



Adsorption of Naphtol Blue Black (NBB) Dye over Immobilized Chitosan from Shrimp Shells onto Glass Plate

Adsorpsi Zat Warna Naphtol Blue Black (NBB) Menggunakan Kitosan dari Cangkang Udang yang Terimobilisasi pada Pelat Kaca

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ABSTRACT

The adsorption of naphtol blue black (NBB) dye using immobilized chitosan on the glass plates had been investigated. The chitosan is derived from chitin deacetylation shrimp shells waste with the degree of deacetylation of chitosan is 75.7%. The produced chitosan were analyzed using FTIR and SEM. The effects of different reaction parameters such as mass of adsorbent, initial pH of solution and initial dye concentration were studied for the adsorption NBB dye. The results from this research showed that 30 mg of adsorbent mass at initial pH 6.0 yielded the optimum conditions for the adsorption of 30 mg/L NBB dye solution at the immobilized chitosan interface with the percentage removal of the dye is 97.187%. The equilibrium adsorption data of this research were analyzed by Langmuir and Freundlich isotherm models. The maximum adsorption capacity is obtained by using Freundlich isotherm with a correlation coefficient (R²) for 0,989 is greater than the value (R²) 0.968 of Langmuir isotherm which the n_F and K_f values were 3.56 and 41.78 L/g respectively. The maximum adsorption capacity (q_{max}) calculated from the Langmuir model is found to be 45,45 mg/g. The kinetics of the NBB dye adsorption nicely followed the pseudo-first rate which demonstrates that physisorption is the possible rate-limiting step controlling the adsorption process in this research.

Keywords : Chitosan; Adsorption; Naphtol Blue Black (NBB); Adsorption isotherms; Adsorption Kinetics

ABSTRAK

Adsorpsi zat warna Naphtol Blue Black (NBB) Menggunakan khitosan terimobilisasi pada pelat kaca telah diteliti. Khitosan diperoleh dari deasetilasi khitin pada kulit udang dengan derajat deaasetilasi khitosan sebesar 75,7%. Khitosan yang dihadlikan dianalisis menggunakan FTIR dan SEM. Pengaruh perbedaan parameter reaksi seperti massa adsorben, pH awal larutan dan konsnetrasi awal zat warna dipelajari untuk adsorpsi zat warna NBB. Hadil dari penelitian ini menunjukkan bahwa 30 mg massa adsorben pada pH awal 6,0 menghadilkan kondisi optimum untuk adsorpsi 30 mg/L larutan zat warna NBB pada khitosan terimobilisasi dengan persentase penyerapan zat warna sebesar 97,187%. Kesetimbangan data adsorpsi dari penelitian ini dianalisis dengan model isotherm Langmuir dan Freundlich. Kapasitas adsorpsi maksimum diperoleh menggunakan isoterm Freundlich dengan nilai koefisien korelasi (R²) 0,989 lebih besar dibandingkan nilai (R²) 0,968 dari isoterm Langmuir dimana nilai n_F dan K_f masing-masing 3,56 dan 41,78 L/g.

Kapasitas adsorpsi maksimum (q_{max}) dihitung menggunakan model Langmuir yaitu 45,45 mg/g. Kinetika dari adsorpsi zat warna NBB baik mengikuti laju kinetika ode satu semu yang menunjukkan bahwa fisisorpsi kemungkinan sebagai laju pembatas yang mengontrol proses adsorpsi pada penelitian ini.

Kata kunci : Khitosan; Adsorpsi; Naphtol Blue Black (NBB); Isoterm Adsorpsi; Kinetika Reaksi

PENDAHULUAN

Indonesia was a developing country in industry and technology. The rapid development of industry and technology had led to increased environmental pollution in air, water and soil. However, most of the waste was disposed of in the running water environment. This waste caused water sources to become unsafe to use both for household purposes and for drinking water (Rustan *et al*, 2019).

