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Removal of triphenylmethane dye from aqueous solutions through an adsorption process over waste materials

Ng Hou Kit [1], Tony Hadibarata [1,*], Adhi Yuniarto [2], Ajeng Arum Sari [3]

[1] Department of Environmental Engineering, Faculty of Engineering and Science, Curtin University, Malaysia, CDT 250, 98009 Miri Sarawak, Malaysia

[2] Department of Environmental Engineering, Faculty of Civil, Planning, and Geo-engineering, Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia

[3] Research Unit for Clean Technology, Indonesian Institute of Sciences, Jalan Cisitu Lama, Komplek LIPI Gedung 50, Bandung 40135, Indonesia

*corresponding author e-mail address: ***hadibarata@curtin.edu.my*** | Scopus ID 16233109100

ABSTRACT

Water pollution is the most significant issue due to rapid growing industrial development especially textile dye industry. Therefore, the adsorption process experiment was conducted to determine the removal ability of the adsorbent chosen. The removal rate and adsorption capacity of Phenol red and Cresol were analyzed by using eggshell adsorbent in the adsorption process. The experiment was conducted with parameters of initial concentration, dosage, pH and contact time. Results indicated that the removal rate achieved more than 90% and the adsorption capacity exceeded more than 5 mg/g. The functional group before adsorption process eggshell adsorbent and after adsorption process eggshell adsorbent was analyzed by using FTIR (Fourier Transform Infrared Spectroscopy). The study of adsorption isotherm and kinetics model was carried out to identify the efficiency of the eggshell adsorbent reacting with the dye solution. The adsorption isotherm that applied in this research was Langmuir isotherm, Jovanovic isotherm and Freundlich isotherm. Moreover, Pseudo-first-order and Pseudo-second-order chosen were conducted to determine the kinetic studies. In short, eggshell adsorbent is highly effective on dye removal through adsorption capacity. The functional group of the eggshell adsorbent was found such as alcohols, phenol, alkanes, carbonyls, ester, saturated aliphatic, aldehydes, aromatics, 2°amines and phosphorus. For kinetics study, Freundlich isotherm was analyzed as the best fit isotherm model as it achieved the highest R2 value which is closed to 1 and Pseudo-second-order was analyzed as the best fit kinetic model in this experiment. Therefore, eggshell adsorbent is highly effective in dye removal.

Keywords: *triphenylmethane, Langmuir, Jovanovic, Freundlich, eggshell.*

1. INTRODUCTION

Water pollution is a tremendous issue that is concerning developing modern society. The global demand for needs drives the development in industries and agriculture activities which bring consequence of generating pollutants that are toxic to the environment such as polycyclic aromatic hydrocarbons, pesticide, and synthetic dyes [1-4]. For instance, dye from textile industry plays a main contribution to water pollution as the dye effluent did not undergo treatment before discharge. Dye industry pollution is the best example that classified as point source pollution. The amount of water consumption that dyeing industry takes up produces huge amount wastewater or effluent that contains highly toxic content of chemicals and coloring compounds which cause pollution to water. The color compound in the dye effluent is visible when it is contacting with water despite the color compound in the dye effluent is low in concentration [5-7]. The high toxicity of the dye effluent is harmful to the aquatic organisms and the quality of the water will be affected. Hence, it is important to manage the wastewater by conducting wastewater treatment process before proceeding to discharge. Dyes and pigment are widely being used in the industry to manufacture the products that commonly used by human. Most of the colored products and material that produced involve in using dye and pigments. The application of the usage of synthetic dye in the fabric and textile industry was broadly been adapted due to the advantages of production in bright colors and easy application with low costing. The application of synthetic dyes are formed and applied in aqueous solution so that a mordant to occur a better fastness of the dyes on fabrics and textile [6,8-10] .

