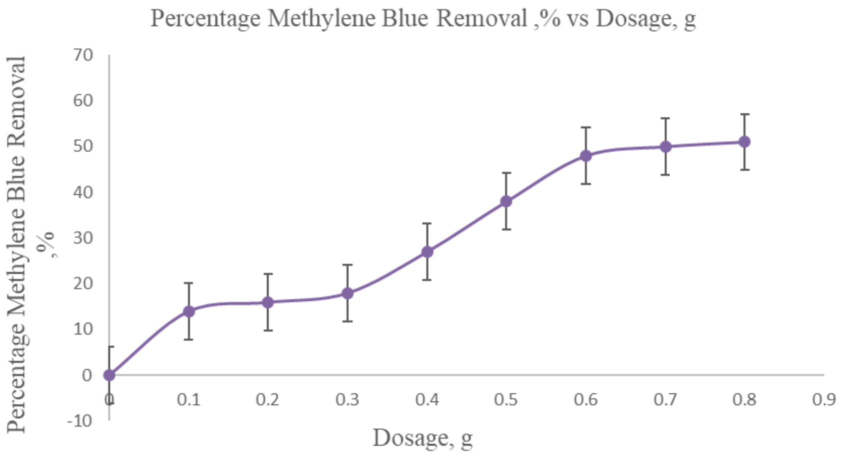


Fig. 5. Effect of adsorbent dosage at the range of 0.1–0.8 g.

3.3. Adsorption kinetic study

The most common method to study the behavior of activated carbon is through kinetic and adsorption equilibrium models. The rate constants were calculated by using the pseudo-first-order and pseudo-second-order kinetic models. The parameters of the non-linear pseudo-first-order and pseudo-second-order models are shown in Table 3. The anticipated outcomes of the non-linear pseudo-first-order and pseudo-second-order kinetic models are shown in Fig. 6.

The amount of dye adsorbed at equilibrium can be represented as q_e. Meanwhile, the amount of dye adsorbed at any time can be represented as q_t. K_1 is the pseudo-first-order rate constant (min^{-1}). From Fig. 6, the plots for both graphs are linear but do not pass through the origin. The deviation of the plot of q_t vs. t and t/q_t vs. t proved that the adsorption process was controlled by film diffusion instead of intra-particle diffusion.

The pseudo-first-order kinetic model yielded a q_e value of 0.5333, whereas the pseudo-second-order kinetic model yielded a q_e value of 3.4048. The adsorption capacities for the pseudo-second-order kinetic model were greater than for the pseudo-first-order kinetic model. On the other hand, the pseudo-first-order kinetic model better obeys the adsorption kinetic data than the pseudo-second-order kinetic model. This was since the correlation coefficient for the pseudo-first-order model, R^2 = 0.9854, gave a strong fit and was enough for explaining kinetic data. Meanwhile, the correlation coefficient for the pseudo-second-order model, R^2 = 0.9017, was less than 0.98. This indicated a weak correlation. Thus, the best kinetic model that fitted well for methylene blue adsorption was calculated using the non-linear pseudo-first-order kinetic models.

Table 3
Parameters of non-linear pseudo-first-order and pseudo-second-order models

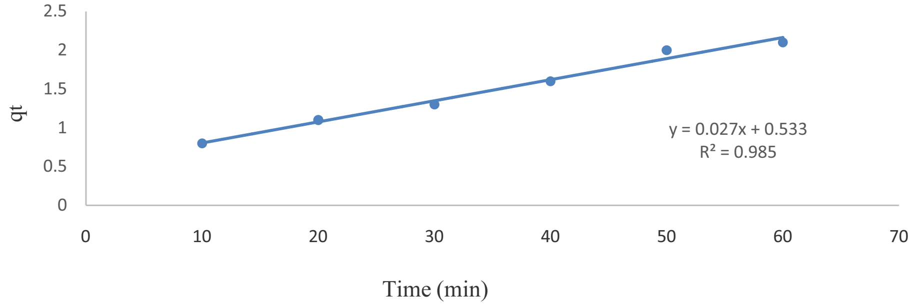
Parameter	Kinetic models	
	Pseudo-first-order	Pseudo-second-order
R^2	0.9854	0.9017
K_1 (min^{-1})	0.0521	–
K_2 (min^{-1})	–	7.32×10^{-3}
q_e (mg/g)	0.5333	3.4048

