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Alkali and magnetite modified fly ash as granular adsorbent for removal of naphthol AS dye from aqueous solution

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Graphical abstract

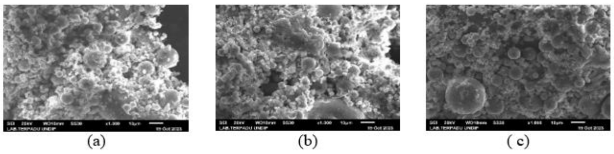

Figure 1. SEM analysis of granular adsorbent from alkali and magnetite modified fly ash with alginate (a), chitosan (b), and carrageenan (c) binder.

Abstract

The presence of dye pollutants in the aquatic environment, apart from causing aesthetic problems, can also cause health problems. Removal of dye pollutants in industrial wastewater can be done using the adsorption method, which is a simple, effective and low-cost process. Fly ash is a solid waste from the coal combustion process which has been widely used as an adsorbent in wastewater treatment containing dyes. In this research, fly ash was used as an adsorbent for naphthol AS dye through modification with alkali and magnetite, and granulation with a binder so that it would facilitate its application on a large scale. The influence of the type of binder (alginate, chitosan, carrageenan) and adsorption variables (pH, contact time, initial concentration of dye) have been studied in this research in addition to studying the adsorption kinetics and isotherms. Granulation of alkali and magnetite modified fly ash was best obtained with carrageenan binder compared to alginate and chitosan binders. Granular alkali and magnetite modified fly ash with carrageenan binder have the best adsorption ability of naphthol AS dye of 91.56% at pH 3, initial concentration of 50 mg/L, and contact time of 120 minutes and follow the pseudo-second-order adsorption kinetics model and the Freundlich adsorption isotherm model.

Keywords: carrageenan, modified fly ash, granular adsorbent, naphthol AS dye

1. Introduction

Dye pollutants are one of the causes of water environmental pollution. Pollution of dye pollutants in the aquatic environment, apart from causing aesthetic problems, can also result in increased oxygen demand (BOD and COD), bioaccumulation, and the formation of mutagenic/carcinogenic compounds which can cause health problems such as allergies, skin irritation, and even cancer (Berradi *et al*., 2019; Gita *et al*., 2017; Lellis *et al*., 2019; Saini, 2017; Maruthai *et al*., 2025).

Sources of dye pollutants include the textile, pulp, paper and pharmaceutical industries. Removal of dye pollutants in industrial wastewater can be carried out using physical (adsorption, filtration, reverse osmosis), chemical (oxidation, coagulation) and biological methods (Gita *et al*., 2017, Saini, 2017; Maruthai *et al*., 2025; Selvanarayanan *et al*., 2024). The adsorption method is widely used because it has advantages such as a simple, effective and low-cost process. Dye adsorbents that have been widely used are activated carbon, zeolite, and fly ash (Siyal *et al*., 2018).

Fly ash, which is solid waste from the coal combustion process, has been widely used as an adsorbent in wastewater treatment containing heavy metals, dyes and organic materials (Ali *et al*., 2012; Yao *et al*., 2015). Valorization of fly ash as an adsorbent is usually in powder form, either with or without modification. Fly ash modification that has been widely carried out is modification with alkali, usually NaOH solution, which aims to reduce crystallinity and increase the pore surface area of fly ash (Purbasari *et al*., 2022; Nugroho *et al*., 2022). The application of fly ash as an adsorbent in powder form on a large scale has problems with the adsorbent separation process after the adsorption process. To overcome this problem, fly ash can be modified with magnetite (Fe_3O_4) compounds. The addition of magnetite to fly ash, apart from increasing the adsorption capacity of fly ash, will also facilitate the separation process due to its magnetic properties (Harja *et al*., 2021; Amodu *et al*., 2015).

Another modification that can be made to fly ash is to increase the size of the fly ash particles. Enlarging the particle size can be done by granulation process using binders derived from polysaccharides such as alginate, chitosan, and carrageenan (Shanmugam, 2023). Apart from being a binder, polysaccharides also show the ability to act as adsorbents. The macromolecular chains in polysaccharides can link together to form a three-dimensional network structure so that the adsorbate will be easier to bind to the functional groups in the network (Ge *et al*., 2023; Hassan *et al*., 2023).

