Modification of the coffee industry sludge-based adsorbent using acid treatment for the removal of tartrazine dye from aqueous solution

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ABSTRACT

The massive amount of industrial sludge produced annually poses an environmental concern, and improper sludge disposal may harm the environment. To address this issue, sludge has been converted into a cost-effective adsorbent for treating wastewater containing dyes. This study aims to modify the coffee sludge-based adsorbent using various treatment methods for tartrazine dye removal. The raw sludge was modified through physical treatment (PT) via oven drying and calcination, chemical treatment (CT) using phosphoric acid and nitric acid, and physicochemical treatment (PCT) method. The modified sludge adsorbents were characterised using Micromeritics ASAP 2020 for nitrogen adsorption analysis. Subsequent batch adsorption experiments were performed using the best-modified adsorbent of PCTS-HNO$_3$ prepared by physicochemical treatment method with nitric acid to assess the effect of various factors, including initial pH (3-11), adsorbent dosage (0.05-0.25 g/L), and initial concentration of tartrazine dye (25-100 mg/L), with a contact time of 2 hours. The best process conditions were achieved at 0.15 g/L of adsorbent dosage, initial pH of 3 and initial concentration of 50 mg/L with almost 100% dye removal. The characterization results revealed that the BET surface area of the modified adsorbent was significantly increased from 363.32 m^2/g of RS to 599.64 m^2/g for PCTS-HNO$_3$ adsorbent. The Langmuir isotherm model provided an excellent fit to the adsorption isotherm data, with correlation coefficients R$^2 \geq 0.99$ and a maximum adsorption capacity (q$_{max}$) of 99.01 mg/g. The kinetic study observed that the adsorption

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process adheres remarkably well to the pseudo-second-order kinetic model, signifying chemisorption adsorption. The results of this study indicate that the modified coffee sludge-based adsorbent proves to be a viable and cost-efficient solution for eliminating tartrazine dye from aqueous solutions.

1.   INTRODUCTION

Dyes are generally described as coloured substances that chemically bond on a substrate and form various complex structures to the substrate. The dye's global production is approximately more than 10,000 tonnes annually, and it is expected to cause about 1-10% loss in production that is discharged to the environment [1-2]. The untreated dyes in industrial effluent discharged directly into natural water bodies have significant adverse effects on photosynthetic activity in aquatic ecosystems and endanger human health [2]. According to the Environmental Quality (Industrial Effluent) Regulations 2009, the permitted colour conditions for discharge of industrial effluent or mixed standard A and B effluent are 100 ADMI and 200 ADMI, respectively [3]. Metals and aromatics compounds in the dye structure create a mutagenic or teratogenic interaction with aquatic life and organisms [2, 4]. Furthermore, exposure to these substances can pose significant risks to human health, including kidney diseases, allergies, carcinogenic effects, and dermatitis [5].

Tartrazine, also recognized as FD & C Yellow No.5, is an anionic dye produced by combining a synthetic lemon-yellow azo dye and trisodium salt [6]. This type of dye is widely used in the food industry products such as soft drinks, chips, gum, gelatine, and mustard. Tartrazine offers high stability and is a cheaper alternative dye than natural food dyes, making this synthetic dye the second most popular additive food colouring agent [7]. The synthetic dye of tartrazine typically contains aromatic ring structures and an azo functional group, which harms human health [8]. Thus, controlling tartrazine usage and excess discharge to the environment is crucial.

The situation becomes increasingly alarming with the projected estimate that 47% of the global population will encounter significant challenges related to clean water scarcity by the year 2030 [9]. Various treatment methods and advanced technologies have been developed to solve the problem of dye present in the water bodies, such as chemical treatment using the oxidation process, biological treatment using microbial cultures, and physical treatment by adsorption [10]. Applications of these available approaches are discovered to have some weaknesses, such as the filtration techniques may result in high possibilities of clogging the membrane system, and the oxidation treatment requires energy and chemical agents to operate the system, resulting in a high capital and operating cost [11]. Adsorption is widely regarded as an efficient method for dye removal, offering numerous advantages such as low capital investment, ease of operation, selective pollutant removal, and lower formation of reaction intermediates [12]. Yagub et al. (2014) found that adsorption was superior to other methods in terms of design flexibility, insensitivity to harmful pollutants and good removal of various dyes [11].

The choice of adsorbent plays a crucial role in the adsorption process, as it directly influences the adsorption rate and the percentage of dye removal from the aqueous solution. Industrial sludge, classified as a carbonaceous material, has demonstrated its efficacy as an adsorbent for efficiently removing dyes from wastewater effluent [13]. Moreover, using the industrial sludge-based adsorbent is anticipated to offer enhanced environmental and economic feasibility [14] . Several studies have used industrial sludge-based adsorbent from textile effluent, sewage treatment, and wastewater treatment [12,14-15]. A previous study by Oke and Mohan revealed that industrial sludge derived from textile effluent treatment exhibited significant potential as an efficient adsorbent, demonstrating an impressive methylene blue dye removal capacity of up to 123.6 mg/g [12].