The physical treatment methods in treating dye wastewater effluent are conventionally adapted. One of them is the membrane-filtration processes which involve in reverse osmosis, nano-filtration and electrodialysis for adsorption techniques [11-14]. It was found that the membrane-filtration processes are constructive and fulfilling the satisfactory for the adaptation of it. However, there are drawbacks to this method. The issue is addressed that the treated effluent is hardly to discharge directly into the water resources as the small dissolved solids forms an accumulation in the treatment which is harmful. Besides, the lifespan of the membrane filter is limited as it could cost more in maintenance by replacing the membrane filter regularly [15,16]. Based on research that carried out, the relationship between membrane-filtration process and adsorption is effective as adsorption process and the equilibrium processes performed an effective way to remove dye effluent. Additionally, the process of adsorption does not involve external additional chemical substances throughout the process. To the extent of that, with proper methodology of the adsorption process and low cost adsorbent that is easy to obtain, it will bring an outcome in producing the optimum result of treated effluent. Waste materials defined as unwanted or unusable materials which discarded after the primary usage which makes it worthless. Most of the waste materials ended up in landfills especially the eggshells. The amount of eggs been used is tremendous in food manufactures and food industry which end up a huge eggshell wastes produced. The findings were reported that approximately 250,000 tonnes of eggshell produced annually as waste globally which mostly ended up in the landfills [16-18]. Reports showed that 20% of all egg products sent to commercial breaking operations to manufacture egg related products. The eggshell by-product was caused by the breaking operation which indicates a substantial waste for processing industry. Due to high nutrition contents of calcium, magnesium and phosphorus, some percentage of the eggshell are reused as fertilization [18,19].

There are many research done in the past to determine the potential of waste materials as alternative adsorbents to replace activated carbon, up to now not much efforts was made to analyze the poultry by-products which is eggshell waste in terms of removal rate, adsorption capacity, isotherm and kinetic studies. In addition, least attention was paid in the process of adsorption to remove the pollutants from dye mixtures despite the industrial dye effluents contained pollutants [20]. Therefore the eggshell was chosen as adsorbent for this research as it is considered low cost and economical with minimum processing and widely abundant to the nature as it commonly becomes as a waste generated from the industry.

The aim of this study was to apply eggshell waste as potential adsorbent to adsorb the triphenylmethane red phenol red and cresol red. Various parameters condition on the adsorption, adsorption isotherm, kinetic studies and chemical characteristic were also being examined.

2. MATERIALS AND METHODS

2.1. Chemicals and materials.

The highest available grade of phenol red and cresol red was obtained from Sigma-Aldrich (Milwaukee, USA). All solvent used in this experiment was high purity and purchased from Qrec (New Zealand). The stock dye solution was prepared by adding 1 gram of dyes powder of each Phenol red and Cresol red with 1000ml of distilled water. The prepared stock dye solution is then kept at room temperature for further procedures. Table 1 shows the properties of phenol red and cresol red. A set of stock dye solution with different concentration was prepared in advance before proceeding to conduct the experiment. The eggshell as an adsorbent was prepared by washing with distilled water to get clean any leftovers on the surface of the waste material to ensure the cleanliness of the adsorbent. The adsorbent was put in the oven with 105 °C for 24 hours to remove the moisture or until completely dried. The dried adsorbent was ground in the blender to form fine powder. The adsorbent powder was stored in a separated container and kept at an enclose place with room temperature.

2.2. Adsorption experiment.

Adsorption experiment was conducted by preparing 0.5g of adsorbent with 50 ml dye into the 100-ml conical flask. The aluminum foil was used to cover each top of the conical flask to prevent any dust particles to pollute the solutions. All conical flasks were put on to the rotary shaker with agitated speed of 150 rpm at room temperature. After filtration using Whatman filter paper, the dye removal was analyzed by UV-Vis spectrophotometer (Perkin Elmer Lambda Bio+) at λ_{max} 365nm (phenol red) and λ_{max} 367nm (cresol red). The formulas for both adsorption capacity and the percentage rate on removal for each sample are shown below:

$$\text{Removal rate (\%)} = \frac{Co - Cx}{Co} \times 100$$

$$\text{Adsorption capacity } \left(\frac{mg}{g}\right) = \frac{Co - Cx}{M} \times V$$

where M indicates the mass of adsorbent used, V is the dye solution volume used, C_o indicates the concentration of the dye solution and C_x indicates the dye solution concentration after adsorption process. Various experimental parameters were summarized in Table 2.