One of the pollution in the environment was dye waste. The common dye used is Naphtol blue black (NBB). These compounds include aromatic diazo chemical compounds which were classified as hazardous chemicals due to its carcinogenic characteristic. In the laboratory, NBB was used as a protein dye on nitrocellulose membranes and as an indicator of the presence of protein in the blood, while on an industrial scale it is used as a dye for textiles, inks, paints, plastics and leather. These dyes were very dark in color and resistant to chemical degradation. photochemical and biological (Ferkous et al, 2015). Thus, highly colored waste water and hazardous when disposed into water bodies without any waste treatment process will affect photosynthesis, aquatic organisms and human health and cause carcinogenic and genotoxic effects. Dye in the water to prevent the

occurrence of photosynthesis of aquatic plants because the dye can inhibit sunlight reaching aquatic plants stomata (Ruzicka, 2014). Therefore, it was essential to eliminate the harmful dye compounds in waste water before discharge into water bodies.

There were several methods that had been used in the sewage treatment process to remove dyestuffs, adsorption was the most practical and effective process to produce good quality effluent (Nawi *et al*, 2010). Several types of adsorbents were usually used to remove dyes such as activated carbon (Sheilatina *et al.*, 2021), wood (Emil *et al.*, 2021), bentonite (Saeed *et al.*, 2019) and silica (Selvaggi *et al.*, 2015). However, the adsorbent is difficult to regenerate (Kamari *et al.* 2009). Therefore, using a biopolymer adsorbent (chitosan) which had a strong chelating ability to pollutants (Sadeghi *et al.*, 2013).

Chitosan is made from chitin through a deacetylation process. Chitin is isolated from the shells of crustaceans such as lobster, crab and shrimp (Zhao *et al.*, 2012). Chitosan as a dye adsorbent was used widely, due to its behavior such as a large particle structure, physico-chemical properties, chemically stable, high reactivity and excellent selectivity. In addition, chitosan had the capacity to physically and chemically bind to various molecules (Artioli (2008) and Ngah *et al.* (2008)).

Research on the adsorption of dyes using chitosan powder had been widely reported. However, retrieving chitosan from water samples was very difficult and ineffective. In addition, chitosan also cannot be reused after the adsorption process and it is also difficult for storage chitosan. Therefore, immobilization of chitosan on a support will be able to overcome this problem (Nawi et al., 2010). Immobilization chitosan onto glass plates was used as an adsorbent to study the adsorption characteristics of textile dyes, in this research NBB dyes (anionic dyes), especially isotherms and its adsorption kinetics as well as the optimum conditions for absorption of NBB dyes. Glass plate was chosen as a supporting material due to its low cost, available, corrosion resistant, chemically inert, and it does not interfere with the adsorption process (Amar (2006) and Ngoh (2010)).

MATERIALS AND METHODS Materials

The materials used in this research were shells from the shrimp waste to make chitosan, NaOH, HCI, acetone, dye naphtol blue black (NBB), acetic acid, and distilled water. The molecular structure of naphtol blue black (NBB) is shown in Figure 1.



Figure. 1. The molecular structure of Naphtol Blue Black

The equipment used in this study include various appliance glass, glass plate, pipette, water pump, analytical balance, FT-IR, SEM, BET, Genesys 10 UV spectrophotometer, pH meter and oven.

Preparation of chitosan

Preparation of chitosan is conducted according to the procedure that had been performed by Rahmi (2007).

Preparation formulation and fabrication of immobilized chitosan

About 6 g of chitosan flakes was dissolved in 400 mL of 5% acetic acid aqueous solution and stirred continuously until dissolved chitosan. Before that, the cleaned glass plates with dimension of 47 mm x 70 mm x 2 mm were prepwered by cleaning and rinsing the glass plates with acetone and ultra pure water to remove any organic and inorganic material on the surface of glass plates. And then the glass plate is dried in the oven for a while, and cooling at ambient temperature after which its weight was finally measured.

The produced clear gel was then casted evenly onto the surface of the clean glass plates at different wet weight and dried completely at ambient temperature (27 °C). The drying process took at least 2 days or longer for a thicker weight of chitosan. The dry weight of chitosan was determined by the difference in the weight of the glass plates before and after the complete drying of the immobilized chitosan. The dry weight of immobilized chitosan was taken as the adsorbent weight or loading for all study during the experiment. The fabrication of immobilized chitosan on glass plates was hereafter known as CS/glass one layer. These CS/glass plates were conditioned by soaking the plates in ultra pure water at pH 4 for 1 h prior to use.