The expansion of the beverage industry, including the coffee industry, has necessitated the establishment of a Wastewater Treatment Plant (WWTP) to comply with the effluent standard requirement by the Department of Environmental [16]. Activated carbon is used in secondary treatment to remove the colour and odour from wastewater from the coffee processing industry. The generated sludge from the treatment processes, primarily containing activated carbon, can be recycled and used as an adsorbent in the dye removal adsorption study. As far as the author knows, no previous studies have explored sludge utilisation from wastewater treatment plants in the coffee industry as a prospective adsorbent. However, raw coffee industrial sludge has a low surface area, limited porosity, and poor adsorption capacity. Thus, the modification of raw coffee industrial sludge is needed to enhance the physico-chemical characteristics of the adsorbent.
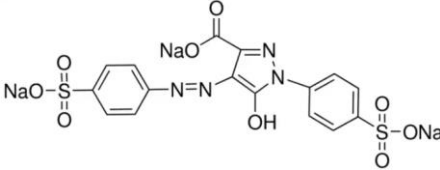
This study aims to modify the coffee sludge-based adsorbent using physical, chemical and physicochemical treatments to remove tartrazine dye from an aqueous solution. The purpose of modifying the industrial sludge-based adsorbent was to augment both the adsorption capacity and surface area of the adsorbent, thereby improving its efficiency in dye removal [17]. The characteristics and adsorption performance of the modified adsorbent with tartrazine dye were examined via nitrogen adsorption analysis and batch adsorption study, respectively. In this study, the adsorption isotherm and kinetic study were also conducted to evaluate the maximum adsorption capacity of the modified adsorbent and investigate the adsorption mechanism involved in removing tartrazine dye.

2. MATERIAL AND METHODS

2.1 Chemicals and materials

In this study, tartrazine dye was selected as a model pollutant of the azo dyes. The characteristics of tartrazine dye are shown in Table 1. A stock solution of tartrazine dye at 1000 mg/L was prepared and further diluted to achieve the desired initial concentrations, ranging from 15 mg/L to 100 mg/L for conducting the adsorption studies. The chemicals used for sludge modification were phosphoric acid (H_3PO_4) and nitric acid (HNO_3), with 85% and 70% purity, respectively. pH of the solution was adjusted using hydrochloric acid (HCl) and sodium hydroxide (NaOH). All the chemicals used were purchased from Qrec, Sdn. Bhd. Meanwhile, the sludge was collected from the coffee industry wastewater treatment plant of Syarikat Hang Tuah Sdn Bhd, located at Tasek Gelugor, Pulau Pinang. The wastewater treatment plant used Poly-Aluminum Chloride (PAC) as a coagulant and activated carbon (AC) to remove the colour of their wastewater.

Table 1. Characteristics of Tartrazine dye

Molecule structure	
Molecule formula	$C_{16}H_9N_4Na_3O_9S_2$
Molecular weight (g/mol)	534.4 g/mol
λmax (nm)	425

2.2   Physical treatment sludge (PTS)

The sludge was subjected to drying in an oven (Memmert UF110 Universal Oven) at 105 °C for 24 h to eliminate the moisture content, and it was denoted as raw sludge (RS). The RS was then crushed, sieved into less than 125 μm particle size, and calcinated at 600 °C for 1 hour in the furnace (Carbolite CWF1100). The calcined sludge was stored in the sample container and known as physical treatment sludge (PTS) adsorbent.

2.3   Chemical treatment sludge (CTS)

For chemical treatment sludge (CTS), 10 g of RS was mixed with 100 ml of 0.5 M phosphoric acid (H_3PO_4) for 12 - 24 hours at room temperature. The mixture was filtered and washed using distilled water until the pH reached 6-7. Then, the CTS was dried in an oven at 105 °C for 12 hours and sieved to less than 125 μm of particle size. The sample was labelled as CTS-H_3PO_4. Similar procedures were then repeated using 0.5 M nitric acid (HNO_3), and the sample was denoted as CTS-HNO_3 adsorbent.

2.4   Physico-chemical treatment sludge (PCTS)

Physico-chemical treatment sludge (PCTS) was prepared using physical and chemical treatment methods. At room temperature, 10 g of PTS was mixed with 100 ml of 0.5 M phosphoric acid (H3PO4) for 12 to 24 hours. The sample was filtered using filter paper and washed using distilled water until pH became 6-7. Then, the sample was dried at 105 °C for 12 hours using an oven and sieved to less than 125 μm of particle size, known as PCTS-H_3PO_4. Similar procedures were then repeated using 0.5 M nitric acid (HNO_3), and the sample was known as PCTS-HNO_3 adsorbent.

2.5   Adsorbent characterization

The Brunauer-Emmett-Teller (BET) surface area and pore structure of raw (RS) and modified adsorbents (PTS, CTS-HNO_3, CTS-H_3PO_4, PCTS-HNO_3 and PCTS-H_3PO_4) adsorbents were analyzed by nitrogen adsorption analysis using Micromeritics ASAP 2020. The degassed condition for the analysis was set under a vacuum at a temperature of 250 °C for 1 hour.

