Isotherm and Kinetic Studies on the Adsorption Behavior of Metanil Yellow Dyes onto Modified Shrimp Shell-Polyethylenimine (SS-PEI)

Rahmiana Zein[1*], Zulkarnain Chaidir[1], Zilfa Zilfa[1], Syiffa Fauzia[2], Putri Ramadhani[1]

[1]Department of Chemistry, Faculty of Mathematics and Natural Science, Andalas University, Limau Manis, Pauh, Kota Padang, Sumatera Barat 25163 Indonesia

[2]Research Center for Chemistry, National Research and Innovation Agency of Republic of Indonesia, Jakarta, 10340 Indonesia

Corresponding author: rzein@sci.unand.ac.id or mimiedison@yahoo.co.id

Abstract

The present study investigated the ability of modified shrimp shells by Polyethylenimine (PEI) for enhanced removal of metanil yellow. The modification was carried out using citric acid as a crosslinker. The removal of metanil yellow by modified shrimp shell-PEI was conducted by batch method and investigated some parameters that affected adsorption, including pH, initial dye concentration, and contact time. The optimum conditions were achieved at pH 5, an initial dye concentration of 1200 mg/L, and a contact time of 90 minutes. The adsorption isotherm study showed that the adsorption of metanil yellow dye by modified shrimp shell-PEI followed the Langmuir isotherm model with a maximum adsorption capacity (q_m) of 121.951 mg/g. The kinetic study indicated that the adsorption process suited the pseudo-second-order model. The characterization results revealed the differences in the adsorbent characteristics before and after the adsorption of metanil yellow dye. The cross-linked PEI onto shrimp shell provided more active sites (amine groups) to bind dye molecules. It can be concluded that modified shrimp shell by PEI has increased its ability in metanil yellow removal.

Keywords: Adsorbent, Metanil yellow, Modification, Polyethylenimine, Shrimp shell.

1. INTRODUCTION

The presence of synthetic dyes in the water bodies originating from textile industry activities is a challenge for the government and researchers to solve these problems. Disposal of dye wastewater into the environment will threaten the ecosystem because it is resistant to aerobic degradation, not sensitive to light and heat, and cuts-off sunlight penetration for the photosynthesis process of aquatic plants. Further impacts cause skin irritation, cancer, and genetic disorders in humans and other living things (Niero et al., 2019).

Metanil yellow is an anionic dye with 377.39 g/mol molar mass. This dye was generally applied as leather dyes, varnishes, waterproof inks, and textiles. The presence of metanil yellow dye in waters harms the ecosystem even in low concentrations. Dye wastewater treatment can be carried out through several methods such as electrocoagulation, chemical precipitation, anaerobic reduction, membrane filtration, photodegradation, and adsorption (Simi et al., 2014; Zilfa et al., 2018; Sadik, 2019). The adsorption process was considered valuable compared to other methods because it was easier to use, short-time operation, and environmentally friendly. It employed natural materials such as organic solid waste to reduce costs and make it easy to regenerate.

Several studies were reported regarding the use of organic solid waste as dye adsorbent, such as water hyacinth (Guerrero-Coronilla et al., 2019), Ketapang shells (Hevira et al., 2021), shrimp shells (Ramadhani et al., 2020), activated carbon from white teak bark (Isiuku, 2017), silica-BSA (Zein et al., 2020), activated carbon from snail shells (Ikhazuangbe et al., 2017), rambutan seeds (Zein et al., 2015), soursop seeds (Fauzia et al., 2015), peanut shells (Nurhasni et al., 2018), activated carbon from oak leaves (Sulyman et

al., 2014) and durian seeds (Chaidir et al., 2015). However, the adsorption capacity was still low, below 100 mg/g. Previous studies have reported using shrimp shells activated with 0.01 M HNO_3 as a biosorbent for metanil yellow dye with an adsorption capacity of 69.307 mg/g (Ramadhani et al., 2020). For this reason, it is necessary to make further efforts to increase the ability of the adsorbent to adsorb dyes.

The high levels of consumption of seafood such as shrimp, crab, and shellfish produce by-products in the form of shells which can cause environmental problems. The accumulation of waste affects the environmental aesthetic value. The abundant resources make the shrimp shell a promising adsorbent for dye removal. The modification of primary materials from organic solid waste into other forms will increase the ability and value of these materials, such as by adding functional groups or active sites to solid materials and linking the molecular chains to each other (Kyzas et al., 2015). This modification can increase the ability of the adsorbent compared to the adsorbent without modification.

Several studies on adsorbent modification have been reported, one of which was used polyethylenimine as a modifier (Zhang et al., 2016; Wong et al., 2019). Polyethylenimine is a polymer containing primary (25%), secondary (50%), and tertiary (25%). The PEI, an amine-rich group, makes this compound have a strong anion exchangeability under various conditions (Santos et al., 2017). The presence of the amine group in PEI will be advantageous if it is used as a shrimp shell modifier to increase the adsorption capacity of metanil yellow dye through electrostatic interaction. Thus, in this study, shrimp shell waste (SS) was modified with polyethylenimine (PEI) to induce the amine functional groups (functionalization) in shrimp shells. The novelty in this research was acquiring a new adsorbent with a higher adsorption capacity than in the former study (shrimp shell q = 69.307 mg/g), as reported by Ramadhani et al. (2020). In this research, citric acid was also used as a crosslinker between functional groups in shrimp shells and PEI to increase the stability of the adsorbent. This paper will discuss the ability of SS-PEI as an adsorbent for metanil yellow dye sorption in a batch system. The characterization of the adsorbent before and after adsorption was characterized using Fourier Transform Infra-Red (FTIR) and Scanning Electron Microscopy Energy-Dispersive X-ray (SEM-EDX). The adsorption equilibrium test was analyzed using the Langmuir and Freundlich isotherm model. The adsorption kinetics was studied using the Pseudo-first-order and Pseudo-second-order kinetics models.