Characterization

The synthesis chitosan was characterized using FTIR analysis. Meanwhile, determination of the surface morphology of immobilized chitosan onto the glass plate was analyzed by Scanning Electron Microscope (SEM), then the results were compwered between the samples with other samples.

Experimental Set up

The reactor was made of glass with a size of 5 cm x 1 cm x 8 cm which can accommodate 30 mL dye solution naphtol blue black (NBB) for the adsorption process. And the tank was used to pump water agitation system of the dye solution which connected to PVC tube. The schematic setup is shown in Figure 2.



Figure 2. The schematic experimental set up

Adsorption studies

a. Determination of the optimum adsorbent mass

Variation of the dry mass of chitosan immobilized on a glass plate were 20, 40, 60 and 80 mg. Chitosan was immobilized on the glass plate, the insert into the glass reactor containing 30 mL of 30 mg/L NBB dye solution. Aeration tank using the water pump conducted to spread NBB dye in the reactor. NBB absorbance of the dye is measured using a spectrophotometer UV-Vis at a wavelength of 618 nm every 15 minutes for 120 minutes

b. Determination of optimum pH

The optimum mass of chitosan immobilized on glass plates (obtained in section a) was used to determine the optimum pH in the adsorption process of NBB 30 mL of 30 mg/L. The variation in pH of the solution used were 4, 5, 6, 7 and 8. The pH is adjusted by adding 0.1 M NaOH and HCI 0.1 M.

c. Determination the effect of initial concentration.

This study was conducted to determine the effect of the initial concentration of the NBB aqueous solution in this process. Variation concentrations of NBB solution were 10, 20, 30, 40 and 50 mg/L. The process of adsorption is carried out at optimum conditions (mass chitosan and pH).

Study of adsorption isotherms and kinetics.

Study of the adsorption isotherms of NBB solution performed using variations of the initial concentration of NBB solution (10-50 mg/L) with a contact time of 120 minutes (using an interval time of 1-120 minutes) to reach equilibrium.

RESULT AND DISCUSSION

Chitosan can be obtained from shrimp shell waste through the isolation process of chitin, then carried out by three processes, namely deproteination, demineralization and deacytellation. Deproteination process is a removal of the proteins which exists in the shrimp head waste. The process forms a stabilization in shrimp shell waste which can improve the quality of dissolved protein, thus resulting the optimum product.

The next process was demineralization, which removal of inorganic compounds (minerals) from shrimp shell waste. The main minerals in shrimp shells were CaCO₃ and less Ca₃(PO)₄ (Rahmi, 2007). The reaction that occurs between hydrochloric acid and minerals produces calcium chloride (CaCl₂) precipitates. Demineralization reaction can be written as:

CaCO ₃ + 2 HCl	\rightarrow	CaCl ₂ +
H2CO3 H2CO3	\rightarrow	H2O +
CO ₂ Ca ₃ (PO ₄) ₂ + 6 HCl + 2(H ₃ PO ₄)	\rightarrow	2 CaCl ₂

Table 1. Yield of chitin and chitosan isolation

Berat Awal	Khitin		Khitosan		
10 gram	Gram	%	gram	%	
	3,8	38%	2,1	21%	

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Chitin was produced from deproteination and demineralization processes. Table 1 showed the weight of chitin obtained is 3.8 grams from the initial weight of 10 grams. Then the amount of the resulting yield was 38%. Meanwhile, the weight of chitosan obtained was 2.1 grams. The chitosan vield was 21%. Chitosan was generated from the deacetylation process of chitin. Using NaOH solution with high concentration would cause a hydrolysis reaction of an amide in chitin, then chitosan would be produced with a better of The deacetylation degree. purpose of deacetylation process was for removing the acetyl group (-COCH₃) from the chitin molecule so as to produce chitosan with a high degree of chemical reactivity from the amine group. The degree of deacetylation indicates the content of free amino acid groups in chitosan (Purwanti, 2014). Chitin and chitosan produced were then analyzed by FTIR instrument.