2.6   Batch adsorption study

The adsorption study for RS, PTS, CTS-HNO_3, CTS-H_3PO_4, PCTS-HNO_3 and PCTS-H_3PO_4 adsorbents was conducted in a batch system to study their ability to remove tartrazine dye from aqueous solution. In the batch adsorption experiments, a range of parameters were systematically investigated, including initial dye concentrations from 25 to 100 mg/L, initial pH spanning 3 to 11, and adsorbent dosages varying between 0.05 to 0.25 g/L. Raw sludge without modification (RS) was used as the control for the adsorption study. Initially, 0.2 g of adsorbent was mixed with 200 mL of 50 mg/L tartrazine dye solution in 250 ml conical flasks. The flasks were then closed and located in an incubator shaker (SI-300) at 25 °C with 150 rpm rotation speed for 120 min to ensure adsorption equilibrium. At regular intervals of 15 minutes, the samples were withdrawn from the conical flask using a 0.45 μm membrane syringe filter. The concentration of the samples was analyzed using a spectrophotometer (HACH DR2800) at a maximum wavelength of 425 nm. The amount of tartrazine dye adsorbed at equilibrium, q_e and time t, q_t, was measured using Eq. (1) and Eq.(2) [18].

$$q_t = \frac{V(C_0 - C_t)}{w} \times 100\%$$ (1)

$$q_e = \frac{V(C_0 - C_e)}{w} \times 100\% \tag{2}$$

The percentage of dye removal was determined using Eq. (3).

$$\% \ removal \ of \ dye = \frac{C_0 - C_t}{C_0} \times 100\% \tag{3}$$

where V is the total volume of solution (L), w is the adsorbent dosage (g), C_0 is the initial dye concentration (mg/L), C_t is the dye concentration at t time (mg/L), C_e is the dye concentration at equilibrium (mg/L). The best adsorbent was selected based on the highest percentage of dye removal for further analysis in batch adsorption, isotherm, and kinetic study. The optimum adsorption conditions were determined using one factor at a time for each parameter studied to obtain the maximum percentage removal of tartrazine dye.

2.7 Adsorption isotherm

During this experimental study, the adsorption data were subjected to modelling using the Langmuir and Freundlich isotherms to ascertain the equilibrium behaviour of the adsorption process. To validate the experimental data and its fitting to the Langmuir and Freundlich models, linear regression was employed. The Langmuir isotherm is monolayer adsorption with homogenous energy at binding sites. The Langmuir equation is given by Eq. (4) [10].

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{4}$$

The linearized equation of Langmuir isotherm model for plotting and analysis is expressed by Eq. (5).

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \tag{5}$$

where C_e is the concentration of the tartrazine dye solution at equilibrium (mg/L), q_e is the quantity of adsorbate adsorbed at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g) at monolayer coverage, and k_L is Langmuir adsorption constant.

Meanwhile, the Freundlich expression isotherm model considers an exponential relationship as a general heterogeneous adsorption surface energy distribution. The Freundlich isotherm model is given by Eq. (6) [10].

$$q_e = k_f C_e^{\frac{1}{n}} \tag{6}$$

The linearized equation of Freundlich isotherm model for plotting and analysis is expressed by Eq. (7):

$$ln q_e = ln k_f + \frac{1}{n}(ln C_e) \tag{7}$$

where k_F is the Freundlich adsorption constant, and n corresponds to the affinity of the adsorbate in the adsorbent.

2.8 Adsorption kinetic study

The linear equation corresponding to the Pseudo-first-order kinetic model is presented in Eq. (8) [19]:

$$ln \, (q_e \, - \, q_t \,) \, = \, ln \, (q_e) - \, k_1 t \tag{8}$$

where q_e is the quantity of adsorbate adsorbed at equilibrium (mg/g), q_t is the quantity of adsorbate adsorbed at time t (mg/g), and k_1 is the first-order rate constant of adsorption (1/h) or (1/min). The values of q_e and k_1 can be obtained from the linear plot graph of ln (q_e - q_t) vs. t plots.

The linear equation corresponding to the Pseudo-second order kinetic model is represented in Eq. (9) [19].

$$\frac{t}{q_t} \, = \, \frac{1}{k_2 q_e^2} + \, \frac{1}{q_e} t \tag{9}$$

where k_2 is the second-order rate constant of adsorption (g/mg.h) or (g/mg.min).

3. RESULTS AND DISCUSSION

3.1 Characterization of modified adsorbent

The Brunauer-Emmett-Teller (BET) surface area and pore structure of raw sludge and modified adsorbent were analyzed using Micromeritics ASAP 2020. Table 2 represents the physical characteristics of the adsorbent before and after several modification processes. It was observed that the BET surface area, average pore diameter and pore volume of physical treatment sludge (PTS) and physico-chemical treatment sludge (PCTS) were significantly increased with an increment of more than 180 m^2/g and 0.11 cm^3/g compared to the raw sludge. The significant increase in the surface area and pore volume of the modified adsorbent (PTS and PCTS) primarily resulted from the physical treatment, which led to the decomposition of organic compounds that existed in the adsorbent [20], followed by further treatment with the chemical agents. The modified adsorbents (PTS and PCTS) exhibited a remarkable increase in both surface area and pore volume.

Table 2. The physical characteristics of modified adsorbents.

	RS	PTS	CTS-HNO₃	CTS-H₃PO₄	PCTS-HNO₃	PCTS-H₃PO₄
Surface area (m^2/g)	363.32	540.76	368.48	342.27	599.64	571.10
Average pore diameter (nm)	3.36	3.11	3.51	3.59	3.02	3.08
Pore volume (cm^3/g)	0.31	0.42	0.32	0.31	0.45	0.44

In comparison to all different modification methods, the physico-chemical treatment using acid nitric (PCTS-HNO₃), which is the combination of physical and chemical treatment methods, has the highest increase in BET surface area and pore volume from 363.35 m^2/g to 599.64 m^2/g and 0.30 cm^3/g up to 0.45 cm^3/g, respectively. Meanwhile, PCTS-HNO₃ shows the lowest average diameter of 3.02 nm, corresponding to the mesopores range suitable for liquid phase adsorption. The finding obtained was in line with the previous study from Oke and Mohan [12], which reported that the BET surface area and pore

volume were increased from 84.33 m^2/g to 123.65 m^2/g and 0.16 cm^3/g to 0.36 cm^3/g after physicochemical modification using phosphoric acid (H$_3$PO$_4$).