This research aims to utilize fly ash as naphthol AS dye adsorbent through modification with alkali and magnetite as well as granulation with a binder so that it is hoped that it will facilitate its application on a large scale. Naphthol AS dye is one of the dyes that is often used in the batik (traditional cloth) industry in Indonesia. The influence of binder type as well as adsorption variables such as pH, contact time and dye initial concentration will be studied. Apart from that, the kinetic and equilibrium models of adsorption isotherms will also be studied.

2. Methods

Materials used in this research were fly ash from power plant in East Java, Indonesia; NaOH flakes; Fe_3O_4 powder; alginate; chitosan; carrageenan; naphthol AS dye; distilled water. All chemicals used were of analytical grade and were used as received.

Fly ash was washed first and dried in oven at 110 °C for 4 hours. Fly ash then was sieved with standard sieve of 100 mesh. Fifty grams of fly ash was modified by mixing with 300 mL of 2 M NaOH solution at 60 °C for 2 hours. Alkali modified fly ash was washed until washing solution was neutral and dried at 110 °C for 3 hours. Alkali modified fly ash was mixed with Fe_3O_4 (weight ratio of 9:1) in a planetary ball mill at a stirring speed of 300 rpm for 4 hours. Alkali and magnetite modified fly ash was then washed and dried at 60 °C for 24 hours (Harja *et al*., 2021). Granulation of alkali and magnetite modified fly ash was carried out by adding a binder, namely a solution of alginate, chitosan and carrageenan amounting to 10% of the mass of alkali and magnetite modified fly ash. After the alkali and magnetite modified fly ash was mixed with the binder, it was molded into granules with a diameter of $\pm$1 cm and then dried at 60 °C for 2 hours. Characterization was conducted on granular alkali and magnetite modified fly ash with different binder by scanning electron microscopy (SEM) analysis using JEOL JSM-6510LA equipment.

Naphthol AS dye was adsorbed by granular alkali and magnetite modified fly ash with carrageenan binder in batch process at dosage of 1.2 g adsorbent per 25 ml of naphthol AS dye solution with variation of pH, contact time, and initial concentration. The concentration of naphthol AS dye solution was measured by Ultraviolet-Visible (UV-Vis) spectrophotometer using Shimadzu UV-1601 equipment.

Naphthol AS adsorption efficiency can be calculated using Equation (1).

$$Adsorption\,efficiency = \frac{C_0 - C_e}{C_0} x100\% \quad (1)$$

C_0 is the concentration of naphthol AS solution at initial condition and C_e is the concentration of naphthol AS solution at equilibrium condition.

Adsorption kinetics studies were carried out using pseudo-first-order kinetics model and pseudo-second-order kinetics model with equations (2)-(3) for each model. Meanwhile, adsorption isotherm studies were conducted using Langmuir isotherm model and Freundlich isotherm model with equations (4)-(5) for each model (Benjelloun *et al*., 2021; Wang and Guo, 2020; López-Luna *et al*., 2019).

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad (2)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (3)$$

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

At those equations, q_e and q_t are adsorption capacity at equilibrium and at time *t*, respectively. The adsorption capacity can be calculated with equation (6).

$$q = \frac{\left(C_0 - C_e\right)V}{W} \quad (6)$$

V is volume of naphthol AS dye solution and *W* is mass of adsorbent (alkali and magnetite modified fly ash). As for q_m is maximum adsorption capacity.

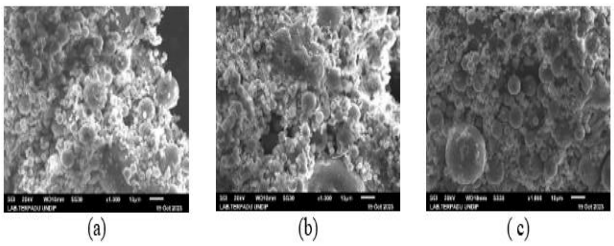

Figure 1. SEM analysis of granular adsorbent from alkali and magnetite modified fly ash with alginate (a), chitosan (b), and carrageenan (c) binder.