2.3. Isotherm and kinetic studies.

Adsorption isotherm and kinetics models are mathematical equation that performed to indicate the efficiency of the adsorbents that interacting with the dye solution by optimizing the surface characteristics, adsorption capacity and the effectiveness towards adsorption system. Furthermore, for kinetics models, the effect of contact time with the range of 10 to 50 minutes was calculated towards the rate of removal on dye. Moreover, three adsorption models, Langmuir, Jovanovic and Freundlich isotherm was selected in this study while pseudo-first-order and pseudo-second order were analyzed for kinetic studies.

Langmuir isotherm is to calculate the surface coverage by complementary the relative rates of adsorption and desorption. The Langmuir equation is written in linear form:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m}$$

where C_e is the concentration of adsorbate at equilibrium (mg/g), q_e is the amount of the adsorbate at equilibrium, q_m is maximum adsorption capacity, and K_L is Langmuir rate constant (mg/g).

Jovanovic isotherm is to analyze the probability of the mechanical contacts among the adsorbate and adsorbent. The Jovanovic isotherm is written in linear form:

$$\ln q_e = \ln q_{max} - K_J C_e$$

where q_e is the amount of adsorbate at equilibrium (mg/g), q_{max} is the adsorbate maximum uptake from plot ln q_e versus C_e, K_j is the Jovanovic constant, and C_e is the adsorbate concentration at equilibrium (mg/g)

Freundlich isotherm applies to the adsorption processes that happen on the heterogonous surfaces. The equation is written below:

$$log\ q_e = log\ K_F + \frac{1}{n}\ log\ C_e$$

where K_F is the adsorption capacity (L/mg), q_e is the amount of adsorbate at equilibrium (mg/g), C_e is the adsorbate concentration at equilibrium (mg/g), and 1/n is the adsorption intensity

For kinetic models, the adsorption process was analyzed with the pseudo-first-order and pseudo-second-order as follows:

Pseudo-first-order : $\ln(q_e - q_t) = \ln q_e - K_1 t$

Pseudo-second-order : $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$

Where q_e is the amount of the adsorbate at equilibrium (mg/g), q_t is maximun uptake of adsorbate from plot ln q_e versus C_e, K_1 is the pseudo-first-order rate constant, k_2 is the pseudo-second-order rate constant, and t is the contact time with adsorbent (min).

2.4. FTIR.

An analysis to determine the functional group of the raw adsorbents and adsorbents after decoloring Phenol red and Cresol red was conducting by using Fourier Transform Infrared Spectroscopy (FTIR) (Spectrum one, Perkin Elmer, USA) recorded in the spectral range of 400-4000 cm^{-1}.

Table 1. Physical and chemical characteristics of CV and PR.

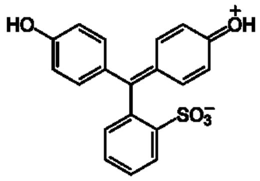
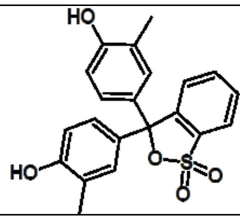
Properties	**Physical-chemical**	
Name	Phenol Red	**Procion Red MX-5B**
Structure		
Molecular formula	$C_{19}H_{14}O_5S$	$C_{21}H_{18}O_5S$
Appearance	Red Powder	Red Powder
Molecular weight	354.38 g/mole	382.43g/mole
Melting point	205 °C	300ºC
Absorption, λ_{max}	590 nm	538 nm

Table 2. Summarizes for all experiments of batch adsorption.

Parameters	**Initial pH**	**Dosage (g)**	**Time (min)**	**Initial Concentration (mg/L)**	
				PR	**CR**
Effect of Initial pH	3 – 11	0.5	240	30	30
Effect of Dosage	7	0.1 - 0.5	240	30	30
Effect of Contact Time	7	0.5	10 - 50	30	30
Effect of Initial Concentration	7	0.5	240	10-50	10-50

3. RESULTS

3.1. Absorption experiment.

The adsorption of phenol red and cresol red with effect of initial concentration, dosage, pH and contact time is shown in Figure 1. The first parameter of the experiment was initial concentration (Fig. 1A). The dye removal rate was determined by conducting with a different initial concentration of 10mg/L, 20mg/L, 30mg/L, 40mg/L and 50mg/L for both phenol red and cresol red. The constant variables for this experiment were fixed at 0.5g of eggshell adsorbent correspondingly, room temperature at ±27°C, a contact time of 240 minutes, dye pH were set at pH 7 and with an agitation speed of 150rpm. The results significantly indicated that the rate of removal decreases when the initial concentration is higher. In this experiment, the graph trend occurred as inversely proportional for both Phenol red and Cresol red as the initial concentration increases, the dye removal rate decreases.