However, the chemical treatment method using acid nitric (CTS-HNO$_3$) and phosphoric acid (CTS-H$_3$PO$_4$) did not significantly increase the adsorbents' surface area and pore volume. This was due to the chemical treatment primarily affecting the surface chemistry rather than the physical structure of the adsorbent. Furthermore, this treatment entails modifying functionality and impregnation with specific chemicals that do not much affect the physical properties of the sludge, such as porosity, particle size, and pore arrangement [21]. Therefore, the effect of chemical treatment tends to be minimal on the surface and pore volume of the chemically modified sludge adsorbents.

A substantial increase in the adsorbent's BET surface area and pore volume was anticipated to enhance the adsorption capacity and reduce diffusion resistance [22]. The greater availability of binding sites on the adsorbent material, resulting from the improved surface area and pore volume, enhanced adsorption performance. Thus, PCTS-HNO3 was expected to have the maximum adsorption capacity in removing the tartrazine dye among all the modified adsorbents.

3.2   Adsorption equilibrium studies

Effect of different adsorbent preparation methods

This study prepared several sludge-based adsorbents using different modification methods, including physical, chemical and physicochemical treatment. The different types of modification are expected to have variations in adsorption performance due to the different physical characteristics obtained from the characterization analysis. Therefore, a batch adsorption study was conducted using RS, PTS, CTS-HNO$_3$, CTS-H$_3$PO$_4$, PCTS-HNO$_3$ and PCTS-H$_3$PO$_4$ adsorbents to investigate their adsorption performance in removing the tartrazine dye at a constant pH of 3, an adsorbent dosage of 0.2 g, an initial concentration of 50 mg/L and 120 min of contact time.

Fig. 1 shows the percentage of tartrazine dye removal by time for RS, PTS, CTS-HNO$_3$, CTS-H$_3$PO$_4$, PCTS-HNO$_3$ and PCTS-H$_3$PO$_4$ adsorbents. An increase in the percentage removal of dye was observed for all tested adsorbents as time progressed. After 120 minutes of adsorption, PTS, PCTS-HNO$_3$, and PCTS-H$_3$PO$_4$ adsorbents demonstrated a near-complete dye removal of 100%. Notably, PCTS-HNO$_3$ exhibited the highest percentage of dye removal, reaching 97.42% within the initial 30 minutes, surpassing the performance of other adsorbents. This finding corresponded to the BET surface area of PCTS-HNO$_3$, which possesses the highest surface area compared to other adsorbents, which can provide a higher adsorption capacity. Thus, PCTS-HNO$_3$ adsorbent was chosen for further investigation in the subsequent adsorption studies.

Effect of different initial pH

The initial solution's pH is a critical factor that significantly impacts the adsorption capabilities of the adsorbent. To assess the impact of initial pH on the percentage of dye removal, the study explored a pH range of 3.0 – 11.0 while maintaining constant initial concentrations of 50 mg/L and adsorbent dosage of 0.2 g of PCTS-HNO$_3$. Fig. 2 depicts the effect of pH variation on the percentage of tartrazine dye removal over time. The finding revealed that the percentage of dye removal for tartrazine increased as the pH value of the solution decreased. The highest percentage of tartrazine dye removal, 99.78%, was observed at pH 3, while the lowest removal percentage, 41.40%, was recorded at pH 11 after 120 minutes of adsorption.

The pH value largely influences adsorption efficiency, as it governs the magnitude of the adsorptive molecule's electrostatic ionisation and the adsorbent's binding site properties [23]. At pH 3, the adsorbent surface carries a positive charge due to the acidic solution, fostering a strong electrostatic interaction with tartrazine, an anionic dye [24-25]. This favourable electrostatic interaction between the positive ion on the

adsorbent surface and the negative ion in the dye group leads to the highest adsorption performance under acidic pH conditions. On the other hand, at higher alkaline pH levels, OH- ions interact with the negatively charged dye particles, resulting in repulsive interactions that significantly reduce the percentage of dye removal. Consequently, it can be deduced that pH 3 represents the optimal initial pH for achieving the best adsorption of tartrazine dye using the PCTS-HNO₃ adsorbent.
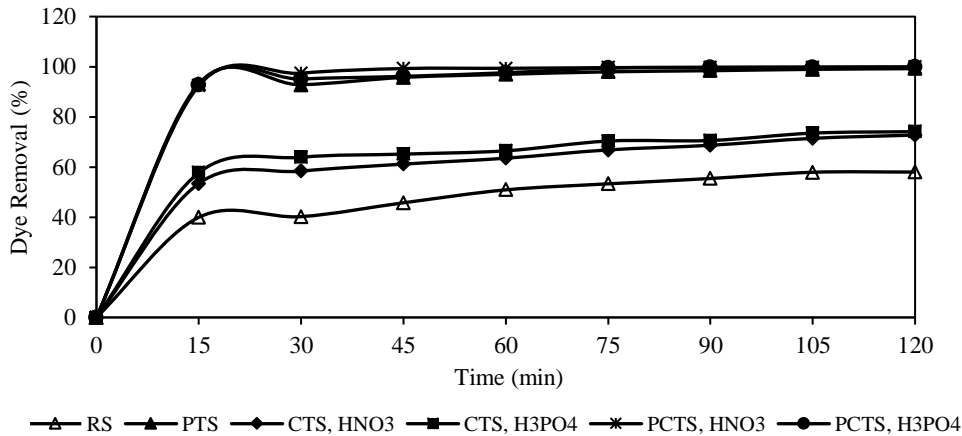