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3. Results and discussion

3.1. Characterization of granular adsorbent from alkali and magnetite modified fly ash

Characterization of granular alkali and magnetite modified fly ash was done by SEM analysis with magnification of 1000x as shown in **Figure 1**. The microstructure of the granular adsorbent from alkali and magnetite modified fly ash with different binders is relatively the same, namely showing a continuous phase of the binder covering the fly ash which is shaped like a ball. The adsorption ability of the three granular adsorbents on naphthol AS dye is relatively the same as shown in **Figure 2.** Adsorption of naphthol AS dye by granular adsorbent took place at pH 3 with adsorbent dose of 1.2 g per 25 mL of 50 mg L^{-1} dye solution for 180 minutes. However, the adsorption test of the granular adsorbents shows that the granular adsorbents with alginate and chitosan binders are relatively less strong because the granular adsorbents experience decomposition after the adsorption process. Thus, in the subsequent dye adsorption process using alkali and magnetite modified fly ash granulated with carrageenan binder.

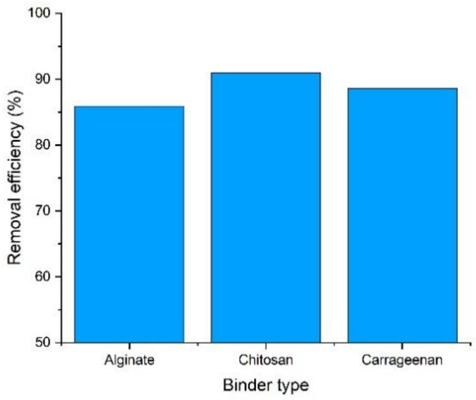

Figure 2. Adsorption ability of naphthol AS dye by granular adsorbents from alkali and magnetite modified fly ash with different binders

3.2. Characterization The effect of pH on the adsorption of naphthol AS dye by granular adsorbent from alkali and magnetite modified fly ash with carrageenan binder

Granular adsorbent from alkali and magnetite modified fly ash with carrageenan binder was used to adsorb naphthol AS dye with pH variations at adsorbent dose of 1.2 g per 25 mL of 50 mg L^{-1} solution for 180 minutes, the results of which are shown in **Figure 3**. The lower the pH, the higher the adsorption efficiency obtained. At low pH, the surface of adsorbent will be positively charged and showed a tendency to attract anionic species. Naphthol AS dye is anionic or negatively charged dye (Benammar *et al*., 2021) so it will be easily attracted to the positively charged surface of the adsorbent. The removal efficiency results at pH 2 and 3 were relatively the same, so pH 3 was chosen for the adsorption process of naphthol AS dye.

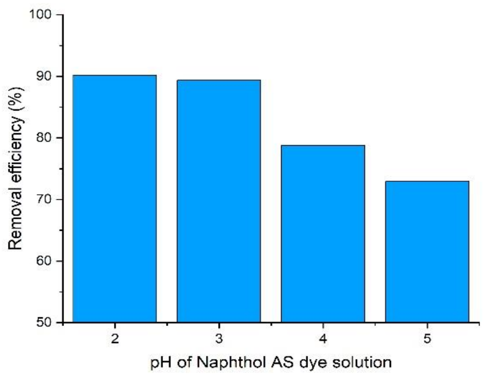

Figure 3. Effect of pH on the adsorption efficiency of naphthol AS dye with granular adsorbents from alkali and magnetite modified fly ash with carrageenan binder

3.3. The effect of contact time on the adsorption of naphthol AS dye by granular adsorbent from alkali and magnetite modified fly ash with carrageenan binder

The adsorption process with variation of contact time was carried out at pH 3 and adsorbent dose of 1.2 g per 25 mL naphthol AS dye solution with initial concentration of 50 mg L^{-1}. Based on **Figure 4**, the longer the contact time, the more the adsorption efficiency will increase. A significant increase occurred in the first 60 minutes of contact time and after that the increase in adsorption efficiency did not change much after a contact time of 120 minutes. At the beginning of the adsorption process there are still many active sites available so that it is able to adsorb naphthol AS dye quickly. However, the longer the adsorption time, the more adsorbate is adsorbed so that the active sites on the adsorbent become more saturated and reach the equilibrium point (Fernandes *et al*., 2020).