The highest removal rate for Phenol red was achieved at 85.16% with the initial concentration of 10mg/L and the lowest removal rate for Phenol red was achieved at 63.55% with the initial concentration of 50mg/L. Besides, the highest removal rate for Cresol red was achieved at 67.36% with initial concentration of 10mg/L and the lowest removal rate for cresol red was achieved at 51.37%.

Furthermore, the trend for adsorption capacity appeared to be directly proportional to both phenol red and cresol red as the adsorption capacity increases along with the initial concentration. The highest adsorption capacity for phenol red was achieved at 6.67 mg/g and the lowest adsorption capacity for Phenol red was 1.72mg/g. Moreover, the highest adsorption capacity for cresol red was as high as 5.39mg/g and the lowest adsorption capacity for cresol red was at 1.36mg/g. The effectiveness of the eggshell towards Phenol red was higher compared to cresol red as the overall removal rate and adsorption capacity for phenol red is higher than cresol red. Based on the trend indicated, the removal rate decreases as the initial concentration increases because the adsorbent achieved at the range of maximum adsorption capacity when reacting in the dye solution [21-23].

Despite high concentration solution reduces the removal rate of the dye solution, the adsorption capacity increases continuously due to the ratio of dye particles and the surface of the adsorbent are relatively low in higher concentration solution which resulted least chances that the dye particles attached to the adsorbent during adsorption process [24,25].

The effect of the eggshell dosage was clearly shown in Figure 1B. This figure indicated the effectiveness of the removal rate for phenol red and cresol red with different dosage of eggshell adsorbent. The highest removal rate for Phenol red was 80.03% and the lowest removal rate for Phenol red was 73.91%. For cresol red, the highest rate of removal was recorded at 76.20% whereas the lowest rate of removal was recorded at 61.76%. Both dyes achieved the highest removal rate at an eggshell dosage of 1.50g and the lowest removal rate at a dosage of 0.50g.

The relationship between the dosage of adsorbent and adsorption capacity was inversely proportional to both dye phenol red and cresol red. This can be explained when the dosage of eggshell increased, the adsorption capacity decreased. The highest adsorption capacity was calculated for Phenol red was 4.57mg/g with the least dosage of 0.5g whereas the lowest adsorption capacity was calculated as 1.65mg/g with 1.5g of dosage. Furthermore, the highest adsorption capacity for cresol red was calculated at 3.82mg/g with only 0.5g of dosage while the lowest adsorption capacity was calculated at 1.57mg/g with 1.5g of dosage. The effectiveness of eggshell reacting with phenol red is higher compared with cresol red. Generally, this can be explained that the dosage increment extended the surface areas of the adsorption resulted in a higher removal rate. The high availability of adsorption sites or pores for the dye particles caused a better result in color removal [26,27].

The effect of pH on the percentage of dye removal rate and adsorption capacity for both phenol red and cresol red was shown in Figure 1C. According to the result obtained, the dye removal rate decreased as the pH of the solution increased which the solution became more alkaline. The figure shows the effectiveness of the removal rate with different pH value for phenol red and cresol red. In this experiment, the relationship between the pH and removal rate was inversely proportional as it can be explained that when the pH value increased, the removal rate for both dyes decreased. The highest removal rate for phenol red was recorded at 84.53% which the solution is acidic at pH 3 whereas the lowest removal rate was obtained at 38.87% which the solution is alkaline at pH 11. Moreover, the highest removal rate for cresol red was achieved as high as 91.28% at acidic condition of pH 3 in the treated solution while the lowest removal rate was 31.88% at alkaline condition of pH 11 in the treated solution. Both of the dye achieved the highest removal rate at acidic condition and lowest removal rate at alkaline condition.

