

## Isotherm, kinetics, and thermodynamics modelling for the removal of chemical oxygen demand, colour, and $\text{NH}_3\text{-N}$ from coffee processing wastewater by ion exchange resins

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### ABSTRACT

Coffee processing wastewater (CPW) is a highly polluted industrial wastewater that can be detrimental to the environment when it is discharged into a watercourse without treatment. The present study looks at the performance of a strong acid cation exchange resin and a strong base anion exchange on the removal of chemical oxygen demand (COD), colour, and ammoniacal nitrogen ( $\text{NH}_3\text{-N}$ ) from CPW using batch experiment. The experiments were carried out with varying pH, resin dosage (g), contact time (min), temperature ( $^{\circ}\text{C}$ ), and shaking speed (rpm). It was observed that over 70% reduction of  $\text{NH}_3\text{-N}$  was achieved under optimal conditions by cation exchange resin, while more than 70% COD, 60% colour removal was attained by anion exchange resin. Langmuir, Freundlich, and Brunauer–Emmett–Teller isotherm models were applied to determine the COD, colour and  $\text{NH}_3\text{-N}$  removal behaviour from CPW using cationic and anionic resins. The findings revealed that the Langmuir equation was the best-described isotherm model for removing COD, colour and  $\text{NH}_3\text{-N}$  from CPW using both cationic and anionic resins. The kinetic study showed that the removal of COD, colour, and  $\text{NH}_3\text{-N}$  was well-fitted with the pseudo-second-order kinetic model. Furthermore, it was observed that the diffusion was the rate-controlling process. The determination of the thermodynamic properties analyses showed that the COD, colour and  $\text{NH}_3\text{-N}$  removal from CPW using cationic and anionic resins was spontaneous and endothermic. The study suggests that both ion exchangers could reduce the concentration of pollutants in the coffee processing wastewater.

*Keywords:* Kinetics; Ion exchange resin; Chemical oxygen demand; Colour;  $\text{NH}_3\text{-N}$

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## 1. Introduction

Coffee production and processing have continuously gained a place worldwide. It is mainly produced in the tropics and consumed in the temperate region [1]. Globally, coffee is the second-largest most traded commodity after petroleum [2]. The production process involves using a large quantity of water, which results in a large volume of organically polluted wastewater. The constituent of coffee processing wastewater (CPW) include toxic chemicals such as polyphenols (3,000–4,000 mg/100 g) and caffeine (400–4,500 mg/100 g). The presence of sugars, proteins, and minerals in coffee, makes it a suitable substrate for organic pollution. During the roasting process, coffee bean components undergo structural changes leading to the formation of melanoidins. These are high molecular weight nitrogenous and brown-coloured compounds [3]. The dark brown coloured coffee wastewater poses a threat to aquatic life due to its high organic pollutants load, and thereby decreasing the supply of dissolved oxygen pollutants. Furthermore, the effects of the high organic pollutant load in CPW include skin irritation and breathing problems in human [4], retarded germination and growth in plants [5], and a reduction in aquatic diversity [6]. Thus, the treatment of CPW is necessary before discharge into a watercourse.

Conventional biological treatment processes are commonly employed to treat the CPW because of its low cost [1,7,8]. Nonetheless, the biological treatment processes for CPW have not been effective due to high concentrations of non-biodegradable compounds such as caffeine, lignin, tannins and humic acid [9,11]. Alternatively, physicochemical treatment processes have also been applied to remove contaminants from CPW such as electrocoagulation, electro-oxidation [10], Fenton, and photo-Fenton [11], zero-valent [12], advanced oxidation [13,14], coagulation/electro-oxidation [15], activated carbon [16,17]. These technologies are yet to be implemented in large-scale operations due to their high treatment cost, the toxic sludge they generate, and high energy demand.

Ion exchange resins are insoluble polymers that incorporate acidic or basic functional groups and have the ability to exchange counter ions within an aqueous solution around them [18]. The ion exchange process is an adsorption phenomenon where the mechanism is electrostatic [19]. Ions are adsorbed onto the charged functional groups of the ion exchange resins by electrostatic force on a 1:1 charge ratio basis [20]. The resins are made from an organic polymer substrate backbone. They are available in the form of small beads (1–2 mm). The bead is generally porous, providing a high surface area of 30–60 m<sup>2</sup>/g to maintain electro-neutrality. Ion exchangers have a fixed ionic group that is balanced by the counter ion. The selectivity characteristics of ion exchange are expressed in Eq. (1):



where A<sup>+</sup> is the counter ion, and (R<sup>-</sup>) B<sup>+</sup> represents the ion exchange resin. The ion exchange resin can be used to remove ionisable species from aqueous solutions [21]. It has also been reported that the strongly basic anion exchanger with quaternary ammonia functional groups could effectively remove

the colour from artificial wastewater [22]. Another study reported the effective removal of colour from textile wastewater using cation exchanger resin [23]. Numerous studies reported removing complex mixtures of organic compounds such as humic substances, dissolved organic matter, and natural organic matter using ion exchange resin [24–26]. Ion exchange resin was also used to successfully remove Nitrate-nitrogen in synthetic wastewater using three different strong base anion resin [27].