2.   MATERIALS AND METHODS
Materials
The materials used in this study were shrimp shells (*Metapenaeus monoceros*) was obtained from Padang, West Sumatera, metanil yellow (MY) dye, aquadest, HNO_3 (Merck), NaOH (Merck), Citric Acid ($C_6H_8O_7$) (Merck), polyethylenimine (PEI) (Sigma Aldrich), and filter paper (Whatman 42).

Equipments
The equipment used in this study were analytical balance (Kern & Sohn GmbH), pH meter (Metrohm), rotary shaker (Edmun Buhler 7400 Tubingen), crusher (Fritsch, Germany), mortar grinding (Fritsch, Germany), and glassware was used in the laboratory. The sample analysis equipment is Fourier Transform Infrared (FTIR) (Unican Mattson Mod 7000 FTIR), Scanning Electron Microscopy Energy-Dispersive X-ray (SEM-EDX) Hitachi S-3400N, United Kingdom), UV-Vis Spectrophotometer (Genesys 20 Thermo Scientific).

FTIR evaluated the functional groups present in the adsorbent. Meanwhile, the morphology was studied using SEM-EDX. The FTIR test was carried out by inserting the sample into the sample holder, and then it was analyzed. The SEM-EDX test placed the adsorbent powder into the sample holder and coated it with Au through the sputtering method. After that, the samples were placed in the SEM-EDX tool to observe the morphology.

Pretreatment of shrimp shells
The shrimp shells were first cleaned to remove the remaining dirt and flesh, then washed several times with tap water. The cleaned shrimp shells were air-dried, then crushed with a grinder, and then sieved 160 μm. Furthermore, the shrimp shells powder was activated by soaking the shrimp shells in 0.01 M HNO_3 (ratio, 1:3) for 3 hours. After that, it was washed with distilled water until the pH was neutral, then filtered and air-dried.

The activated shrimp shell is ready to be modified with Polyethylenimine (PEI) (Suhaili et al., 2016).

Modification of Shrimp Shell with Polyethylenimine (SS-PEI)

4 grams of activated shrimp shell were soaked and stirred in 100 mL of 4% PEI for 24 hours. Then, 200 mL of 1% citric acid was added to the mixture and let it sit for 30 minutes. The mixture was washed with 600 mL of distilled water, then air-dried. Then, it was ready to be used (Liu et al., 2011).

Determination of pHpzc of SS-PEI adsorbents

Determination of the pHpzc value was carried out by the solid addition method. The procedure was carried out by adding 0.1 grams of SS-PEI into 10 ml of 0.1 M KCl solution at a different pH (1-10). The final pH value was measured after stirring for 24 hours. The point of intersection of the pH versus ΔpH (pH$_f$ – pH$_i$) with the X-axis gives the zero charge point (pHpzc) (Reddy et al., 2012).

Batch study of adsorption metanil yellow by SS-PEI

The adsorption process was carried out using the batch method and investigated different parameters such as the effect of pH (3-8), initial concentration of dye (60-1600 mg/L), and contact time (15-120 minutes). The pH of the solution was adjusted by adding a solution of NaOH or HNO$_3$. For each variation in the pH of the dye solution, a buffer solution was added. The adsorption study was conducted by contacting 0.1 gram of SS-PEI with 10 mL of MY dye solution in Erlenmeyer with pH, concentration, and contact time by each test parameter. Then the mixture was stirred with a rotary shaker at 100 rpm. After reaching the specified stirring time, the mixture was filtered. The filtrate was analyzed by UV-Vis spectrophotometer (wavelength 435 nm) to determine the final concentration of MY dye. The adsorption capacity of the adsorbent (q, mg/g) was determined using the following equation:

$$q = \frac{(C_e - C_0)V}{m} \qquad (1)$$

where C_0 is the initial concentration of the dye (mg/L); C_e is the concentration of dye in equilibrium in solution (mg/L); V is the volume of the solution (L); m is the mass of the adsorbent (g) (Chaidir et al., 2015).

Adsorption Isotherm Study

The adsorption studies were executed using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) model. These models' approach can provide an overview of the distribution process of the adsorbate between the liquid phase and the solid phase. In addition, this modeling can give information about the adsorption process that occurs in equilibrium at a constant temperature. The linear form of the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich adsorption isotherm model equation can be written as follows (Inyinbor et al., 2015; Iryani et al., 2017) :

$$\frac{1}{q_e} = \frac{1}{k_L q_m C_e} + \frac{1}{q_m} \qquad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (3)$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \qquad (4)$$

$$\ln q_e = \ln q_m - K_{DR} \, \varepsilon^2 \qquad (5)$$

$$E = \frac{1}{\sqrt{2 K_{DR}}} \qquad (6)$$

Where q_m is the maximum adsorption capacity of the adsorbent (mg/g); C_e is the final concentration of adsorbate at equilibrium (mg/L); q_e is the adsorption capacity of the biosorbent at equilibrium (mg/g); K_L is the constant of the Langmuir isotherm model (L/mg); K_F and n are Freundlich's constants; b is the Temkin constant (J/mol); K_T is a constant related to the foremost isotherm constant (L/mg); T is the temperature (K); R is the ideal gas constant (8.314 J/mol K); K_{DR} is a constant associated with the free energy of adsorption (mol^2/J^2); ε is the polyanion potential (J/mol); E is the free energy of adsorption per adsorbate molecule (kJ/mol).