Identification of the shift in functional groups of chitosan and also for calculating the degree of deacetylation of chitosan was performed by using FTIR instrument. The FTIR spectrum of chitin compounds showed in Figure 3.a, while the spectrum of chitosan in Figure 3.b.



Figure 3. FTIR Spectrum of (a). Chitin and (b) Chitosan

The FT-IR spectrum of chitin showed sharp peaks at the absorption of 1658.7 cm⁻¹ which indicated the presence of stretching of the amide group (C=O), and the absorption of 2927.7 cm⁻¹ showed the presence of a CH group. Absorption that extends above 3000 cm⁻¹ indicated the presence of a hydroxyl or OH group in chitin (Rinaudo, 2006).

The FTIR spectrum of chitosan showed sharp peaks at a wave number of 3444.6 cm⁻¹ which indicated overlapping hydroxyl (-OH) and amine (-NH₂) strain vibrations. The absorption

band at wave number 2920.16 cm⁻¹ showed the C-H strain vibration on aliphatic CH_2 which was strengthened by the emergence of CH_2 bending vibration absorption at wave number 1419.5 cm⁻¹. At a wave number of 1658.7 cm⁻¹, it showed the stretching of the carbonyl group of the amide. The complete spectrum of chitin and chitosan showed in Table 2.

Jenis Vibrasi	Agustina, 2015		Penelitian Ini		
	Khitin	Khitosan	Khitin	Khitosan	
OH Streching	3500	3450	3449,5	3444,6	
NH (-NH ₂) Streching	-	3400	-	3444,6	
NH (-NHCOCH ₃) Streching	3265, 3100	-	3109,2	-	

CH (CH ₃) Streching	2961 (lemah)	-	2962,5	-
CH (-CH ₂ -) Streching asym	2928	2926	2927,7	2920
CH (-CH ₂ -) Streching sym	2871	2864	2889,2	2889,2
C=O(-NHCOCH ₃) Streching	1655	1650 (lemah)	1658,7	1658,7
NH (-NHCOCH ₃) bending	1560	-	1558,4	-
CN (R-NH ₂) bending	1310	-	1315,4	-
NH (R-NH ₂) bending	-	1596	-	1577,7
CN Streching	-	1200-1020	-	1080,1
CH (-CH ₂) bending asym	1426	1418	1427,2	1423,4
CH (-CH ₂ -) bending sym	1378	1377	1380,0	1380,9
C-O (-C-O-C-) Streching asym	1077	1082	1072,3	1080,1
C-O (-C-O-C-) Streching sym	1024	1033	1029,9	1033,8

Table 2. Chitin and Chitosan FTIR Shifting Data

The difference between chitin and chitosan lies in the intensity of the hydroxyl group and carbonyl group of the amide. In chitosan the intensity of %T for the hydroxyl group is 10.71 and the %T for the amide group is 42.1. Meanwhile, in chitin, the hydroxyl group's %T intensity is 9.79 and the %T amide is 22.98. This difference results in different values of the degree of deacetylation. The main purpose of deacetylation is the removal of the amide group in chitin to obtain chitosan which had an amine group. The results of the preparation of making chitin into chitosan were not completely successful in converting the amide group into an amine, so the presence of an amide group still showed in the spectrum.

The degree of deacetylation is determined by comparing the absorbance of the amide group (1659.10 cm⁻¹) with the absorbance of the hydroxyl group (3400 cm⁻¹) contained in the FTIR spectrum of chitosan (Figure 3.b). The amide group in chitosan showed the measurement of the acetyl group, while the hydroxyl group (-OH) as a correction of water absorption by chitosan in the deacetylation process. The method used for the calculation is the base line method using the Domszy and Robert equations (Domszy, 1985).