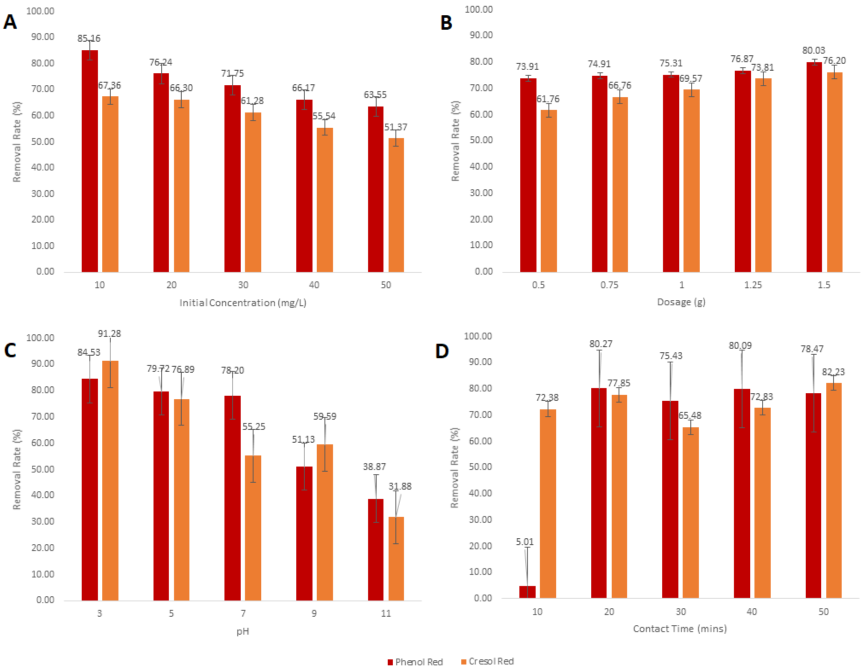


Figure 1. Effect of some parameter on adsorption of phenol red and cresol red by eggshell: Initial concentration (A), adsorbent dosage (B), pH (C), contact time (D).

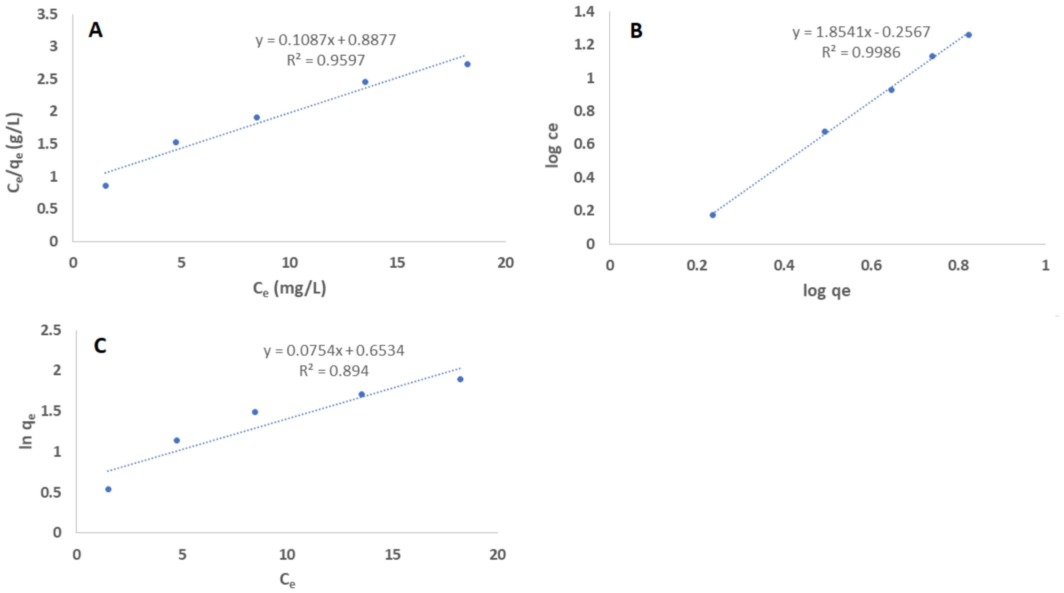


Figure 2. Isotherm studies of phenol red adsorption on eggshell: Langmuir (A), Freundlich (B), Jovanovic (C).