Adsorption Kinetic Studies

The data related to the contact time between adsorbent and adsorbate were employed to study the adsorption kinetic using pseudo-first-order and pseudo-second-order. It is essential to analyze the adsorption kinetics

model to determine the appropriate experimental adsorption capacity (q_e) value. In addition, it can be predicted that the adsorption process occurs chemically or physically. The linear form of the pseudo-first-order and pseudo-second-order adsorption kinetics model equations can be written as follows (Naghizadeh et al., 2017):

$$-\ln (q_e-q_t) = k_1.t - \ln q_e \qquad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (8)$$

Where q_e is the optimum adsorption capacity, q_t is adsorption capacity at time t (minutes), k_1 is pseudo-first-order constant and k_2 is pseudo-second-order constant.

3. RESULT AND DISCUSSION
Characterization of SS-PEI Adsorbent

The characterization of the functional groups contained in the SS-PEI adsorbent before and after the adsorption of metanil yellow dye was analyzed using FTIR. The analysis was carried out in the range of wavenumbers 4000-400 cm^{-1}. The FTIR spectra of SS-PEI can be seen in Figure 1.
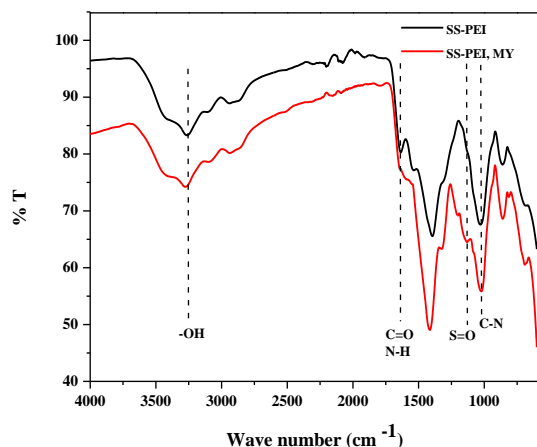

Figure 1. FTIR spectra of SS-PEI before and after metanil yellow adsorption

The peak in the range of 3000-3500 cm^{-1} indicated the presence of O-H. Peaks confirmed the N-H group at 1800-2239 cm^{-1} and 1631 cm^{-1} regions, which showed the presence of N-H bonds in NH$_2$. The appearance of a peak at 1386 cm^{-1} indicated the presence of C-H bonds in ethylene and methylene contained in the PEI structure. It

proved that the amino groups in PEI have been grafted onto the surface of the shrimp shells. The peak at 1030 cm^{-1} indicates a C-N group stretching, and the peak at 2800-2900 cm^{-1} region indicates a C-H stretching. After the adsorption process, there was a shift at the wavenumber, indicating an interaction between SS-PEI and metanil yellow dye. The disappearance of peaks at 1800-2239 cm^{-1} and 1630 cm^{-1} was evidence of the binding process of the metanil yellow anion by the amine group of PEI. Possible interactions that occurred on the surface of the adsorbent were through electrostatic interactions between protonated amine groups (NH$_3^+$) and metanil yellow dye anions in acidic conditions (D-SO$_3$-) (Chatterjee et al., 2011; Zhang et al., 2016). The peak at 1128.60 cm^{-1} can prove the presence of the S=O functional group originated from the metanil yellow dye structure (Berber-villamar et al., 2018; Nandiyanto et al., 2019).

The difference in the surface of the adsorbent before and after adsorption was analyzed by Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX). The results of the SS-PEI surface morphology analysis before and after adsorption were showed in the Figure 2.