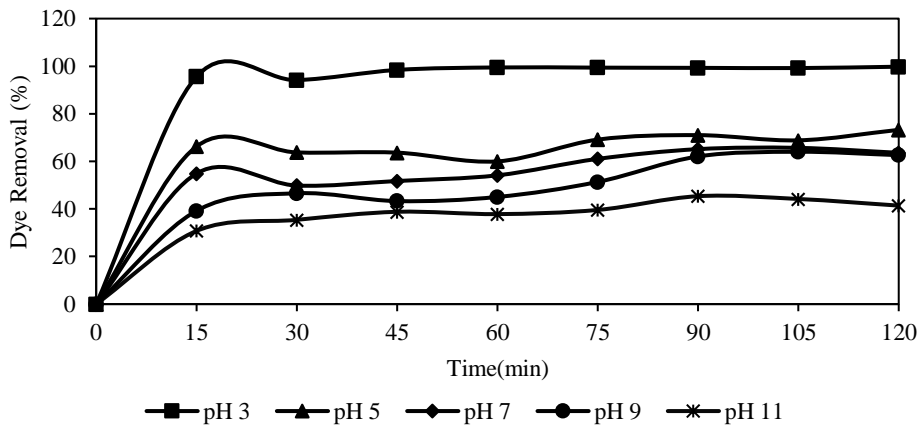Fig. 1. Effect of different modification treatments on the percentage removal of tartrazine dye.

Fig. 2. Effect of different initial pH on the percentage removal of tartrazine dye.

Effect of different adsorbent dosages

In this study, the investigation of adsorbent dosage aimed to assess the performance of the adsorbent and its ability to adsorb the dye effectively while also considering the economic feasibility of the optimum dosage. The effect of adsorbent dosage on the percentage of dye removal was investigated by varying amounts of PCTS-HNO₃ adsorbent from 0.05 g to 0.25 g at a fixed initial concentration of 50 mg/L and a pH of 3. As shown in Fig. 3, the dye percentage removal increased from 73.68% to nearly 100% with the escalation of adsorbent dosage from 0.05 g to 0.25 g. Based on the results, the adsorption process rapidly

increased during the initial 15 minutes, attributed to the easy accessibility of available sites on the adsorbent surface. Subsequently, as the surface adsorption sites gradually depleted, the uptake rate slowed, ultimately reaching equilibrium after 30 minutes of contact time.
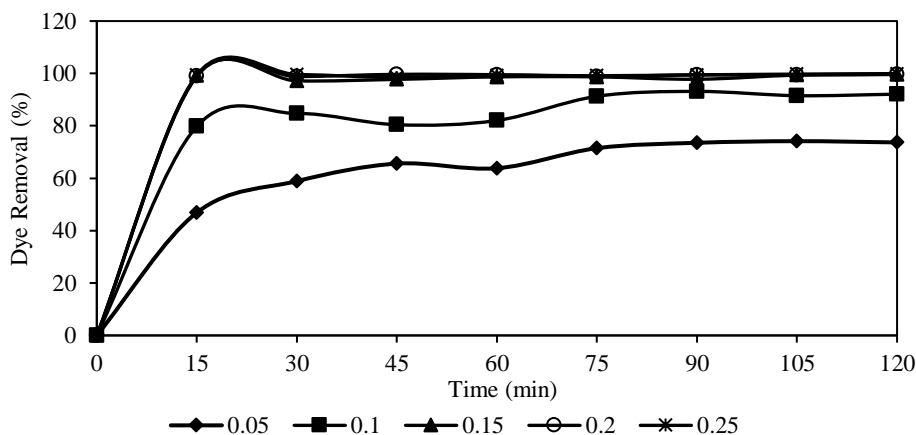

Fig. 3. Effect of different adsorbent dosages on the percentage removal of tartrazine dye.

Furthermore, the percentage of dye removal for 0.15 g, 0.20 g, and 0.25 g of PCTS-HNO$_3$ adsorbent was closer to each other by more than 99% after 120 min of contact time. This could be because all dye ions were completely absorbed by the active sites of the modified sludge-based adsorbent at 0.15 g and above. The findings aligned with previous research, demonstrating that higher adsorbent dosages lead to increased sorption sites across the adsorbent's surface area, thereby contributing to a higher percentage of dye removal [26]. Consequently, the optimal adsorbent dosage for tartrazine dye removal was found to be 0.15 g, as it achieved the maximum dye removal of up to 99.71%.