The trend of the adsorption capacity indicated as inversely proportional for both Phenol red and cresol red as the treated solution increased from acidic to alkaline, the adsorption capacity decreased. According to the result, the highest adsorption capacity was calculated in phenol red as 5.22mg/g which was the solution in acidic condition of pH 3 while the lowest adsorption capacity was calculated as 2.40mg/g at the alkaline condition of pH 11. For cresol red, the highest adsorption capacity was calculated as 5.641mg/g at the condition of acidic of pH 3 whereas the lowest capacity was calculated as 1.97mg/g at the alkaline condition of pH 11. In addition, the effectiveness of the eggshell reacting in both dyes, cresol red indicated more effective compared with phenol red.

The overall removal rate and adsorption capacity of cresol red are higher than phenol red. The trend of pH indicates that removal rate is higher at acidic solution and lower in alkaline solution. This can be explained as the electrostatic attraction in acidic solution increases due to the interactions between the adsorbent with positive charged and the negative charged of the dye particles [7,28]. Nevertheless, a high concentration of negative charged sites in alkaline solution contains excessive OH^- ions which caused the highly negative charged adsorbent reacting less effective in adsorption process due to strong electrostatic repulsive forces that exist [29]. Therefore, it can be concluded that adsorption process performed effectively in acidic solution compared with alkaline solution.

The effect of contact time on the percentage of dye removal rate and adsorption capacity for both phenol red and cresol red was shown in Figure 1D. Based on the result obtained in phenol red, removal rate was 5.01% at contact time of 10 minutes and drastically increased to 80.27% at the contact time of 20 minutes. The removal rate decreased at contact time of 30 minutes at 75.43% and increased to 80.09% after that. At contact time of 50 minutes, the removal rate decreased slightly to 78.47%. The highest removal rate was 80.27% at the contact time of 20 minutes and the lowest removal rate was 5.01% at a contact time of 10 minutes.

Furthermore, the rate of removal for cresol red achieved 72.38% at the contact time of 10 minutes and increased to 77.85% at the contact time of 20 minutes. The removal rate decreased to 65.49% at contact time of 30 minutes and increased steadily to 72.83% and 82.23% at contact time of 40 minutes and 50 minutes. The highest removal rate was achieved at 82.23% at contact time of 50 minutes whereas the lowest removal rate was 65.48% at contact time of 30 minutes because the eggshell had achieved an equilibrium state at contact time of 20 minutes for phenol red and contact time of 10 minutes for Cresol red. This indicated that at equilibrium state, the maximum availability of the adsorbents attached to the dye particles on the binding sites were not much adsorption process on-going [9, 30]. The trend of the adsorption rate for both Phenol red and cresol red was similar to the removal rate. The highest adsorption capacity for phenol red was calculated as 4.96mg/g at contact time of 20 minutes and the lowest adsorption capacity was 0.31mg/g at contact time of 10 minutes. For cresol red, the highest adsorption capacity was 5.08mg/g at contact time of 50 minutes and the lowest adsorption capacity was 4.05mg/g at contact time of 30 minutes.

3.2. Adsorption isotherms and kinetics parameters.

The adsorption isotherms parameters were conducted to analyze the interaction between the eggshell adsorbents and both phenol red and cresol red dyes. When the interaction between both dyes and eggshell achieved at equilibrium state, the adsorption isotherms were performed in order to analyze the mechanism of the adsorption response. Langmuir isotherm, Jovanovic isotherm and Freundlich isotherm were used as the application for this research. Langmuir isotherm was performed to find the differences and to compute the adsorption capacity of the adsorbent. Jovanovic isotherm was performed to analyze the mechanical contacts among adsorbate and adsorbent. Freundlich isotherm was applied to determine the surface heterogeneity and distribution of the adsorbent's active site [31].