The surface morphology of SS-PEI before adsorption (Figure 2 (a)) showed that SS-PEI had pores and a rough surface. These surface characteristics provided an excellent opportunity for the adsorption of metanil yellow dye on the surface of SS-PEI. It can be proven based on the results of the characterization of SS-PEI after the adsorption of metanil yellow dye, as shown in Figure 2 (b). The surface of SS-PEI after adsorption has a smoother texture and smaller pore size. The differences in the surface characteristics prove that metanil yellow dye has been adsorbed on the SS-PEI surface, causing the concentration of MY dye in the solution was decreased. The percentage of the dominant elements on the surface of SS-PEI before and after adsorption was indicated in Figure 2. The results of the EDX analysis showed that the dominant elements on the SS-PEI surface were C, O, Mg, P, and Ca. These elements were the main components in shrimp shells that played a role in adsorbing metanil yellow dye removal (Ramadhani et al., 2020).
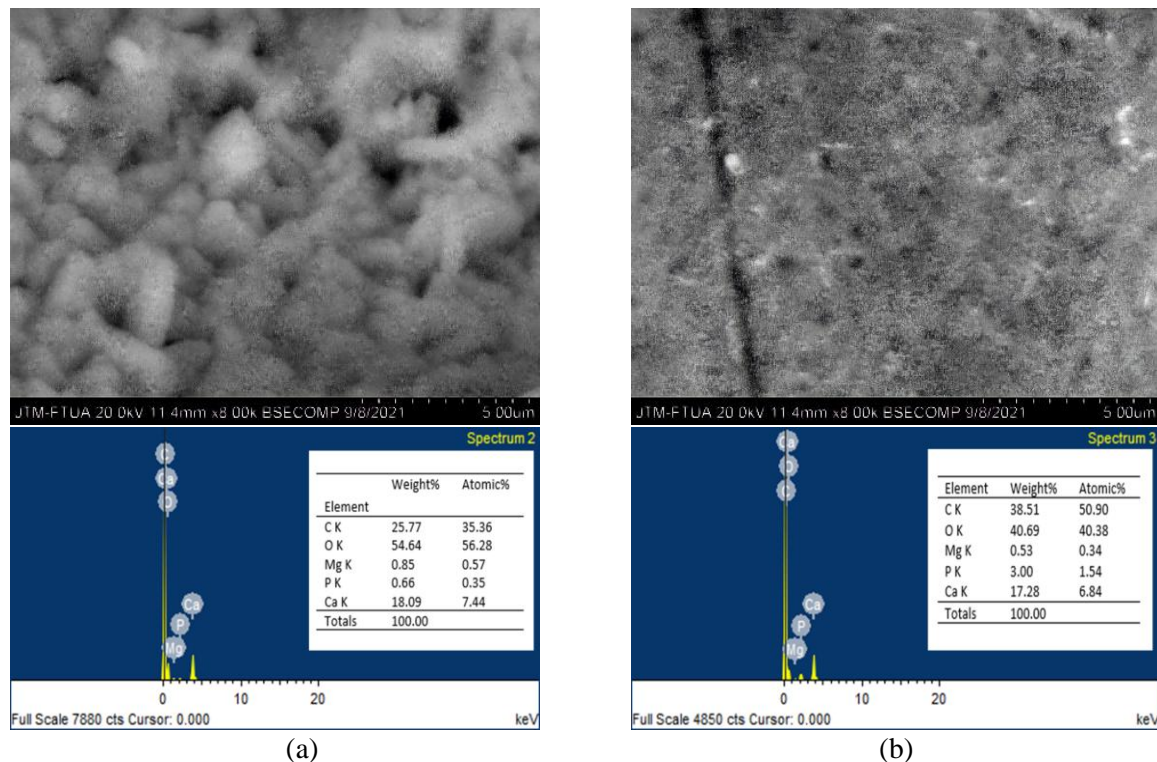
(a)　　　　　　　　　　　　　　　　　　　(b)

Figure 2. Surface morphology of SS-PEI before (a) and after adsorption (b) of metanil yellow dye

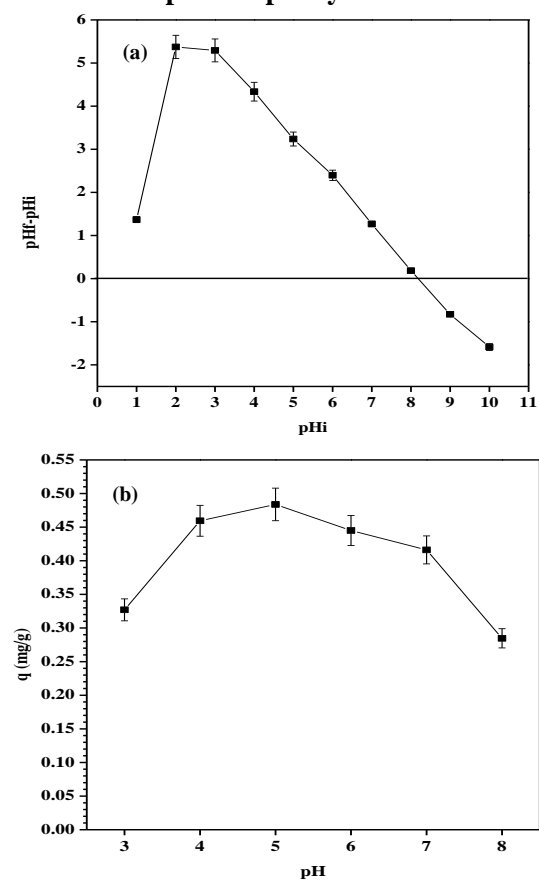## Analysis of pHpzc value and the effect of pH on the adsorption capacity

Figure 3. (a) pHpzc curve and (b) the effect of contact time on metanil yellow adsorption onto SS-PEI.

The advantages of the solid addition method are that it is fast and easy to operate (Bakatula et al., 2018). At the pHpzc value, the adsorbent surface has equal positive and negative charges. The pHpzc value can predict that the adsorption process will occur optimally in the appropriate pH range (Hevira et al., 2021).

The pHpzc of SS-PEI was obtained at pH 8.1 (Figure 3 (a)). When the pH value was lower than pHpzc 8.1, the surface of the adsorbent became positively charged. The low pH caused an increase in the amount of H+ on the surface of the adsorbent, which encouraged the adsorption of adsorbate anions through electrostatic interactions. Increasing the pH value (pH>pHpzc) caused the number of negative charges to increase, which caused electrostatic repulsion between similar ions, thus providing lower adsorption capacity. Based on the pHpzc value, it can be predicted that the adsorption process for metanyl yellow dye by SS-PEI will take place optimally at low/acidic pH. Ribeiro et al. (2015) have also reported the optimal adsorption of 5G reactive blue anionic dye at pH<7.6 (Ribeiro et al., 2015).