3.3.1. Adsorption isotherm

The adsorption isotherm demonstrates how the adsorption molecules dispense between the solid and liquid phases when the adsorption process reaches an equilibrium state. Adsorption isotherm also can be described as the equilibrium concentration of the substrate that came in contact with the adsorbent. To find a suitable model for the process, the analysis of the isotherm data was calculated using different isotherm models [31]. The two typical adsorption isotherms are shown in Fig. 7, the adsorption isotherm, Langmuir isotherm, and Freundlich isotherm. Table 4 shows the parameters of kinetic models.

From Fig. 7, The Langmuir isotherm fitted the adsorption process better than the Freundlich isotherm. The R^2 value for Langmuir was 0.8255, while Freundlich isotherm was 0.0151. The R^2 values for the Freundlich isotherm were too small to be considered best fits. This means that the adsorption of methylene blue dye is favorable to the

(a) Pseudo-First Order



(b) Pseudo-Second Order

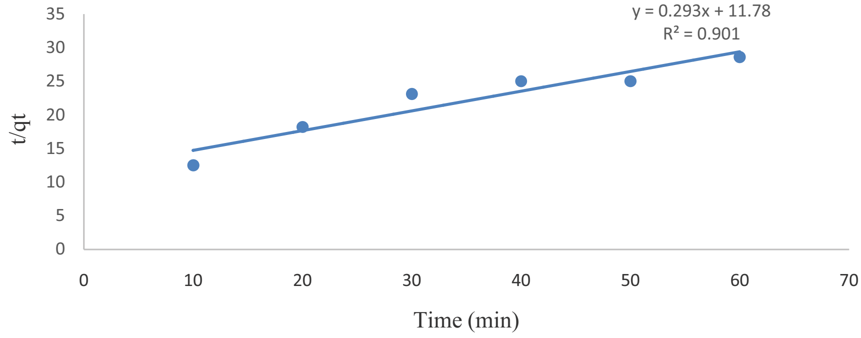
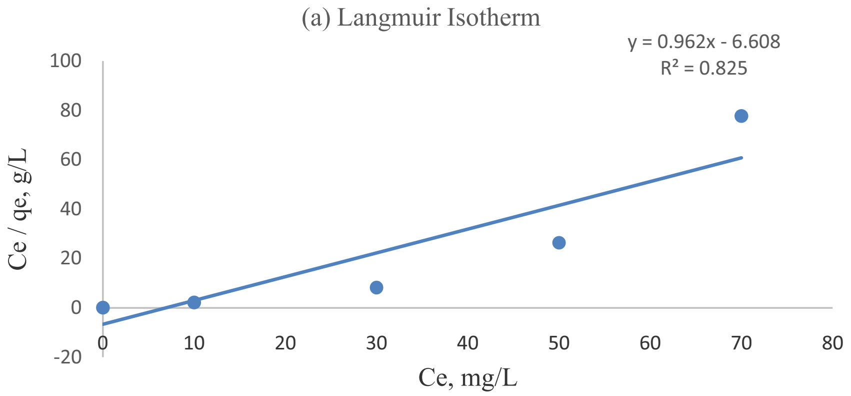


Fig. 6. Adsorption kinetics (a) pseudo-first-order and (b) pseudo-second-order.