Effect of initial concentration of tartrazine dye

The initial dye concentration significantly influences the extent of dye removal. The impact of the initial dye concentration was examined concerning the availability of binding sites on the adsorbent surface area, which is directly related to the concentration of the dye solution [27]. Thus, the initial dye concentration was investigated within the 15-100 mg/L range at a fixed adsorbent dosage of 0.15 g and pH of 3. The effect of initial tartrazine dye concentration on the percentage of dye removal and adsorption capacity (mg/g) are illustrated in Fig. 4 (a) and Fig. 4 (b), respectively. The study revealed that an increase in the percentage of dye removal was associated with a decrease in initial dye concentration. At lower initial dye concentrations of 15, 25 and 50 mg/L, the percentage of dye removal was achieved by almost 100%. Increasing the initial concentration to 75 and 100 mg/L, on the other hand, resulted in slightly lower dye removal of 84.22% and 74.74%, respectively. Meanwhile, the adsorption capacity of the adsorbent showed a significant increase, rising from 20.67 mg/g to 99.61 mg/g as the initial concentration ranged from 15 to 100 mg/L, as shown in Fig. 4 (b).

Generally, the percentage of dye removal diminishes as the initial dye concentration increases, likely due to the saturation of adsorption sites across the adsorbent surface. The lower dye removal observed at higher initial dye concentrations of 75 and 100 mg/L can be attributed to the fixed available surface area of the adsorbent at a constant adsorbent dosage. The limitation of surface area reduces the adsorption capacity to uptake the number of moles of dye in the solution. On the other hand, a lower initial dye concentration offers weaker resistance to dye uptake, resulting in a higher mass transfer driving force, which in turn

promotes a higher adsorption rate [28]. Thus, the fixed dosage adsorbent used in adsorption cannot completely adsorb the excess mole of tartrazine dye at a high concentration solution.
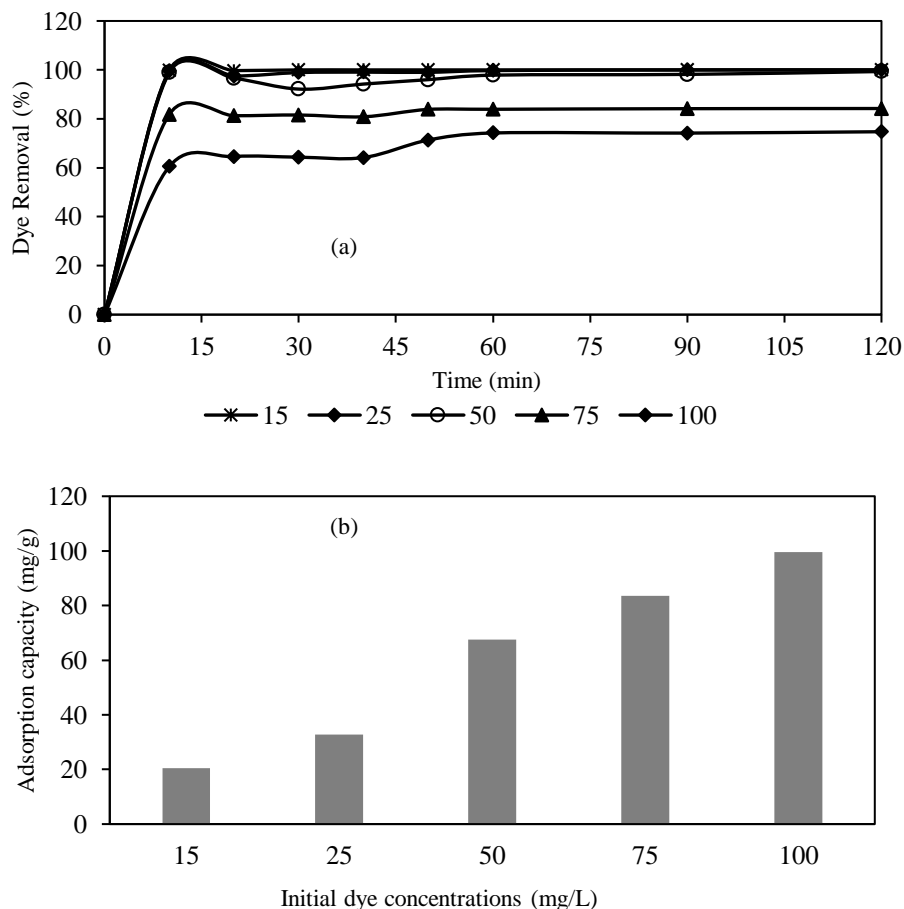

Fig. 4. Effect of different initial concentrations on the (a) percentage removal of tartrazine dye and (b) adsorption capacity (mg/g).

Adsorption isotherm

The adsorption isotherm study is essential in describing the adsorption mechanism of the adsorbate. This term refers to the distribution of adsorbate molecules between the solid and liquid phases at constant temperature and pH, respectively [29]. The capability of adsorbent adsorbing the adsorbate can be described via the equilibrium sorption isotherm. The surface characteristics and affinity of the adsorbent are distinguished by the specific constant obtained from the isotherm. To evaluate the reliability of the experimental data, the Langmuir and Freundlich adsorption isotherm models, expressed in Eq. (5) and Eq. (7), respectively, were employed.