The pH effect on the adsorption capacity of metanil yellow was studied in the range of 3-8 (Figure 3 (b)). The optimum

condition was obtained at pH 5. This indicated suitability with the results of the determination of the pHpzc value. The pH condition of the acidic solution affected the protonation of the amine group in SS-PEI. The presence of a protonated amine group will encourage the electrostatic interaction of the positive charge of the amine with the negative charge of the sulfonate group on the metanil yellow dye molecule. The decreasing adsorption capacity with increasing pH indicated a competition between OH^- and the anion of metanil yellow dye on the active site of SS-PEI. In addition, increasing the pH of the solution can cause the deprotonation of the amine group so that its reactivity is reduced to bind the anion of the metanil yellow dye. The same result has been reported by Borhade & Kale, 2017 regarding decreasing the eggshell adsorbent's ability to adsorb Rhodamine B, Eriochrome black T, and Murexide dyes with increasing pH solution. (Borhade et al., 2017).

Effect of initial concentration on the adsorption capacity and adsorption isotherm study of metanil yellow by SS-PEI

The effect of dye concentration on the adsorption capacity of metanil yellow was studied in the concentration range of 60-1600 mg/L. The adsorption process was carried out at the optimum pH (pH 5), 0.1 gram mass, 60 minutes contact time, and 100 rpm stirring speed. The effect of the concentration of MY on the adsorption capacity of SS-PEI was indicated in Figure 4.
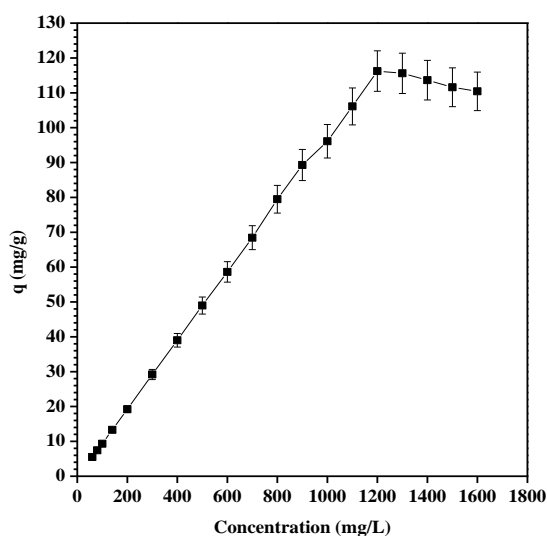

Figure 4. The effect of concentration on metanil yellow adsorption onto SS-PEI.

Figure 4 showed that the adsorption capacity of SS-PEI increased until the concentration of MY 1200 mg/L with an adsorption capacity of 116.23 mg/g. This increase in adsorption capacity was probably caused by the availability of active sites proportional to the amount of adsorbate, thereby increasing the interaction between SS-PEI and the anion of metanil yellow dye. The decrease in adsorption capacity after optimum conditions occurred due to the accumulation of dye molecules on the surface of the adsorbent so that the active site was saturated (Dawood et al., 2016). The same results have been reported by Dai et al. 2017 (Dai et al., 2017).

It was essential to study the isotherm model to predict the adsorption mechanism between the adsorbate and the adsorbent. Adsorption isotherms can explain how the distribution of adsorbate molecules on the adsorbent at equilibrium. The linear curves of the adsorption isotherm model are presented in Figure 5.

The adsorption isotherm model equations were used to obtain the regression equation's value and the coefficient of determination (R^2). The regression equation values were then analyzed to determine the parameters of the Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Temkin (Table 1) adsorption isotherm models related to the mechanism during the adsorption process.