(a) Langmuir Isotherm

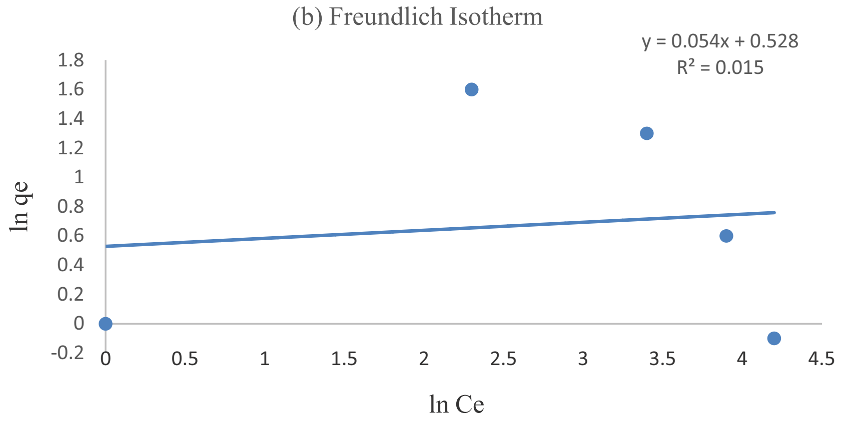

(b) Freundlich Isotherm

Fig. 7. Adsorption isotherm (a) Langmuir isotherm and (b) Freundlich isotherm.

Table 4
Parameters of kinetic models, Langmuir isotherm, and Freundlich isotherm

Parameter	Kinetic models	
	Langmuir isotherm	Freundlich isotherm
R^2	0.8225	0.0151
Q_o (mg/g)	1.0393	–
K_L (L/mg)	0.1456	–
n	–	18.248
K_F (L/mg)	–	–

Langmuir isotherm. The data fit better to the Langmuir model than the Freundlich model. Five gradual increasing initial concentrations (0, 10, 30, 50, and 70 mg/L) of methylene blue were considered for this plot. The parameters, such as K_L, were found to be 0.1456 L/mg.

The amount of methylene blue adsorbed on the activated carbon surface at constant temperature was chemisorption. This was further supported by Langmuir's theory, which is the formation of a monolayer. Because of the monolayer formation, a saturation in adsorption would reach a higher equilibrium concentration of the adsorbate [32]. This type of adsorption occurred due to short-range chemical forces, which do not allow penetration through the primary adsorbed molecules. In other words, for each active site, can be occupied by only one adsorbate molecule.

4. Conclusions

This study had successfully examined the orange peel as an agricultural waste material that can be used as an adsorbent to remove methylene blue from an aqueous solution. Activated carbon orange peel, a low-cost adsorbent, was proven to be effective in removing methylene blue from wastewater that contained textile dye. High level of colour removal achieved within a short time which was 50 min. Hence, by using orange peel as an adsorbent, it can be an alternative for less costly adsorbent used in wastewater treatment and solving waste management issues.

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Conflicts of interest

The authors declare no conflict of interest.

References

[1] E.U. Etim, Removal of methyl blue dye from aqueous solution by adsorption unto ground nut waste, Biomed. J. Sci. Technol. Res., 15 (2019) 11365–11371.

[2] O.S. Bayomie, H. Kandeel, T. Shoeib, H. Yang, N. Youssef, M.M.H. El-Sayed, Novel approach for effective removal of methylene blue dye from water using fava bean peel waste, Sci. Rep., 10 (2020) 7824, doi: 10.1038/s41598-020-64727-5.

[3] M. Berradi, R. Hsissou, M. Khudhair, M. Assouag, O. Cherkaoui, A. El Bachiri, A. El Harfi, Textile finishing dyes and their impact on aquatic environs, Heliyon, 5 (2019) e02711, doi: 10.1016/j.heliyon.2019.e02711.

[4] S.M. Kanawade, R.W. Gaikwad, Removal of methylene blue from effluent by using activated carbon and water hyacinth as adsorbent, Int. J. Chem. Eng. Appl., 2 (2011) 317–319.

[5] L. Baloo, M.H. Isa, N.B. Sapari, A.H. Jagaba, L.J. Wei, S. Yavari, R. Razali, R. Vasu, Adsorptive removal of methylene blue and acid orange 10 dyes from aqueous solutions using oil palm wastes-derived activated carbons, Alexandria Eng. J., 60 (2021) 5611–5629.

[6] S. Giraldo, I. Robles, L.A. Godínez, N. Acelas, E. Flórez, Experimental and theoretical insights on methylene blue removal from wastewater using an adsorbent obtained from the residues of the orange industry, Molecules, 26 (2021) 2021, doi: 10.3390/molecules26154555.

