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Kinetic and Equilibrium Study of Synthetic Dye Adsorption Using Alkali-Activated Scallop Shells as Sustainable Adsorbents

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Abstract. Scallop shells are abundant in Indonesia, particularly along the northern coast of Java Island in Pekalongan Regency. These shells serve as natural adsorbents for removing synthetic textile dyes from aqueous solutions due to their high mineral content, especially calcium carbonate. Adsorption experiments were conducted to evaluate the potential of scallop shells as adsorbents for removing vat dye solutions. Adsorption kinetics were analyzed using pseudo-first-order and pseudo-second-order models in both linear and non-linear forms. The results showed that the non-linear pseudo-first-order model best described the adsorption process, with a qe value of 0.98982 mg/g. Equilibrium studies using Langmuir, Freundlich, and Jovanovic isotherm models indicated that the linear Freundlich model provided the best fit, with an R^2 of 0.99969, suggesting a heterogeneous adsorption process. These findings confirm that scallop shells are effective and eco-friendly adsorbents for textile dye removal and hold promise for sustainable water treatment. Further studies are suggested under real industrial conditions.

Keywords: adsorption, equilibrium studies, kinetic analysis, synthetic textile dyes, scallop shell

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1. Introduction

Indonesia is rich in marine resources, including the northern coast of Java Island. One of them is Pekalongan Regency, which is abundant in marine animal products. Marine animal waste, such as scallop shells commonly found along the fish auction sites in Wonokerto, Pekalongan Regency, is often

seen discarded. Scallop shells are currently underutilized as accessories. Fishermen typically only harvest the meat from scallops for sale in markets.

As natural adsorbents derived from fishery by-products, scallop shells have gained attention as a sustainable alternative for removing dyes using natural materials. The abundant availability of scallop shells in Pekalongan Regency offers a promising solution. Scallop shells are rich in minerals, such as sodium as a micro-mineral and calcium as a macro-mineral. They also contain an abundance of calcium carbonate ($CaCO_3$) [1]. Additionally, scallop shells act as antibacterial agents without causing environmental harm [2]. Their abundance, low cost, and eco-friendly properties make them an attractive alternative for addressing dye pollution challenges.

Water pollution caused by synthetic dyes, especially from the textile industry, has become a significant environmental concern [3]. Vat dyes, are commonly used in the batik dyeing process in Indonesia, particularly in Pekalongan Regency, a famous city for its batik industry. Other studies have shown that heavy metals, such as Ni, Cr, and Cu, are commonly found in batik wastewater, especially from textile dyes [4]. Discharging dyes into the water system causes serious ecological threats to the surrounding ecosystem and human health. Thus, it is crucial to develop efficient and eco-friendly techniques for dye removal from wastewater.

Previous studies have demonstrated the potential of scallop shells for various applications. They have been utilized as eco-friendly biodiesel [5], stabilizers in remediating arsenic (As) and heavy metals (Pb and Zn) in contaminated soil [6], biosorbents for removing heavy metals like cadmium (Cd) [7], radioactive strontium (Sr^{2+}) [8], Cr (VI) [9], and Streptococcus mutans [10]. Chitosan/nanohydroxyapatite composites derived from scallop shells have also been used to treat mercuric ions [11] and Safranin O dye [12].

For the treatment of synthetic dye waste, previous research references various methods, including bioremediation using Aspergillus sp. [13] for Indigosol Blue 04B waste degradation. Activated carbon has also been applied in batik wastewater treatment [14]. Scallop shell nanocomposites have been shown to remove Direct Red 81 dye [15], and Acid Red 14 [16].

This study treated scallop shells with an alkali solution. In previous research [17], the addition of alkali was chosen because it could remove impurities effectively with minimal concentration, sufficient for the relatively small mass of the adsorbent [18]. The difference in our study is the focus on using a 0.25 M NaOH solution, whereas previous studies typically used untreated adsorbents or adsorbents in the form of chitosan compounds.