The value of each parameter of the adsorption isotherm model (Table 1) was used to predict the adsorption mechanism during the process. The Langmuir isotherm model assumed that the adsorption process occurred on a homogeneous adsorbent surface, forming a monolayer (Uzunoğlu et al., 2016). Table 1 showed the coefficient of determination of the Langmuir isotherm model, which was R2 0.955, close to 1, indicating that the adsorption process followed the Langmuir model. The adsorption process of metanil yellow dye on the surface of SS-PEI can occur chemically by forming a monolayer layer on the surface of a homogeneous SS-PEI. The value of R_L ($0 < R_L < 1$) in this model can indicate that the adsorption process of metanil yellow dye by SS-PEI was favorable.
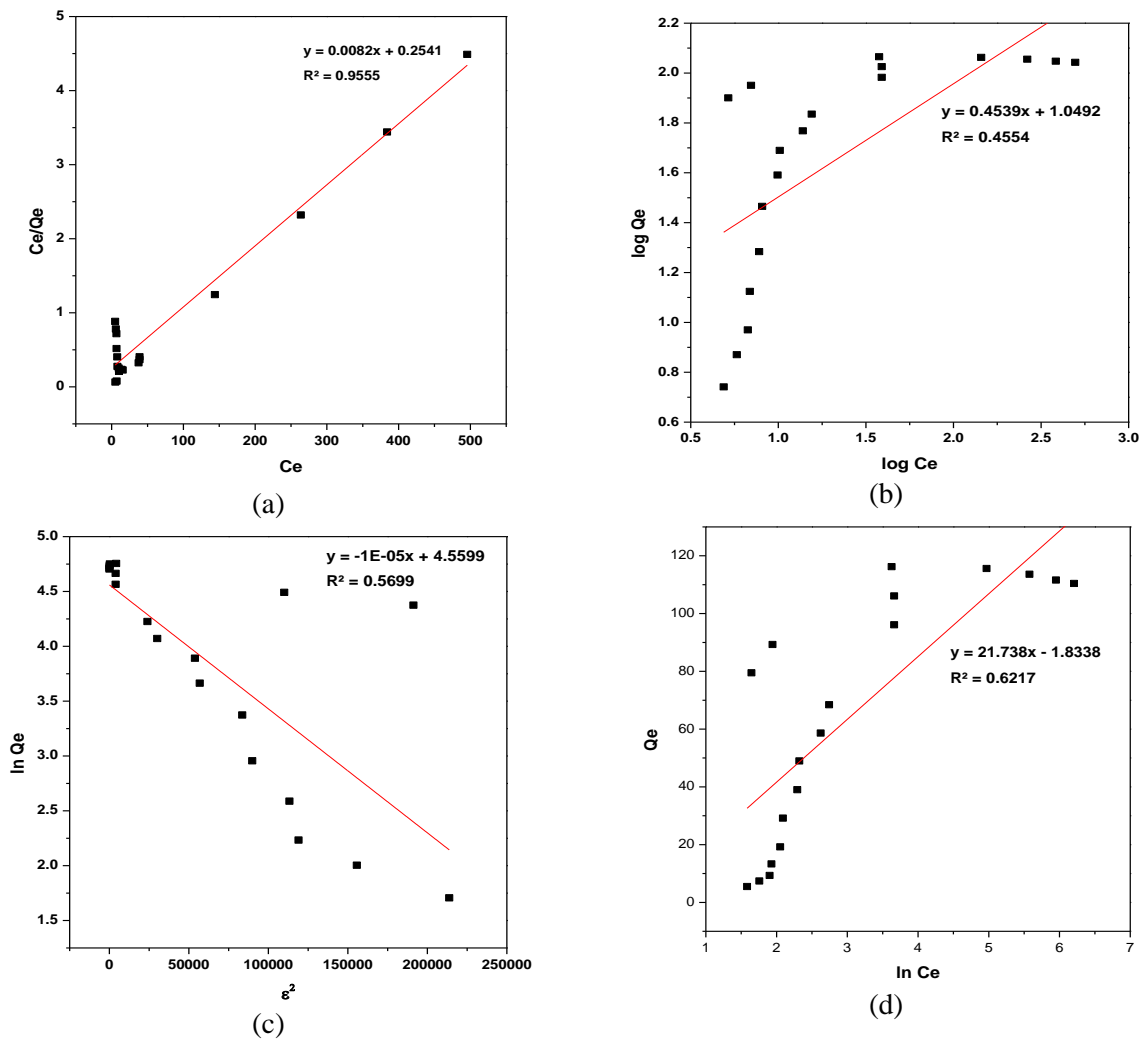
(a)

(b)

(c)

(d)

Figure 5. The adsorption isotherm model of (a) Langmuir, (b) Freundlich, (c) Dubinin-Radushkevich and (d) Temkin for adsorption of metanil yellow by SS-PEI.

Table 1. Parameters of isotherm model Langmuir, Freundlich, Dubinin-Radushkevich (D-R) Temkin for adsorption metanil yellow dye by SS-PEI

Langmuir				Freundlich		
q_m (mg.g^{-1})	K_L (L.mg^{-1})	R^2	R_L	K_F	n	R^2
121.951	0.032	0.955	0.019-0.341	11.199	2.203	0.454
D-R				**Temkin**		
q_m (mg.g^{-1})	K_{DR} (mol^{-2}/J^{-2})	E (kJ.mol^{-1})	R^2	K_T (L.mg^{-1})	b (J.mol^{-1})	R^2
95.573	1 x 10^{-5}	0.223	0.569	0.919	113.974	0.621

The adsorption process by forming a multilayer on the surface of a heterogeneous adsorbent can be explained by the Freundlich isotherm model (Mangaleshwaran et al., 2015). In the Freundlich isotherm model, K_F was the Freundlich isotherm constant related to the adsorption capacity and n was the Freundlich constant related to the degree of inhomogeneity of the adsorbent surface. If the value of n equals 1, then the adsorption process

was linear. If the n value was smaller than 1, it indicated that the adsorption takes place chemically, whereas if the value of n was above 1, then the adsorption process can occur physically (Sadaf et al., 2014). Table 1, the value of was more significant than one described that the adsorbate was well distributed on the surface of the adsorbent so that it can be indicated that the adsorption process was favorable.

The D-R isotherm model was generally used to calculate the adsorption energy and determine whether the adsorption process chemically or physically occurred (Sawasdee et al., 2016). The low R2 value indicates that the adsorption process did not follow the D-R isotherm model. However, based on the E value (E < 8 kJ/mol), it can be described that the adsorption process occurred physically (Joseph et al., 2016).

The Temkin isotherm model explained that as the degree of the adsorption process increased, the heat of adsorption decreased linearly (Wang et al., 2018). In the Temkin isotherm model, the heat of adsorption during the process is indicated by the value of b. The b value obtained was relatively high, b>0 (b=113.974 J/mol). This value can describe that the adsorption process occurred physically and chemically where there was a strong interaction between the dye molecule and the biosorbent. It can be confirmed by the adsorbent characterization data with SEM-EDX, which showed the smoothness of SS-PEI because MY dye molecules have covered the surface. The K_T value was 0.919 L/mg indicating a good affinity during the adsorption of MY dye by SS-PEI. Referring to the coefficient value in the Temkin isotherm model, it can be concluded that the surface of the SS-PEI adsorbent was not homogeneous (Daneshvar et al., 2014).