In this study, batch ion exchange tests using both cation and anion exchange resins were performed to study the removal of COD, colour, NH<sub>3</sub>-N from a CPW. The study further tries to answer how effective the method is in removing or reducing pollutants from CPW. The dynamic behaviour of adsorption on the effect of resin dose, contact time, agitation speed, temperature, and pH, Freundlich, Langmuir, Temkin, and Brunauer–Emmett–Teller (BET) isotherms, adsorption kinetics, and thermodynamics were also investigated.

## 2. Materials and methods

### 2.1. Wastewater sample collection

The CPW was collected using a simple grab method in a polyethylene container from a coffee processing plant in Seberang Perai Pulau Penang, Malaysia. The CPW collected was immediately transported to the laboratory and stored at 4°C to avoid biological changes before analysis, following the standard method for examining water and wastewater).

### 2.2. Materials

Concentrated H<sub>2</sub>SO<sub>4</sub> and NaCl were used for pH adjustment and media pre-treatment. Resins consisting of polystyrene matrix with amine group to form anion exchangers (NR+4 Cl) and sulfonated groups to form cation exchangers (–SO<sub>3</sub><sup>-</sup> H<sup>+</sup>) were obtained Zibo Fengjing International Trading CO., Ltd. Shandong, China for this study. Properties of the resins are given in Table 1. Chemicals used in the present study were of analytical grade, obtained from Sigma-Aldrich, Malaysia.

### 2.3. Batch experimental procedures

In each adsorption experiment, 100 mL of CPW was shaken in a 250 mL Erlenmeyer flask using an orbital shaker (model IKA KS4000i). The moisture content before use was 42%–48% and 45%–50% as given by the manufacturer. The experiment was preceded by rinsing both resins with distilled water to free them from adhering dirt and it was then soaked for 4 h in 100 mL of 1 M concentration of H<sub>2</sub>SO<sub>4</sub> for cation resin and 1 M concentration of NaCl for anion resin as recommended by the manufacturer to activate the nanopore structure. The resin was then rinsed continually with distilled water, and the pH of the supernatant was measured until pH was neutral in both cases. Experiments were carried out to investigate the effect of resin dose (5–50 g), shaking speed (50–400 rpm), contact time (5–210 min), pH (3–12), and temperature (30°C–70°C) under the condition where one parameter was varied, and the others remained constant. The supernatant was then

Table 1  
Properties of the cation and anion exchange resin

S/N	Properties	Cation	Anion
1	Moisture content (%)	45–50	42–48
2	Total exchange capacity (mmol/g)	≥4.5	≥3.5
3	Total exchange capacity (mmol/g)	≥2.0	≥1.35
4	Particle size range (%)	0.315–1.25 mm ≥ 95	0.315–1.25 mm ≥ 95
5	True density (g/mL)	1.26–1.30	1.07–1.10
6	Defined shear rate (%)	≥90	≥90
7	Bulk density (g/mL)	0.78–0.88	0.67–0.73
8	Effective grain size (mm)	0.40–0.70	0.40–0.70
9	Coefficient of uniformity	≤1.6	≤1.6
10	Type	Strong acid styrene gel resin	Strong base anion resin
11	Ionic form	Na <sup>+</sup>	Cl <sup>-</sup>

<sup>a</sup>Properties given by the manufacturer.

filtered through 0.45-micron filter paper using a vacuum pump and analysed for COD, colour, and NH<sub>3</sub>-N. The experiments were conducted in triplicate and the data represent the mean values from the triplicate experimental runs. The control experiment was carried out without the media to quantify the potential losses of contaminants during the experiment. Additionally, to ensure no leaching from the containers, experiments were conducted with a distilled water blank (with resin).