Figure 2 and 3 shows the adsorption isotherm parameters for phenol red on eggshell adsorbent. By comparing the result analyzed, the Freundlich isotherm model was the best fitted to the adsorption data. The R^2 value of the Freundlich isotherm for both dyes was 0.9986 and 0.9746 which the values were closed to 1 compared to Langmuir and Jovanovic isotherms. In certain condition, if the 1/n value is less than 1 which is indicate a nature adsorption, every time the value is near to zero it will become heterogeneous, and value of 1/n exceeding one referring to cooperative adsorption process [32]. From the straight line equation in Figure 2 and 3 indicated Freundlich isotherms of Eggshell for phenol red cresol red, the value 1/n exceeded one, therefore it is indicated as cooperative adsorption. The best fitted adsorption isotherm would be different from other research as the composition of adsorbents reacting with different dye may vary the result.

Table 3 shows the adsorption kinetics for Pseudo-first-order and Pseudo-second order of both phenol red and cresol red. For Pseudo-first-order, the linear plot was plotted in a graph of ln $(q_e\text{-}q_t)$ against t whereas the linear plot was plotted in a graph of t/q_t against t for Pseudo-second-order. The kinetics parameter for Pseudo-first-order and Pseudo-second order were analyzed from the straight line equation from the plotted graph. Based on the result analyzed, Pseudo-second order was the best fitted for eggshell adsorbent compared with Pseudo-first-order. The R^2 value in Pseudo-second-order achieved 0.9611 and 0.3039 compared with Pseudo-first-order which only achieved 0.415 and 0.0647. Hence, it can be concluded that Pseudo-second-order is the best fitted as adsorption kinetics on removal of phenol red and cresol red using the eggshell as adsorbent.

3.3. FTIR (Fourier Transform Infrared Spectroscopy).

The functional groups and the bonding groups of the raw adsorbent and the adsorbent after adsorption process were analyzed with the usage of FTIR. The range of the infrared spectrum that can be obtained by FTIR is between 400-4000 cm^{-1}. Generally, the infrared adsorption spectrum generated by FTIR able to characterized the chemical bonds on the surface of the adsorbent. Table 4 shows the FTIR spectrum for functional group and the bond of raw eggshell and eggshell after phenol red and cresol red adsorption. The raw eggshell achieved a peak at 3272.75 cm^{-1} and change slightly to 3326.65 cm^{-1} after phenol red adsorption and to 3365.79 cm^{-1} after cresol red adsorption. The peaks corresponded to the alcohols and phenol functional group with the bond of O-H (stretch). The second peak for the raw eggshell was found at 2922.23 cm^{-1}. It experienced an insignificant shift to 2918.51 cm^{-1} after undergoing phenol red adsorption and to 2924.10 cm^{-1} after cresol red adsorption.

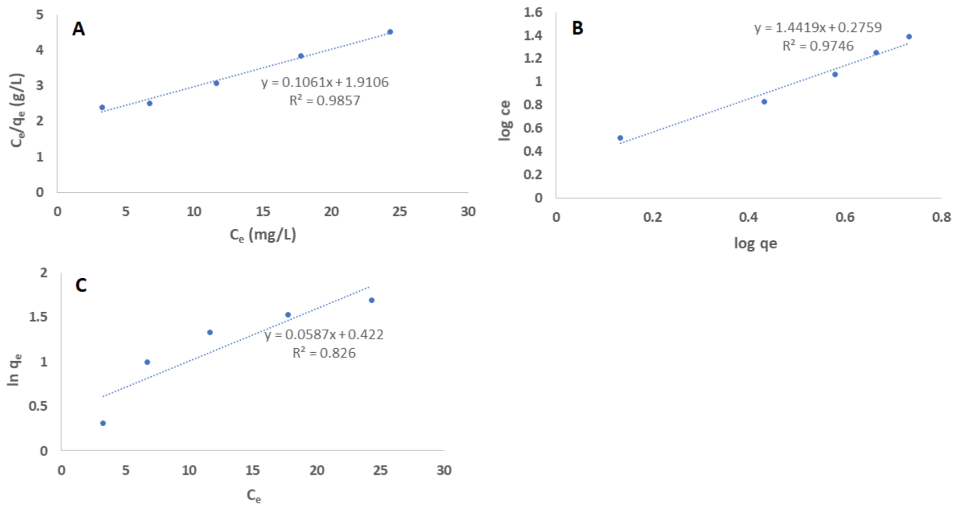


Figure 3. Isotherm studies of cresol red adsorption on eggshell: Langmuir (A), Freundlich (B), Jovanovic (C).