This study focuses on assessing the potential of scallop shells as adsorbents for the removal of synthetic dye solutions. The adsorption kinetics were examined through pseudo-first-order and pseudo-second-order models, considering both linear and non-linear forms. Furthermore, adsorption equilibrium was analyzed using Langmuir, Freundlich, and Jovanovic isotherm models in their linear and non-linear variations. The findings of this research aim to support the advancement of sustainable and effective water treatment methods, especially for industrial dye removal applications.

2. Methods

2.1. Characterization of Dyes

Vat dyes, included in the category of synthetic dyes, were used in this study. Their chemical structure and characteristics are described in Table 1.

Table 1. Basic Characteristics of Vat Dyes

Chemical Name	**Vat Red 1, Solubilized**
Commercial Name	Indigosol Pink IR
CAS Number	3875-72-7
Molecular Formula	$C_{18}H_{13}C_{l2}NaO_8S_4$

2.2. Preparation of Scallop Shell Powder

The scallop shells are washed under running water and sun-dried. They are then finely crushed and sieved using standard ASTM sieves within the 80 to 100 mesh range, resulting in particles sized 149–177 μm, which are used as adsorbents in subsequent experiments [19]. This study uses a scallop shell with the addition of 0.25 M NaOH as an alkali treatment. The use of scallop shells with the addition of 0.25 M NaOH as an alkali treatment serves to enhance the adsorption capacity of the material. Chemically, the alkaline treatment helps in removing organic impurities and increasing the surface roughness, which can lead to a greater number of active sites available for adsorption.

The location of the scallop shell sampling is at the Wonokerto Fish Auction Place with coordinates 109°37’21.46” and 6°50’38.83” located in Wonokerto Kulon Village, Wonokerto District, Pekalongan Regency. The Wonokerto Fish Auction Place can be seen in Figure 1. This location was selected because it is one of the major coastal fishery centers in Pekalongan Regency, where scallop shell waste is abundantly available as a by-product of seafood processing. The high availability of scallop shells ensures a consistent and sustainable raw material supply for the study.

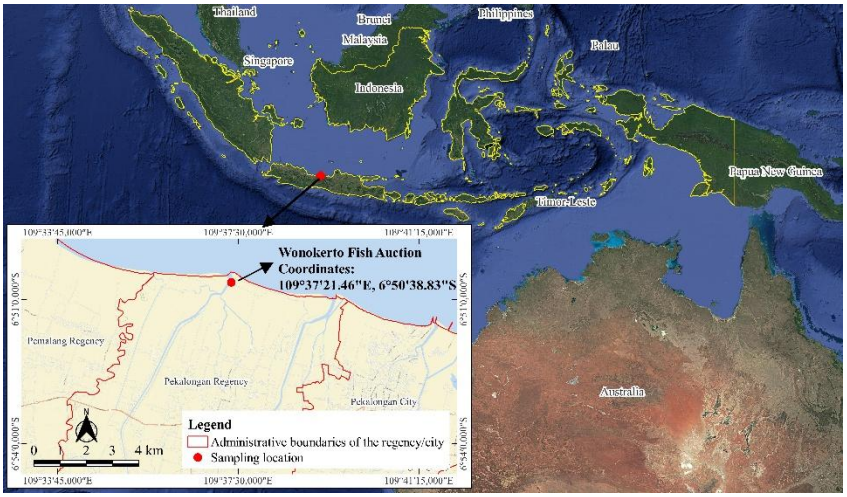

Figure 1. Scallop Shell Sampling Location at Wonokerto Fish Auction

2.3. Adsorption Experiments

All adsorption experiments were conducted at 25°C using the batch method. For each experiment, 50 mL of dye solution with an adjusted pH was transferred into an erlenmeyer flask. After that, variations in the amount of adsorbent were made, ranging from 250 mg. The variations in contact time ranged from 30 minutes, and variations in initial concentration started from 20mg/L are described in Table 1.