Based on the adsorption isotherm model analysis, it can be concluded that the adsorption process occurred mainly through electrostatic interactions between protonated amine groups and metanil yellow dye anions. The distribution of adsorbate molecules occurred on a homogeneous adsorbent surface by forming a monolayer. It was confirmed by FTIR analysis of the adsorbent that showed the wavenumber shifting indicated the interaction between the functional group and the anion of the MY dye.

Effect of contact time on the adsorption capacity and adsorption kinetic study of metanil yellow by SS-PEI

The effect of contact time on the adsorption capacity of metanil yellow dye by SS-PEI was studied within 15-120 minutes. The contact time effect in the adsorption process of metanil yellow dye by SS-PEI is shown in Figure 6.
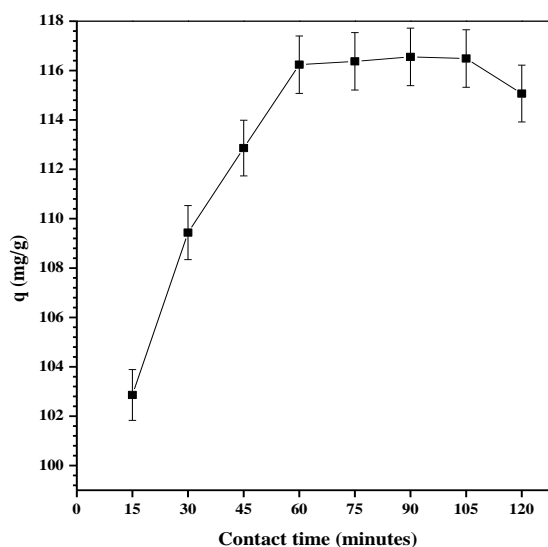

Figure 6. The effect of contact time on metanil yellow adsorption onto SS-PEI

The adsorption rate was an essential parameter in batch adsorption studies. Figure 6 showed that the adsorption rate in the early stages tended to be fast, i.e., 15 to 60 minutes. It was probably due to many active sites available to bind the anion of metanil yellow dye. After that, the adsorption rate tended to be constant. The saturated adsorbent surface caused it. The optimum contact time was obtained at 90 minutes with an adsorption capacity of 116.554 mg/g. The longer optimum time for the adsorption process of metanil yellow indicated that the more functional groups encouraged electrostatic interactions between protonated amine groups (cations) and the anions of metanil yellow dye, causing the increase in adsorption capacity. The decrease in adsorption capacity after the optimum time could be caused by the release of dye anions bound to the SS-PEI surface into the solution, causing the concentration of MY dye to increase. The possible adsorption mechanism between SS-PEI adsorbent and metanil yellow dye was described in Figure 7.

Figure 7 shows the possible mechanisms that occurred during the adsorption process of metanil yellow dye by SS-PEI through electrostatic interactions between the amine group and the anion of metanil yellow dye. The abundant number of amine groups from PEI caused an increase in the solid electrostatic interaction between the protonated amine groups in PEI and the anion of metanil yellow dye. This electrostatic interaction caused an increase in the adsorption

capacity of metanil yellow dye until an equilibrium was reached. Besides that, hydrogen bonding between the O atom in the metanil yellow dye and the H atom in the amine group in PEI. The adsorption process can also occur through the pores on the surface of the adsorbent. It can be confirmed from the characterization of the adsorbent with FTIR and SEM-EDX. The shift in the wavenumber at the specific peak of the FTIR spectrum of the SS-PEI adsorbent after the adsorption of metanil yellow dye may indicate an interaction between the functional group and metanil yellow dye. The results of the surface characterization of the adsorbent after the adsorption of metanil yellow dye with SEM showed a smooth surface and a decreased number of pores. It indicated that the metanil

yellow dye molecule had entered and covered the surface of the SS-PEI. The same finding has also been reported by Ramadhani et al. (2021) regarding the adsorption of metanil yellow dye by chitosan, possibly through electrostatic interactions between the protonated amine group chitosan and the anion of metanil yellow dye (Ramadhani et al., 2021).

Adsorption kinetics data provide information about the adsorption mechanism and the efficiency of the adsorption process. The curve of the adsorption kinetics model (Figure 8) shows the linear regression equation's value, and the coefficient of determination (R^2) was used to determine the value of the adsorption kinetics parameter for metanil yellow dye by SS-PEI.
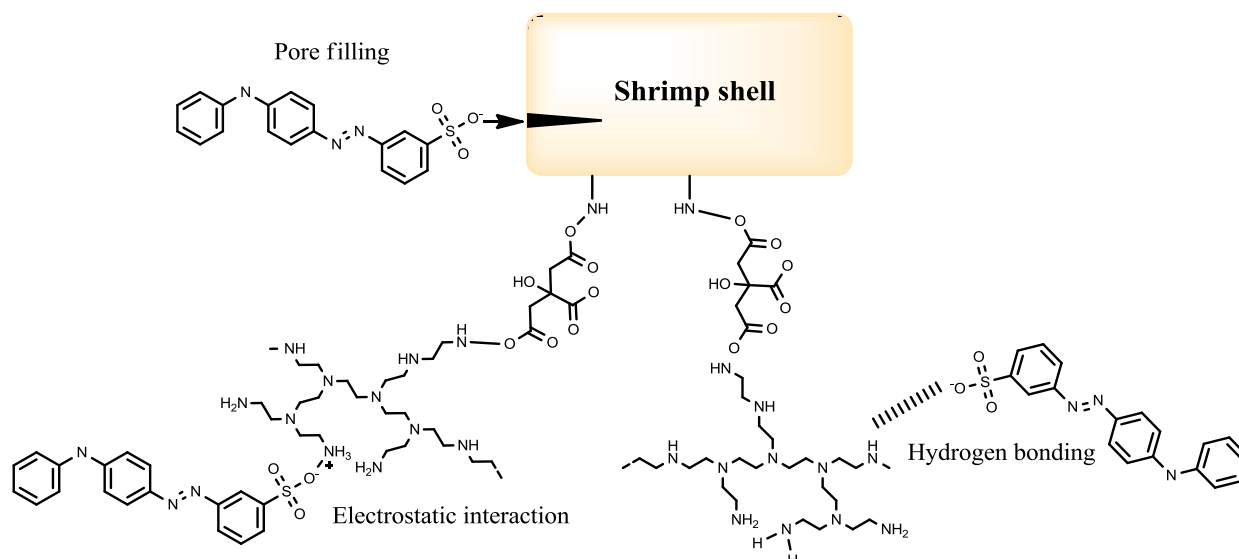