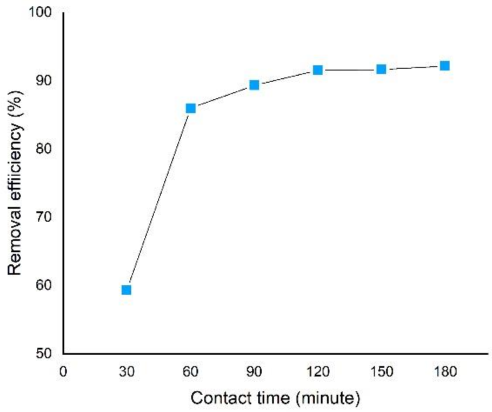

Figure 4. Effect of contact time on the adsorption efficiency of naphthol AS dye with granular adsorbents from alkali and magnetite modified fly ash with carrageenan binder

3.4. The effect of initial concentration on the adsorption of naphthol AS dye by granular adsorbent from alkali and magnetite modified fly ash with carrageenan binder

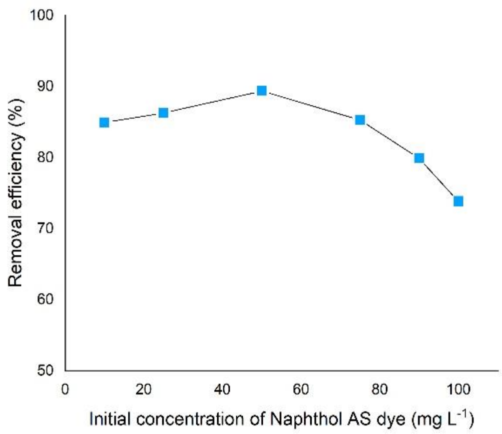

Figure 5. Effect of initial concentration on the adsorption efficiency of naphthol AS dye with granular adsorbents from alkali and magnetite modified fly ash with carrageenan binder

Furthermore, the adsorption process with variation of initial concentration was conducted at pH 3 and adsorbent dose of 1.2 g per 25 mL naphthol AS dye solution for 180 minutes. **Figure 5** shows that increasing the initial concentration of naphthol AS solution from 10 to 50 mg L^{-1} can increase the adsorption efficiency. The increasing initial concentration of adsorbate will provide a driving force which causes an increase in adsorption efficiency. After the initial concentration of the naphthol AS solution is 50 mg L^{-1}, increasing the initial concentration of the naphthol AS solution will cause the adsorption efficiency to decrease because the number of active sites adsorbing the naphthol AS dye decreases and the adsorbent surface becomes increasingly saturated (Purbasari et al., 2023).

3.5. Adsorption kinetics studies

Adsorption kinetics studies to determine the adsorption mechanism of naphthol AS dye by granular adsorbent were carried out using pseudo-first-order and pseudo-second-order kinetic models. **Figure 6** shows the linear plot of the pseudo-first-order and pseudo-second-order kinetic models, while **Table 1** displays the kinetic parameters obtained. Based on the R^2 value which is closest to 1, the adsorption of naphthol AS dye by granular alkali and magnetite modified fly ash with carrageenan binder follows a pseudo-second-order kinetic model which assumes that adsorption is controlled by chemisorption (Benjelloun *et al*., 2021; Wang and Guo, 2020; López-Luna *et al*., 2019).