Table 2. Variation of Adsorption Experiments

Variation	Quantity Used	Details
Contact Time	30 – 150 min	range of values 30 min
Adsorbent Mass	250 – 1250 mg	range of values 250 mg
Initial Concentration	20, 100, 200, 300, 400 mg/L	

Then, the solution was stirred using a magnetic stirrer at a constant speed of 500 rpm. Furthermore, the adsorbent was separated from the aqueous solution, and all samples were filtered using 12 μm of

filter paper. The concentration of the dye remaining in the solution was measured with a UV-Visible Spectrophotometer at a wavelength of 400-600 nm [20].

The Langmuir, Freundlich, and Jovanovic adsorption isotherms were investigated in this study. The variation of initial adsorbate concentration was added to determine the isotherm models. Adsorption isotherm tests determine the maximum adsorption capacity.

In addition, pseudo-first-order and pseudo-second-order kinetics were carried out as adsorption kinetics studies. 1g/50mL at an initial concentration of 20 mg/L for variations of contact time 30, 60, 90, 120, and 150 minutes with the same adsorbent mass, temperature, and pH, respectively. The adsorption kinetics were determined by analyzing the adsorption of the dye from aqueous solution at different time intervals.

3. Results and Discussion

3.1. Characterization of the Scallop Shell Powder

The content of the scallop shell is described in Table 3. It describes that the proximate composition of scallop shell, most components in the scallop shell are minerals. The high mineral content indicates micro and macro minerals, especially calcium as fillers that can form mechanical properties, and sodium as maintaining the balance of body fluids with the surrounding environment. The relatively low protein content is due to the fact that proteins are complex compounds, including amino acids found in matrix proteins, which primarily serve to assist in the biomineralization process [21].

The difference in scallop shell color is not too significant a difference in proximate content [22]. XRD analysis of the scallop shell is 98% calcium carbonate and 2% organic compounds. Meanwhile, SEM analysis of scallop shell nanoparticles has open pores and is evenly distributed [23]. Then, TG/DTA analysis of the scallop shell before calcination, decomposition occurred at temperatures ranging from 600°C to 850°C. The decomposition was likely caused by calcium carbonate ($CaCO_3$) breaking down due to the release of carbon dioxide (CO_2). In XRF analysis, the content of scallop shell calcination produces slightly larger CaO than before calcination, which is around 98.4-98.9% [24]. Scallop shells also contain impurities such as cadmium (Cd) [25].

Table 3. Proximate composition of scallop shell

	Proximate	Composition (%)	Information
Alkali Treatment	Moisture	0,099	Wet Basis
	Mineral	97,47	Dry Basis
	Lipid	0,36	Dry Basis
	Protein	2,17	Dry Basis
	Carbohydrate *(by different)*	0	Dry Basis

3.2. Adsorption Process Analysis

In this study, we used three variations, namely the mass variation of the adsorbent, the contact time of the adsorption process, and the concentration of the adsorbate as shown in Figure 2. The details of the variations have been explained in the method section of the study. It will later be used as data to determine isotherms and adsorption kinetics.

Similar previous studies explained the removal of Reactive Black 5 dye with scallop shell that increasing the amount of adsorbent resulted in higher dye removal efficiency. In addition, the higher the waste concentration, the lower the removal efficiency [26]. According to the present results, the optimal and effective adsorbent concentration was detected to be 1250mg/50mL in a solution concentration of 20mg/L with a contact time of 90 minutes.

In the analysis of the adsorption process time variation, the R^2 value is 0.99999, meaning that 99.9% of the variation in the Removal (%) data can be explained by Box Lucas model, same as one-phase association equation with zero offset, and the Reduced Chi-Square value is 0.0217, indicating that the

difference between the model and the data is very small, so the fit is excellent. Meanwhile, in the mass variation analysis, the R^2 value is 0.99979, meaning that 99.97% of the variation in the data can be explained by the Langmuir model. On the other hand, in the time variation analysis, the R^2 value is 0.93469 when using the linear form, which indicates a good fit.