The FTIR spectrum of chitosan (Figure 3.b) showed the absorbance value of the amide group at wave number 1635.96 cm-1 with a transmittance of 6.2% is 1.21 while the absorbance value of the –OH group at wave number 3430cm⁻¹ with transmittance 9.88% was equal to 1.01. The degree of deacetylation of chitosan obtained was 65.98% while the degree of deacetylation of chitosan was 75.7%.

The resulting chitosan was then immobilized on a glass plate using 5% acetic acid. The results of chitosan with 5% acetic acid produced a gel-shaped mixture which was then dripped on a glass plate. Drying was performed for two days to get complete evaporation of the solvent, so the chitosan would stick perfectly. The purpose of this immobilization of chitosan was to make it easy for separation the adsorbent from the adsorbate, due to the difficulties and expensive cost which required for separation process between the adsorbate and the adsorbent therefore immobilization needs to be conducted.

Immobilized chitosan on a glass plate was then characterized using a Scanning Electron Microscope (SEM). Figure 4 showed the SEM characterization of the immobilized chitosan with variation of mass. The picture pointed that the mass of chitosan with a mass of 50 mg had the most compact structure than the others. Density decreases with smaller chitosan masses such as 10 mg and 30 mg. The denser the immobilized chitosan it will cover the active site of the chitosan so as absorption will be hampered. Adsorption will take place slowly in a thicker mass of chitosan.



(a) 10 mg, (b) 30 mg and (c) 50 mg

The difference in adsorbent loading greatly affects the course of the adsorption process. Determination of the weight of the adsorbent is the first thing that needs to be complete in the adsorption process, because it is to determine the amount of loading of the adsorbent and also to avoid the excessive use of the adsorbent so as the adsorption process would be more effective.



Figure 5. The Curve of the Effect of Adsorbent loading on the absorption of NBB dye solution (pH=6.4 Co=30 mg/L t = 60 minutes)

Figure 5 showed that the optimum adsorbent loading is found at 30 mg with an absorption percentage of 98.187%, a decrease in absorption occurs when the adsorbent mass is increased or decreased, as come about an adsorbent mass of 20 mg with an absorption percentage of 93.108% and at 40 mg with an absorption percentage of 95,429%. The phenomenon occurs due to the limited crosssectional area of the glass plate so that if using an excessive mass of chitosan it will only increase the thickness and density of chitosan on the glass plate. Meanwhile, if using a less weight of chitosan, the formation of chitosan layer under optimal and slightly adsorp NBB dyes. Increasing the thickness and density of the adsorbent lead to the adsorption of Naphthol Blue Black (NBB) dye to be arduous until it reaches the lowest layer of chitosan. So as the percentage of absorption of NBB dyes is reduced (Nawi et al., 2010).

The point that influenced by the adjusment of pH in the adsorption system were the adsorbent and the adsorbate, so this regard to the dye solution and also the surface charge of the adsorbent. Figure 6 illustrated the effect of pH on adsorption dye with a range of 4.0 to 10.0. The adsorption is carried out using a concentration of 30 mg/L NBB and an optimum mass of adsorbent (30 mg) with a contact time of 60 minutes. The initial pH value of NBB dye was 6.4, which had a percent absorption value of 97.187%. The absorption optimum percentage for NBB adsorption using immobilized chitosan is at pH 6.0 with an absorption value of 97,219%. At a pH

between 6.0 and 8.0 NBB dyes will ionize to form anionic compounds.

$NBB\text{--}SO_3Na \rightarrow NBB\text{--}SO_3^- + Na^+$

At pH lower than 6.0 the percentage of absorption of NBB dye was lower due to the surface of the protonated chitosan becomes positively charged at an acidic atmosphere. The density of positively charge on the chitosan surface increases with decreasing pH, so that the adsorption process sensitively pH changeable. Additionally, the condition of immobilized chitosan with the use of pH 4.0 not only caused protonation of the amine group (-NH₂) of chitosan, but also lowered the pH sensitivity of chitosan. The reaction mechanism of chitosan protonation produces cationic amines:

 $R-NH_2 + H^+ \rightleftharpoons R-NH_3^+$

Increasing electrostatic interactions between the active site of chitosan and NBB dyes follows the following reaction:

$NBB-SO_3^- + R-NH_3^+ \longleftarrow NBB-SO_3^- + H_3N^+-R$

The percentage of adsorption also decreases at pH above 6.0, due to the deprotonation of amine group in chitosan thereby reducing the positive charge of chitosan and then debilitating the electrostatic interaction between chitosan and NBB dye molecules. As the NBB compound is in alkaline pH, the NBB active group would react with OH so that the NBB compound becomes less reactive. This is corresponded with previous research conducted by Nawi, 2010.