Fig. 5 and Fig. 6 present the Langmuir and Freundlich isotherm models applied to the adsorption of tartrazine dye using PCTS-HNO$_3$ adsorbent. Meanwhile, the calculated isotherm constant and correlation coefficient are listed in Table 3. The experimental results revealed that the isotherm data are well fitted to the Langmuir isotherm with a correlation coefficient, R^2 of 0.9944 and a maximum adsorption capacity of 99.01 mg/g. Therefore, the adsorption process utilizing the PCTS-HNO$_3$ adsorbent was determined to be

monolayer adsorption. According to the Langmuir model, the adsorbent surface is structurally homogeneous, and the adsorption process leads to a monolayer mechanism where adsorbate molecules selectively attach to a restricted amount of adsorption sites on the surface [29]. Equilibrium is attained in the dye removal process when the adsorption rate becomes equivalent to the desorption rate. Once the adsorption process reaches equilibrium, there is no further interaction between the adsorbent and adsorbate molecules.
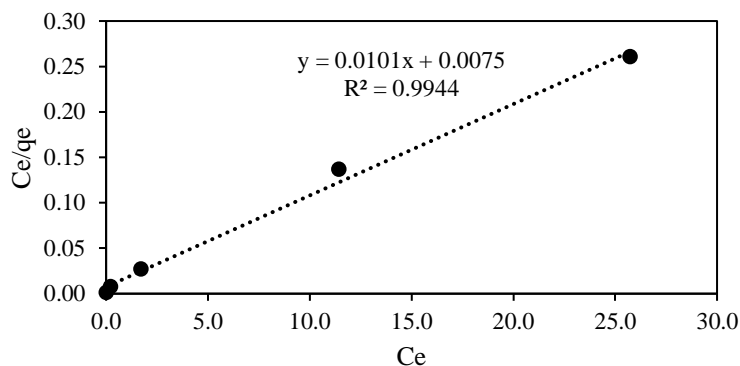

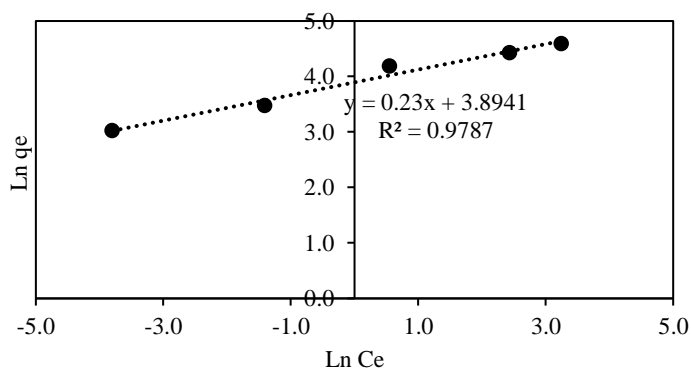Fig. 5. Langmuir model plot for tartrazine dye removal using PCTS-HNO$_3$.

Fig. 6. Freundlich model plot for tartrazine dye removal using PCTS-HNO$_3$.

Table 3. Adsorption isotherm parameter for Langmuir and Freundlich Equation

	Parameter	Value
Langmuir	k_L	1.35
	q_{max}	99.01
	R^2	0.9944
Freundlich	K_F	49.11
	n	4.35
	R^2	0.9787

The comparison of the maximum adsorption capacity (q_{max}) of several types of adsorbents used in the adsorption of the tartrazine dye reported in the previous study is shown in Table 4. The finding demonstrated that PCTS-HNO$_3$ obtained the highest q_{max} compared to the other adsorbents. Thus, PCTS-

HNO_3 was considered an economical and effective adsorbent in removing tartrazine dye from an aqueous solution.

Table 4. The maximum adsorption capacity is q max of several types of adsorbents for tartrazine dye removal.

Adsorbents	Operating conditions			q_{max} (mg/g)	References
	pH	Adsorbent dosage	Initial dye concentration		
Biochar	3	15 mg	50-140 mg/L	85.47	[30]
Boiler Residue	5	10 mg	30-200 mg/L	67.79	[31]
Saw Dust	3	5 g/L	1-15 mg/L	4.71	[32]
Biosorbent	3	0.2 g	25-200 mg/L	90.90	[33]
PCTS-HNO_3	3	0.15 g	25-100 mg/L	99.01	Present study

Adsorption kinetic

The adsorption kinetics is vital in measuring the adsorbent's adsorption rate throughout the process design [29]. The kinetics study further contributes to understanding the rate-limiting step and the mechanism underlying the adsorption of tartrazine dye using PCTS-HNO_3. Fig. 7 and Fig. 8 illustrate the kinetic adsorption data of the pseudo-first order and pseudo-second order models for tartrazine dye removal using PCTS-HNO_3 adsorbent. Table 5 presents the calculated data and parameters for both kinetic models.
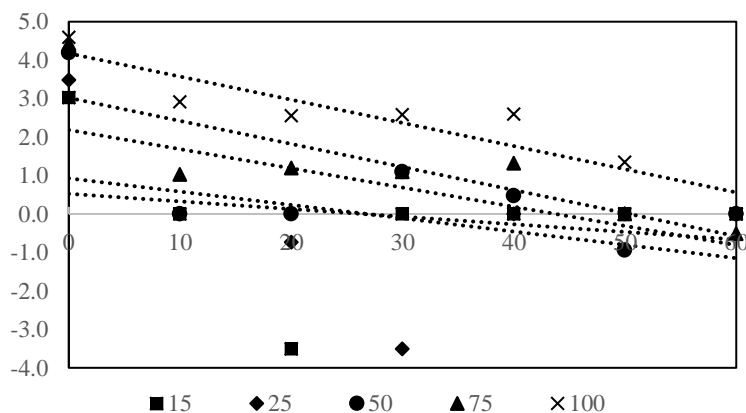

Fig. 7. Pseudo-first order kinetic plot for the removal of tartrazine dye by PCTS-HNO_3.