[7] G. Crini, E. Lichtfouse, Advantages and disadvantages of techniques used for wastewater treatment, Environ. Chem. Lett., 17 (2019) 145–155.

[8] R. Arshad, T.H. Bokhari, T. Javed, I.A. Bhatti, S. Rasheed, M. Iqbal, A. Nazir, S. Naz, M.I. Khan, M.K.K. Khosa, M. Iqbal, M. Zia-ur-Rehman, Degradation product distribution of Reactive Red-147 dye treated by UV/H_2O_2/TiO_2 advanced oxidation process, J. Mater. Res. Technol., 9 (2020) 3168–3178.

[9] M. Contreras, C.D. Grande-Tovar, W. Vallejo, C. Chaves-López, Bio-removal of methylene blue from aqueous solution by *Galactomyces geotrichum* KL20A, Water, 11 (2019) 282, doi: 10.3390/w11020282.

[10] V.L. Er Siong, K.M. Lee, J.C. Juan, C.W. Lai, X.H. Tai, C.S. Khe, Removal of methylene blue dye by solvothermally reduced graphene oxide: a metal-free adsorption and photodegradation method, RSC Adv., 9 (2019) 37686–37695.

[11] K. Gautam, S. Kamsonlian, S. Kumar, Removal of Reactive Red 120 dye from wastewater using electrocoagulation: optimization using multivariate approach, economic analysis, and sludge characterization, Sep. Sci. Technol., 55 (2020) 3412–3426.

[12] M.R. Samarghandi, A. Dargahi, A. Shabanloo, H.Z. Nasab, Y. Vaziri, A. Ansari, Electrochemical degradation of methylene blue dye using a graphite doped PbO_2 anode: optimization of operational parameters, degradation pathway and improving the biodegradability of textile wastewater, Arabian J. Chem., 13 (2020) 6847–6864.

[13] E. Misran, O. Bani, E.M. Situmeang, A.S. Purba, Banana stem based activated carbon as a low-cost adsorbent for methylene blue removal: isotherm, kinetics, and reusability, Alexandria Eng. J., 61 (2022) 1946–1955.

[14] R. Tang, C. Dai, C. Li, W. Liu, S. Gao, C. Wang, Removal of methylene blue from aqueous solution using agricultural residue walnut shell: equilibrium, kinetic, and thermodynamic studies, J. Chem., 2017 (2017) 8404965, doi: 10.1155/2017/8404965.

[15] R. Ahmad, K. Ansari, Comparative study for adsorption of congo red and methylene blue dye on chitosan modified hybrid nanocomposite, Process Biochem., 108 (2021) 90–102.

[16] A. Aichour, H. Zaghouane-Boudiaf, F.B. Mohamed Zuki, M. Kheireddine Aroua, C.V. Ibbora, Low-cost, biodegradable and highly effective adsorbents for batch and column fixed bed adsorption processes of methylene blue, J. Environ. Chem. Eng., 7 (2019) 103409, doi: 10.1016/j.jece.2019.103409.

[17] R. Ahmad, K. Ansari, Polyacrylamide-Grafted *Actinidia deliciosa* peels powder (PGADP) for the sequestration of crystal violet dye: isotherms, kinetics and thermodynamic studies, Appl. Water Sci., 10 (2020) 195, doi: 10.1007/s13201-020-01263-7.

[18] A.H. Jawad, N. Hum, A.M. Farhan, M.S. Mastuli, Biosorption of methylene blue dye by rice (*Oryza sativa* L.) straw: adsorption and mechanism study, Desal. Water Treat., 190 (2020) 322–330.

[19] S. Mohebali, D. Bastani, H. Shayesteh, Equilibrium, kinetic and thermodynamic studies of a low-cost biosorbent for the removal of Congo red dye: acid and CTAB-acid modified celery (*Apium graveolens*), J. Mol. Struct., 1176 (2019) 181–193.