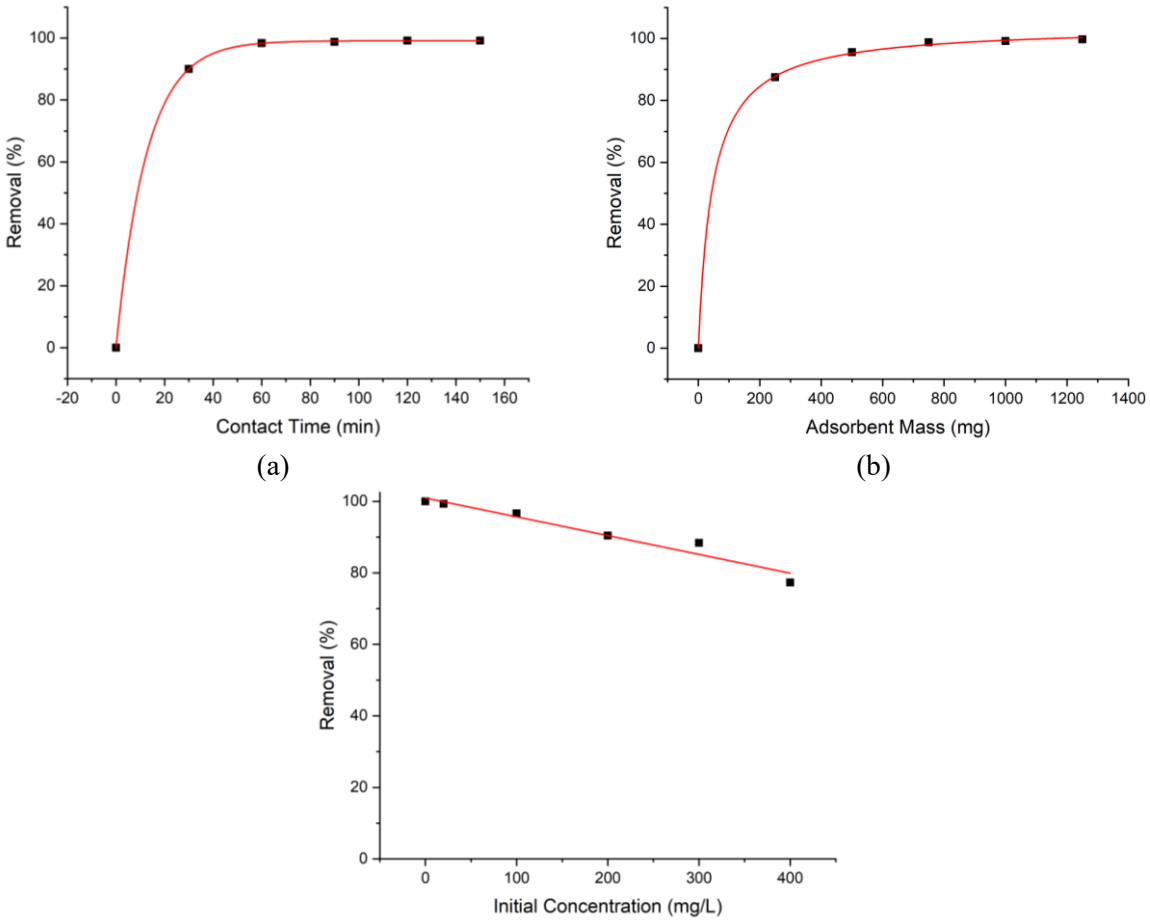

Figure 2. Variation of Treatment on the Removal of Vat Red 1, Solubilized (a) Effect of Contact Time, (b) Effect of Adsorbent Mass, and (c) Effect of Initial Concentration

3.3. Adsorption Kinetics

Adsorption Kinetics in our research uses two kinetic models, pseudo-first-order and pseudo-second-order, respectively linear and non-linear forms are described in Table 4. The best representation of this adsorption is pseudo-first-order non-linear form with a value of R^2 0.9997, which is very close to 1. The substance being adsorbed per unit mass of adsorbent (q_e) is 0.98982 mg/g, which means the process is not too slow, making it quite efficient where equilibrium can be reached within a reasonable time. The rate constant for the adsorption process (K_1) is 0.07199, which suggests that the adsorption occurs at a reasonable rate. In essence, pseudo-first-order indicates that the reaction seems to exhibit first-order behavior concerning one reactant.