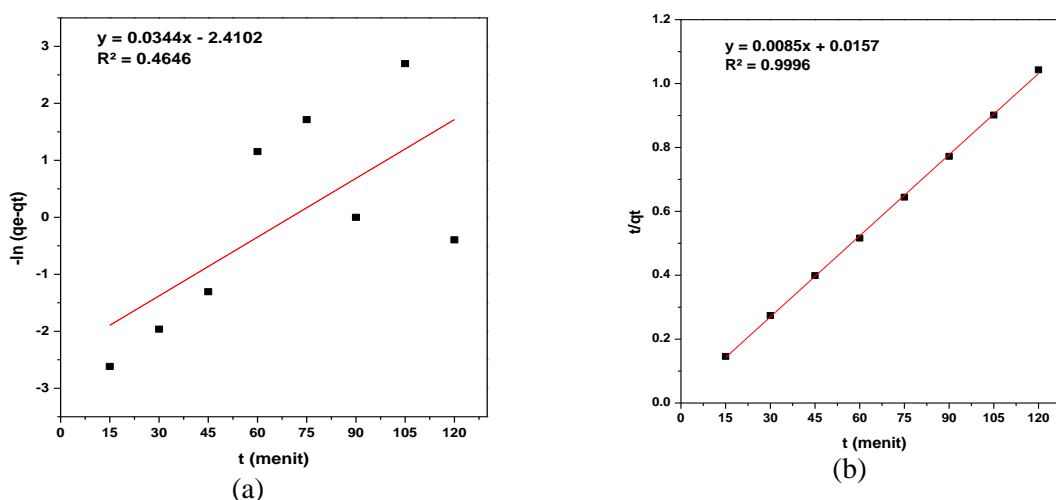**Figure 7.** Possible mechanism of adsorption of metanil yellow dye by SS-PEI with citric acid as a crosslinker

Figure 8. Adsorption kinetics model of (a) *pseudo-first-order* and (b) *pseudo-second-order*.

Table 2. Parameters of kinetic model pseudo-first-order and pseudo-second-order for adsorption metanil yellow dye by SS-PEI.

Pseudo-first order			Pseudo-second order		
K_1 (min^{-1})	Q_e (mg/g)	R^2	K_2 (min^{-1})	Q_e (mg/g)	R^2
0.034	11.136	0.464	0.0046	117.64	0.999

The adsorption kinetics parameters of metanil yellow dye by SS-PEI are presented in Table 2. The value of the coefficient of determination (R2) for the pseudo-first-order model (R^2=0.464) (Table 2) was lower than the pseudo-second-order model (R2=0.999). It showed that the pseudo-first-order model could not successfully describe the adsorption process of metanil yellow by SS-PEI. The calculated adsorption capacity value (Qe) was obtained from the slope of the curve in Figure 7. The Qe value in the pseudo-first-order model was relatively low compared to the experimental adsorption capacity value, indicating a discrepancy between the model and the experiment.

On the other hand, the pseudo-second-order model showed that the adsorption capacity value was insignificant between the experiment and the calculated model. It indicated that the adsorption process followed a pseudo-second-order adsorption kinetics model. In this model, it can be explained that the adsorption process took chemically occurred through hydrogen bonding between metanil yellow dye and amine. Similar results have also been reported by Nausheen et al. 2017 regarding the adsorption of Golden XDL dye following a pseudo-second-order adsorption kinetics model, which shows that the adsorption mechanism occurs chemically (Nausheen et al., 2017).

4. CONCLUSIONS

This study synthesized and characterized shrimp shells modified by PEI as adsorbents for metanil yellow in a batch system. The adsorption isotherm study showed that the adsorption of metanil yellow followed the Langmuir isotherm model with a maximum adsorption capacity (qm) of 121.951 mg/g. The experimental adsorption capacity values and calculated adsorption capacities did not differ significantly, indicating that the process followed a pseudo-second-order adsorption kinetics model. The differences in adsorbent

characteristics before and after the adsorption of metanil yellow dye showed the interaction between the adsorbent and adsorbate. The adsorption process occurred mainly through electrostatic interaction between the protonated amine functional group of PEI and the anion of metanil yellow dye. The increase in the adsorption capacity of metanil yellow dye by SS-PEI occurred due to the increase of active sites (amines) to bind the metanil yellow anion. So it can be concluded that the process of modifying shrimp shells with Polyethylenimine in the presence of citric acid as a crosslinker for adsorption of metanil yellow dye removal was successfully carried out.

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