[20] N.D. Shooto, P.M. Thabede, B. Bhila, H. Moloto, E.B. Naidoo, Lead ions and methylene blue dye removal from aqueous solution by mucuna beans (velvet beans) adsorbents, J. Environ. Chem. Eng., 8 (2020) 103557, doi: 10.1016/j.jece.2019.103557.

[21] I. Fatimah, I. Sahroni, M.S.E. Dahlyani, A.M.N. Oktaviyani, R. Nurillahi, Surfactant-modified *Salacca zalacca* skin as adsorbent for removal of methylene blue and Batik's wastewater, Mater. Today Proc., 44 (2021) 3211–3216.

[22] Y. Dai, K. Zhang, X. Meng, J. Li, X. Guan, Q. Sun, Y. Sun, W. Wang, M. Lin, M. Liu, S. Yang, Y. Chen, F. Gao, X. Zhang, Z. Liu, New use for spent coffee ground as an adsorbent for tetracycline removal in water, Chemosphere, 215 (2019) 163–172.

[23] M.A. Ahmad, M.A.M. Eusoff, M.N.N. Khan, A. Khasri, Microwave-assisted activated carbon from passion fruit peel for methylene blue dye removal, AIP Conf. Proc., 2124 (2019) 30019, doi: 10.1063/1.5117141.

[24] M.A. Ahmad, M.A. Eusoff, P.O. Oladoye, K.A. Adegoke, O.S. Bello, Optimization and batch studies on adsorption of methylene blue dye using pomegranate fruit peel based adsorbent, Chem. Data Collect., 32 (2021) 100676, doi: 10.1016/j.cdc.2021.100676.

[25] A. Kamińska, P. Miądlicki, K. Kiełbasa, M. Kujbida, J. Sreńscek-Nazzal, R.J. Wróbel, A. Wróblewska, Activated carbons obtained from orange peels, coffee grounds, and sunflower husks-comparison of physicochemical properties and activity in the alpha-pinene isomerization process, Mater. (Basel, Switzerland), 14 (2021) 7448, doi: 10.3390/ma14237448.

[26] M.R. Mafra, L. Igarashi-Mafra, D.R. Zuim, É.C. Vasques, M.A. Ferreira, Adsorption of remazol brilliant blue on an orange peel adsorbent, Braz. J. Chem. Eng., 30 (2013) 657–665.

[27] S. Dey, S.R. Basha, G.V Babu, T. Nagendra, Characteristic and biosorption capacities of orange peels biosorbents for removal of ammonia and nitrate from contaminated water, Clean. Mater., 1 (2021) 100001, doi: 10.1016/j.clema.2021.100001.

[28] P. Senthil Kumar, P. Sebastina Anne Fernando, R. Tanvir Ahmed, R. Srinath, M. Priyadharshini, A.M. Vignesh, A. Thanjiappan, Effect of temperature on the adsorption of methylene blue dye onto sulfuric acid–treated orange peel, Chem. Eng. Commun., 201 (2014) 1526–1547.

[29] M. Khodaie, N. Ghasemi, B. Moradi, M. Rahimi, Removal of methylene blue from wastewater by adsorption onto $ZnCl_2$ activated corn husk carbon equilibrium studies, J. Chem., 2013 (2013) 383985, doi: 10.1155/2013/383985.

[30] M.A. Mohammad Razi, M.N.A. Mohd Hishammudin, R. Hamdan, Factor affecting textile dye removal using adsorbent from activated carbon: a review, MATEC Web Conf., 103 (2017) 06015, doi: 10.1051/matecconf/201710306015.

[31] N. Ertugay, E. Malkoc, Adsorption isotherm, kinetic, and thermodynamic studies for methylene blue from aqueous solution by needles of *Pinus Sylvestris* L., Pol. J. Environ. Stud., 23 (2014) 1995–2006.

[32] L. Liu, X.-B. Luo, L. Ding, S.-L. Luo, 4 – Application of Nanotechnology in the Removal of Heavy Metal From Water, X. Luo, F. Deng, Eds., Nanomaterials for the Removal of Pollutants and Resource Reutilization: Micro and Nano Technologies, Elsevier, Amsterdam, Netherlands, 2019, pp. 83–147.