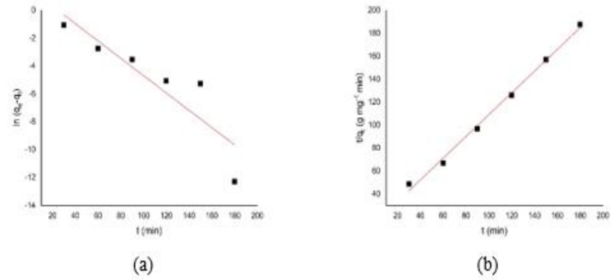

Figure 6. Linear plot of pseudo-first-order (a) and pseudo-second-order (b) kinetic models for the adsorption of naphthol AS dye by granular alkali and magnetite modified fly ash with carrageenan binder

Table 1. Kinetic parameters for the adsorption of naphthol AS dye by granular alkali and magnetite modified fly ash with carrageenan binder

Kinetics model	Parameter	Value
Pseudo-first-order	q_e (mg g^{-1})	4.582
	k_1 (min^{-1})	0.062
	R^2	0.801
Pseudo-second-order	q_e (mg g^{-1})	1.056
	k_2 (g mg^{-1} min^{-1})	0.062
	R^2	0.995

3.6. Adsorption isotherm studies

The adsorption isotherm study was conducted using the Langmuir isotherm and Freundlich isotherm models. The linear plot of the isotherm model on the adsorption of naphthol AS dye by granular adsorbent is shown in **Figure 7**, while the isotherm parameters are shown in **Table 2**. Adsorption of naphthol AS dye by granular adsorbent tends to follow the Freundlich isotherm model based on the R^2 value (~1). Thus, the adsorption of naphthol AS dye by granular alkali and magnetite modified fly ash with carrageenan binder occurs on a heterogeneous surface with multilayer adsorption (Wang *et al*., 2020; López-Luna *et al*., 2019).

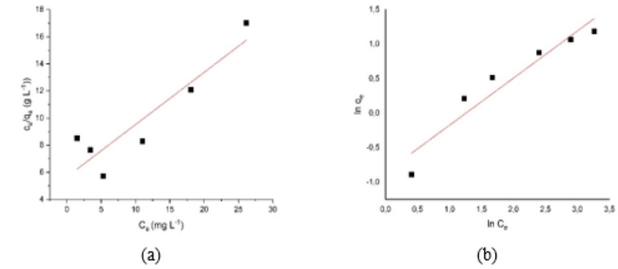

Figure 7. Linear plot of Langmuir (a) and Freundlich (b) isotherm models for the adsorption of naphthol AS dye by granular alkali and magnetite modified fly ash with carrageenan binder

Table 2. Isotherm parameters for the adsorption of naphthol AS dye by granular alkali and magnetite modified fly ash with carrageenan binder

Isotherm model	Parameter	Value
Langmuir	q_m (mg g^{-1})	2.595
	K_L (L mg^{-1})	0.068
	R^2	0.828
Freundlich	$1/n$	0.683
	K_F (mg g^{-1}(L $mg^{-1})^{1/n}$)	0.423
	R^2	0.915

The best result of naphthol AS dye by granular alkali and magnetite modified fly ash with carrageenan binder was obtained at pH 3, initial concentration of 50 mg/L, and contact time of 120 minutes with an efficiency of 91.56%. The efficiency of naphthol dye adsorption obtained is still lower than the adsorption efficiency with iron filings (95.70%), coffee grounds (99.63%), and natural zeolite (99.98%) which are adsorbents in powder form (Ngwu *et al*., 2021; Fitry *et al*., 2024; Imandiani *et al*., 2018). However, granular adsorbents with larger sizes compared to powder adsorbents and having magnetic properties will be easier to apply on a large scale.

4. Conclusions

Fly ash, solid waste from the coal combustion process, had been utilized as an adsorbent for naphthol AS dye through modification with alkali and magnetite, and granulation with carrageenan binder. Granular alkali and magnetite modified fly ash with carrageenan binder had the best adsorption ability of naphthol AS dye of 91.56% at pH 3, initial concentration of 50 mg/L, and contact time of 120 minutes with adsorbent dose of 1.2 g per 25 mL dye solution. The adsorption of naphthol AS dye by granular adsorbent followed the pseudo-second-order adsorption kinetics model and the Freundlich adsorption isotherm model.

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