Table 3. Kinetic parameters for phenol red and cresol red adsorption on eggshell.

Adsorption Kinetics	Adsorption constant	Phenol Red	Cresol Red
Pseudo-1st Order	$q_{e\ calculated}$	2.4650	1.56534
	k_1	0.056	0.0095
	R^2	0.415	0.0647
Pseudo-2nd Order	$q_{e\ calculated}$	2.5069	5.015045
	k_2	0.016486	0.37952
	R^2	0.3039	0.9611

Table 4. FTIR spectral characteristics of phenol red and cresol red adsorption on eggshell.

Eggshell frequency (cm^{-1})			Assignment	Functional Group
Raw	Adsorption of PR	Adsorption of CR		
3272.60	3326.65	3365.79	O–H stretch	Alcohol, phenol
2922.23	2918.51	2924.10	C–H stretch	Alkanes
1636.30	1648.40	1638.16	C=C stretch	Carbonyls, ester, saturated aliphatic, aldehydes
1397.75	1404.50	1390.30	C–C stretch	Aromatic
872.20	881.30	878.45	C–H bending	Alkanes
711.92	707.68	713.63	N–H bending	2°amines
669.06	683.97	674.56	P=S stretch	Phosphorus

The peaks were attributed to C-H (stretch) which is categorized as alkane functional group. This is representing that organic layers are existing which is built from amino acids in the eggshells. The next peak was visible at a frequency of 1636.30 cm^{-1} at raw eggshell. After Phenol red adsorption, the peak achieved at a frequency of 1648.40 cm^{-1} and another peak achieved at a frequency of 1638.16 cm^{-1} after cresol red adsorption. The three peaks at this range are parallel to the C=C (stretch) under the functional group of carbonyl, ester, saturated aliphatic and aldehydes. An intense peak was observed at the frequency of 1397.75 cm^{-1} for raw eggshell. The frequency shifts to 1404.50 cm^{-1} after Phenol red adsorption and shift to 1390.30 cm^{-1} after Cresol red adsorption. The peak corresponded to C-C (stretch) which characterize as aromatics functional group. The intense peak appeared as it is highly affiliated with the occurrence of carbonate mineral in the eggshell matrix [33, 34]. A moderate peak was observed at the frequency of 872.20 cm^{-1} for raw eggshell. After Phenol red adsorption, the frequency shifts to 881.30 cm^{-1} whereas after Cresol red adsorption, the frequency changed to 878.45 cm^{-1}. The function group of this peak is alkanes with the bond of C-H (bend). This can be explained as the deformation of in-plane and out-plane which indicating the existence of calcium carbonate ($CaCO_3$). The eggshell as adsorbent interacted with the dye solution correlated with the carbonate group that existing in the spectrum [24, 33-34].

Moving to another peak, it was observed that a raw eggshell at a frequency of 711.92 cm^{-1} shifted to frequency of 707.68 cm^{-1} after Phenol red adsorption and 713.63 cm^{-1} after the adsorption of Cresol red. This peak can be categorized as the 2°amines functional group with N-H (bend). Lastly, a small peak is appeared and observed in raw eggshell at the frequency of 669.06 cm^{-1}. The frequency changed to 683.97 cm^{-1} after Phenol red adsorption and the frequency of 674.56 cm^{-1} was noticeable after the adsorption of Cresol red. The functional group was phosphorus with the bond of P=S (stretch). This can be concluded that the functional group of alcohols, phenol, alkanes, carbonyls, ester, saturated aliphatic, aldehydes, aromatics, 2°amines and phosphorus are capable in removing the pollutants, especially in color dye.

4. CONCLUSIONS

The eggshell waste had a potential ability as adsorbent to adsorb the triphenylmethane red phenol red and cresol red. Several impact factors like pH, dosage, contact time, and initial concentration were optimized. Adsorption of phenol red was found higher than cresol red on eggshell. Freundlich isotherm model described the adsorption results with high correlation co-efficient R^2 equal to 0.9986 and 0.9746 for phenol red and cresol red. On the other hand, pseudo-second-order model provides R^2 value equal to 0.9611 and 0.3039 for phenol red and cresol red.

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