This study aligns with the research by Yazid, where cuttlefish bone as an adsorbent for Congo Red adsorption was analyzed using both kinetic models, namely the pseudo-first-order model and the pseudo-second-order model, with R^2 values approaching 1 [27]. The pseudo-first-order and pseudo-second-order kinetic models were employed in this study to comprehensively evaluate the adsorption kinetics mechanisms, as both models are commonly applied in dye adsorption studies. Utilizing both

linear and non-linear forms of these models allows for a more accurate analysis of the experimental data fit and offers deeper insights into the adsorption rate and mechanism of the alkali-activated scallop shell-based adsorbent.

Table 4. Adsorption Kinetic on the Removal of Vat Red 1, Solubilized Dyes

Kinetics Model		**Parameters**		
		q_e(mg/g)	K_1	R^2
Pseudo-first-order	Linear Form	0.67348	0.00575	0.7941
	Non-Linear Form	0.98982	0.07199	0.99997
		q_e(mg/g)	K_2	R^2
Pseudo-second-order	Linear Form	1.00143	0.58367	0.99936
	Non-Linear Form	1.03685	0.18894	0.99883

3.4. Adsorption Isotherms

Adsorption Isotherm in equilibrium studies of our research uses three isotherm models, namely Langmuir, Freundlich, and Jovanovic are described in Table 5. The best representation of this adsorption is a Freundlich linear form with a value of R^2 0.99969. The value of n 1.35011 indicates that the adsorption process is favorable, although not extremely strong. For value of K_f 0.88322 indicates relatively low adsorption capacity. Frendlich isotherm model suggests a heterogeneous adsorption process with varying adsorption sites and energies. In contrast, the Langmuir and Jovanovic models were less accurate, indicating that the adsorption was not restricted to a monolayer or a uniform surface and likely involved more complex interactions. These findings are consistent with the study by Sneha Bhagyaraj, which demonstrated that the adsorption of boron from aqueous solution using cuttlefish bone is well represented by the Freundlich isotherm model [28].

Table 5. Adsorption Isotherms on the Removal of Vat Red 1, Solubilized Dyes

Isotherms Model		**Parameters**		
		q_{max}(mg/g)	K_L	R^2
Langmuir	Linear Form	28.74389	0.02337	0.87037
	Non-Linear Form	48.75624	0.00989	0.99684
		n	K_F	R^2
Freundlich	Linear Form	1.35011	0.88322	0.99969
	Non-Linear Form	1.20495	0.82991	0.9994
		q_{max}(mg/g)	K_J	R^2
Jovanovic	Linear Form	1.84138	0.04771	0.794
	Non-Linear Form	29.73605	0.01568	0.99643

4. Conclusion

The study indicates that scallop shells, rich in minerals, are an effective and sustainable adsorbent material for removing Vat Red 1, Solubilized dyes, with optimal conditions determined by the balance between adsorbate concentration and adsorbent mass. The optimal and effective treatment using an adsorbent mass of 1250 mg/50 mL at a concentration of 20 mg/L for 90 minutes can remove 99.7% of the dye concentration. The adsorption process is characterized by fast kinetics and heterogeneous site interactions. The adsorption process follows a pseudo-first-order kinetic model, indicating that the adsorption rate primarily depends on the adsorbate concentration in the solution. This suggests that the adsorption mechanism is governed by surface interactions rather than bulk diffusion. The data aligns

well with the Freundlich isotherm model, highlighting a heterogeneous adsorption process. This implies that the adsorbent surface consists of multiple types of adsorption sites with different energies, allowing varying levels of interaction between the adsorbent and the adsorbate molecules.

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