The Pseudo-first order model did not fit well with the experimental data, as indicated by the relatively low correlation coefficient (R^2) values between 0.05 and 0.84, as shown in Fig. 7. In contrast, the Pseudo-second-order kinetic model exhibited higher correlation coefficient (R^2) values, surpassing 0.99 for all initial dye concentrations ranging from 15 to 100 mg/L. Furthermore, the pseudo-second-order model also exhibited the closest values of adsorption capacity equilibrium, demonstrating excellent agreement between the calculated and experimental data. The pseudo-second-order kinetic model effectively described the rate-limiting step of the adsorption process, indicating that chemisorption governs the uptake of tartrazine dye using PCTS-HNO_3 adsorbent, rather than mass transfer between the fluid phase and adsorbent surface [29]. Meanwhile, the rate constants for the adsorption of tartrazine dye are 2.3620 min^{-1} to 0.0045 min^{-1}, corresponding to initial dye concentrations of 15 mg/L to 100 mg/L. The higher rate constant, k_2, was observed at a lower concentration of 15 mg/L for tartrazine dye due to the less competition among tartrazine dye molecules for surface adsorption sites. In contrast, at higher concentrations, the rate constant becomes

lower due to the limited availability of adsorption sites caused by the increased number of dye molecules [20].
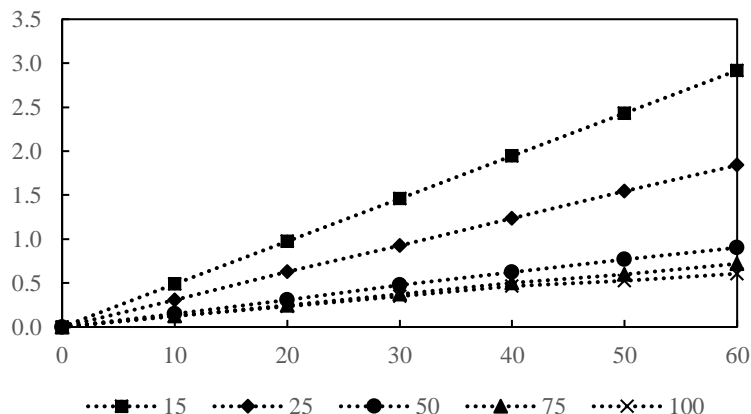

Fig. 8. Pseudo-second order kinetic plot for the removal of tartrazine dye by PCTS-HNO$_3$.

Table 5. Kinetic parameters for the removal of tartrazine dye by PCTS-HNO$_3$

Initial dye concentration (mg/L)	Pseudo-first-order kinetics				Pseudo-second-order kinetics			
	Qe,exp (mg/g)	Qe,cal (mg/g)	k_1 (min^{-1})	R^2	Qe,exp (mg/g)	Qe,cal (mg/g)	k_2 (min^{-1})	R^2
15	20.54	1.69	-0.0198	0.05	20.54	20.58	2.3620	1.00
25	32.38	2.53	-0.0346	0.13	32.38	30.86	0.1207	0.99
50	65.65	8.89	-0.0499	0.42	65.65	66.22	0.0400	0.99
75	83.93	20.49	-0.0599	0.68	83.93	83.33	0.0253	0.99
100	98.93	65.03	-0.0602	0.84	98.93	98.04	0.0045	0.99

4. CONCLUSION

Sludge produced from wastewater treatment plants of the coffee industry was proved to be an efficient adsorbent for removing tartrazine dye from an aqueous solution. Since the coffee industrial sludge has the potential to be used as an adsorbent, it provided a beneficial application to the industry in terms of environmental and economic concerns, as it could reduce mishandling sludge disposal and sludge disposal costs. Further treatment of the raw sludge by physicochemical treatment using acid nitric (PCTS-HNO$_3$) provided a higher BET surface area of 599.64 m^2/g, contributing to a high dye removal efficiency of nearly 100%. The best adsorbent dosage was more than 0.15 g/200 mL to achieve the maximum removal of tartrazine dye. In addition, the acidic condition of pH 3 has a major influence on tartrazine dye removal, providing greater electrostatic interaction between adsorbent and dye molecules. Thus, the best operating conditions for PCTS-HNO$_3$ adsorbent were attained at 0.15 g/L of adsorbent dosage and initial pH of 3 with a maximum adsorption capacity of 99.01 mg/g. The experimental data on tartrazine dye removal exhibited an excellent agreement with the Langmuir isotherm model and the pseudo-second-order model, indicating that chemisorption plays a vital role in removing tartrazine dye. Overall, the modified sludge-based adsorbent with the physicochemical method demonstrated the promising potential as a cost-effective solution for removing tartrazine dye from an aqueous solution.

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6.   CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest in publishing this paper.

7.   AUTHORS' CONTRIBUTIONS

Muhammad Firdaus Mohamad Pesol: Conceptualisation, methodology, investigation, formal analysis, and writing-original draft; **Nurulhuda Amri**: Conceptualisation, methodology, formal analysis, supervision, writing-review and editing; **Faraziehan Senusi**: Conceptualisation, formal analysis, and validation; **Siti Fatimah Abdul Halim**: Formal analysis, and validation; **Mohamad Sabri Mohamad Sidik**: Writing-review and format editing.

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