Figure 6. Curve Effect of pH on Adsorption NBB dye solution (Co=30 mg/L, mcs=30 mg, t=60 minutes)

Figure 7 indicated that the effect of the initial concentration of the NBB solution and the contact time on the adsorption capacity. The increasing of the initial concentration of the dye solution would increase the equilibrium rate. Figure 7 explained that the adsorption capacity for each initial concentration of NBB solution had a different optimum time. The adsorption process is fast at 15 minutes, which means that there is diffusion rapidly to the surface of the adsorbent. This is occurred due to many active sites available on the adsorbent at the beginning of the adsorption. Increasing adsorption time, the adsorption will slow down until it reaches

equilibrium as shown in Figure 7, the initial concentration of the NBB solution (10 mg/L) takes 30 minutes to reach equilibrium. At higher concentrations, the equilibrium time increases. Minutes 45, 60, 75 and 90 were the equilibrium points for concentrations of 20, 30, 40 and 50 mg/L. This conducted because of the increasing concentration of NBB dyes solution lead to the interaction between NBB and the chitosan plate to be stronger. The interaction occurs between the protonated chitosan surface through the strong electrostatic force between $-NH_2$ from chitosan and SO₃ group from NBB dye solution.



Figure 7. Curve effect of time on adsorption capacity at different concentrations

The isotherm obtained from the study of adsorption of NBB dye solution on immobilized chitosan on a glass plate is the Freundlich isotherm which assumes that the adsorption of NBB with glass plate immobilized chitosan occurs physically. The adsorbent forms a multilayer system with heterogeneous surfaces so that the system had different adsorption capabilities.

The calculation results of Langmuir and Freundlich isotherms available in table 3. The

 Q_{max} value reached from the study is 45.45. The greater of the value of Q_{max} indicated the better of the adsorption process. The Q_{max} value in this research is greater than using other adsorbents

but still less than palygorskite modified chitosan as shown in table 4.

Langmuir			Freundlich		
R ²	K _L (L/g)	Q _{max} (mg/g)	R ²	n _F	K _F (L/g)
0.968	22.002	45.45	0.989	3.56	41.78

Table 3. Langmuir and Freundlich adsorption isotherm.

Nama	Adsorben	Adsorbat	Q _{max}	
Bregas,	Abu Sekam	Logam	0 4 4 1 2	
2005	Padi	Pb	0,4412	
Wanyonyi	Akar	Congo		
2014	Eichornia	Dod dvo	1,580	
	crassipes	Red dye		
Rahmi,	Komposit	Fonol	0.208	
2007	Khitosan	Felloi	0,200	
Pengg, 2013	Khitosan-	Vollow		
	Modified	2DC	71,38	
	Palygorskite	343		

Table 4. Comparison of maximum adsorption capacity (Q_{max}) value

The rate and mechanism of the NBB dye adsorption process using immobilized chitosan can be analyzed using a simple kinetic model. The kinetic model used is a pseudo first order and a pseudo second order reaction. Table 5 (a) explained that the parameters of the pseudofirst-order kinetic model with the regression coefficient value (R²≥0.99) with the calculated adsorption value (qe_{ca}l) approach the experimental adsorption capacity value (geexp). The pseudo-second-order kinetics model (Table 5 (b)) had a regression coefficient value ($R^2 \ge 0.99$). The value of (ge_{cal}) is also near to (ge_{exp}) but

lower than the pseudo-first-order kinetic model. This means following pseudo-first-order kinetics with the overall mechanism of absorption of NBB dyes using a chemical reaction process that involves the exchange of electrons between NBB dyes and chitosan. Pseudo-first-order kinetics uses a modeling based on a solid phade with a physisorption mechanism as the controlling step for the adsorption rate. The advantage of pseudofirst-order kinetics is that it can predict the initiation of a reaction as proposed by Asci, 2012.

Konsentrasi	qe _{exp} (ma/a)	k ₁ (ment)	qe _{cal} (mg/g)	R ²
10 mg/L	10.71	0.0990	35.6	0.990
20 mg/L	20.79	0.0668	22.0	0.998
30 mg/L	30.76	0.0622	26.2	0.998
40 mg/L	38.80	0.0576	31.3	0.994
50 mg/L	48.81	0.0553	36.1	0.998

 Table 5 (a).
 Pseudo-First Order Adsorption Kinetics

qe _{exp} (mg/g)	k ₂ (g/mg menit)	qe _{cal} (mg/g)	R ²	h
10.71	0.00508	22.7	0.803	2.62
20.79	0.00075	26.3	0.997	0.52
30.76	0.00021	37.0	0.998	0.29
38.80	0.00010	47.6	0.999	0.23
48.81	0.00005	58.8	0.999	0.17
	qe _{exp} (mg/g) 10.71 20.79 30.76 38.80 48.81	qeexp (mg/g) k2 (g/mg menit) 10.71 0.00508 20.79 0.00075 30.76 0.00021 38.80 0.00010 48.81 0.00005	qeexp (mg/g)k2 (g/mg menit)qecal (mg/g)10.710.0050822.720.790.0007526.330.760.0002137.038.800.0001047.648.810.0000558.8	qeexp (mg/g)k2 (g/mg menit)qecal (mg/g)R210.710.0050822.70.80320.790.0007526.30.99730.760.0002137.00.99838.800.0001047.60.99948.810.0000558.80.999

Table 5 (b). Pseudo-second Order Adsorption Kinetics

CONCLUSIONS

Based on the results of the research that had been carried out, the conclusion is the amount of chitosan yield produced from shrimp shell waste is 2.1%. The degree of deacetylation of chitosan obtained from shrimp shell waste is 75.7%. The optimum condition for the adsorption of NBB dye using immobilized chitosan on a glass plate is 30 mg of adsorbent mass loading and a pH of 6.0 with an absorption percentage of 98.187%. The adsorption isotherm followed by the absorption of NBB dye using immobilized chitosan is the Freundlich isotherm with an R² value of 0.989, an n_F value of 3.6 and a Kf of 41.78 L/g. The appropriate kinetic model for the NBB adsorption process with chitosan immobilization is pseudo-first-order kinetics with a rate constant (k1,ads) of 0.0622 min⁻¹ and adsorption capacity (qe) of 30.76 mg/g.

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REFERENCES

- Agustina, S., Swantara, I.M.D., dan Suartha, I.N. (2015). Isolasi Kitin, Karakterisasi, dan Sintesis Kitosan Dari Kulit Udang. *Jurnal Kimia*. 9(2): 271-278.
- Amar, A. H., (2006). Development of a simple dip coating method for immobilization of TiO₂ onto solid supports using direct TiO₂

powder. *M Sc Thesis*: Universiti Sains Malaysia.

Artioli, Y., (2008). Adsorption. *Encyclopedia of Ecology*.: 60-65.

- Asci Y., Açıkel Ü., Sag Açıkel Y. (2012). Equilibrium, hysteresis and kinetics of cadmium desorption from sodium-feldspar using rhamnolipid biosurfactant. *Environmental Technology*. 1-12.
- Domszy, J.G. and Roberts, G.A.F. (1985). Evaluation of Infrared Spectroscopic Techniques for Analyzing Chitosan. Journal MakromalChem. 186:1671-1677.
- Emil E. Thybring, Charles R. Boardman, Samuel L. Zelinka, Samuel V. (2021). Glass Common Sorption lisotherm Models are not Physically Valid for Water in wood. Colloids and Surfaces A: **Physicochemical** and Engineering Aspects. 627 127214. https://doi.org/10.1 016/j.colsurfa.2021.127214.
- Ferkous, H., Merouani, S., Hamdaoui, O., Rezgui, Y.and Guemini, M. (2015).
 Comprehensive Experimental and Numerical Investigation of The Effect of Frequency and Acoustic Intensity on The Sonolytic Degradation of Naphthol Blue Black in water, *Ultrasonic Sonochemsitry*, 26 (2015) 30-39.
- Kamari, A., Ngah WSW., Liew LK., (2009). Chitosan and Chemically Modified Chitosan Beads for Acid Dyes Sorption. *Journal of Environmental Sciences*. 21:296-302.

- Nawi, M. A., Sabar, S., Jawad, A. H., Sheilatina, Ngah W. S. W. (2010). Adsorption of Reactive Red 4 by Immobilized khitosan on glass plates: Towards the design of immobilized TiO₂-khitosan synergistic photocatalyst-adsorption bilayer system. *Biochemical Engineering Journal*. 49: 317-325.
- Ngah, W. S. W. And Fatinathan, S. (2008). Adsorption of Cu (II) ions in aqueous solution using chitosan beads, chitosan-GLA beads and chitosan-alginate beads. *Chemical Engineering Journal*. 143:62-72.
- Ngoh Y. S., (2010). Immobilization of TiO₂ powder onto glass plate via dip-coating technique using ENR-50/PVC polymer blend as a adhesives and its photocatalytic application. *M Sc Thesis*: Universiti Sains Malaysia.
- Purwanti, Ani., (2014). Evaluasi Proses Pengolahan Limbah Kulit Udang Untuk Meningkatkan Mutu Khitosan yang Dihasilkan. *Jurnal Teknologi*. Vol 7. No.1:83-90.
- Rahmi. (2007). Adsorpsi Fenol pada Membran Komposit Khitosan Berikatan Silang, *Jurnal Rekayasa Kimia dan Lingkungan*, 6:28-34.
- Rinaudo M. (2006). Chitin and chitosan: Properties and applications, *Progress in polymer science journal.* 31: 603-632.
- Rustan, F. R., Sriyani, R., & Talanipa, R. (2019). Analisis Pemakaian Air Bersih Rumah Tangga Warga Perumahan Bumi Mas Graha Asri Kota Kendari. *Stabilita*, 7(2), 151–160.
- Ruzicka, O. dan L. Safira. (2014). Aplikasi Fotokatalis TiO₂ Pada Degradasi Limbah Cair Zat Warna Tekstil, Lomba Karya Ilmiah Sumber Daya Air Tahun 2014.
- Sadeghi, Mousa. Arami, M., Gharanjig, K. (2013). Preparation of chitosan-ethyl acrylate as a biopolymer adsorben for basic dyes removal from colored solutions. *Journal of Environmental Chemical Engineering.* 1: 406-416.

- Saeed, M., Munir, M., Nafees, M., Shah, S. S. A., Ullah, H., and Waseem, A. (2019). Synthesis, characterization and applications of silylation based grafted bentonites for the removal of Sudan dyes: isothermal, kinetic and thermodynamic studies. *Micropor. Mesopor. Mater.* 291:109697. doi: 10.1016/j.micromeso.109697.
- Selvaggi, R., Tarpani, L., Santuari, A., Giovagnoli, Latterini. L. (2015). S., Silica Nanoparticles Assisted Photodegradation Orange Acridine Aqueous of in Suspensions. Applied Catalysis Β, Environmental, 168-169: 363-369.
- Sheilatina, Lubis, S., Fathurrahmi and Oktari, L., (2021). Characterization and Investigation on Photocatalytic Activities of TiO₂/Coconut Shell-Based Activated Carbon, Indonesian Journal of Fundamental and Applied Chemistry, 6 (2), 33-39.
- Zhao, Y., yang, B., Xu, J., Fu, Z., Wu, M., Li, F. (2012). Facile synthesis of Ag nanoparticles supported on TiO₂ inverse opal with enhanced visible-light photocatalytic activity. *Thin Solid Films*. 520 3515–3522.