#### 2.4. Analytical method

Hach DR 2800 spectrophotometer Colorado USA was used to determine the concentration of all studied parameters according to the standard method of water and wastewater examination. The COD was measured based on the closed reflux calorimetric method (method 5220D), colour was calculated as true colour based on method 8025, and NH<sub>3</sub>-N was measured base on Nessler method 8038. The removal percentages of the response were determined based on Eq. (2):

$$\text{Removal}(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where  $C_i$  and  $C_f$  are the initial and final concentrations of COD, colour, and NH<sub>3</sub>-N in untreated and treated CPW, respectively.

#### 2.5. Isotherm modelling

Adsorption isotherms were used to describe the relationship between adsorbent (ion exchangers) and adsorbate (COD, colour, and NH<sub>3</sub>-N) in the solution. Adsorption experiments were carried out by mixing 100 mL of CPW by varying resin dosages (from 5 to 40 g for the cation resin treatment and 5–60 g for the anion resin). The optimum condition for pH, shaking speed and contact time obtained from the adsorption experiment was used to ensure equilibrium conditions for the cation and anion modelling

experiment. The amount of adsorption at equilibrium,  $q_e$  (mg/g), was calculated based on Eq. (3):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where  $q_e$  (mg/g) is the equilibrium adsorption capacity,  $C_0$  and  $C_e$  (mg/L) are the initial and final concentration of the wastewater and  $m$  is the mass of the dry resin in g, and  $V$  is the volume. The Langmuir, Freundlich, and BET adsorption isotherm models were used to describe the sorption equilibrium parameters in this study [27].

##### 2.5.1. Langmuir model

The theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface [28]. It is expressed in Eqs. (4) and (5):

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

The linear form of the equation is given as follows:

$$\frac{1}{q_e} = \frac{1}{Q_o K_L C_e} + \frac{1}{Q_o} \quad (5)$$

where  $q_e$  is the amount of adsorbate per unit mass of adsorbent (mg/g),  $Q_o$  (mg/g), and  $K$  (L/mg) refer to the saturation solid-phase concentration and the rate of adsorption (L/mg).  $C_e$  is the equilibrium liquid phase concentration of the adsorbate (mg/L). A linear graph of  $1/q_e$  was plotted against  $1/C_e$ .

$$R_L = \frac{1}{1 + K_L C_i} \quad (6)$$

The Langmuir isotherm can be expressed using the dimensionless factor  $R_L$  defined as in Eq. (6). The  $R_L$  shows

the type of possible adsorption thus favourable  $0 < 1 < R_L$ , linear  $R_L = 1$ , unfavourable  $R_L > 1$  or irreversible  $R_L = 0$  [29].

### 2.5.2. Freundlich adsorption isotherm

The equation applied to describe the model is expressed in Eq. (7) [30].

$$q_e = K_F C_e^{1/n} \quad (7)$$

where  $K_F$  (L/g) and  $n$  are the Freundlich constants, they reflect the adsorption capacity at  $C_e = 1$  and the adsorption intensity, respectively. The linear form of the Freundlich equation is expressed as in Eq. (8):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

### 2.5.3. Brunauer–Emmett–Teller (BET) model

The theory is an extension of the Langmuir model from a monolayer adsorption system to a multilayer system, where the interactions between molecules of different layers exist [31]. The linear form of the equation is presented in Eq. (9) as follows:

$$\frac{C_e}{(C_i - C_e)q_e} = \frac{1}{K_{\text{BET}} \cdot q_m} + \left[ \frac{K_{\text{BET}} - 1}{K_{\text{BET}} \cdot q_m} \right] \left[ \frac{C_e}{C_i} \right] \quad (9)$$

where  $C_i$  and  $C_e$  denote the concentration of initial and final wastewater,  $K_{\text{BET}}$  is constant,  $q_m$  and  $q_e$  represent the maximum amount adsorbed on a monolayer and the maximum amount adsorbed under equilibrium conditions.

## 2.6. Kinetic and thermodynamic studies

The kinetic experiments were conducted using 100 mL of raw CPW. Samples were taken at different time intervals for measurement; (0–150 min) in the case of treatment via cation exchange resin and (0–240 min) in the case of treatment by anion exchange resin. The amount of pollutant adsorbed onto the resin at time  $t$  ( $q_t$ ) is calculated based on Eq. (10). The kinetic process at different times was described by the pseudo-first-order, pseudo-second-order, and intra-particle model using linear regression.

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (10)$$

where  $q_t$  (mg/g) is the equilibrium adsorption capacity at time  $t$ ,  $C_0$  and  $C_t$  (mg/L) is the initial concentration and the concentration of the adsorbate at time  $t$ .  $V$  is the volume, and  $m$  is the mass of the dry resin in grams. Lagergren pseudo-first-order and pseudo-second-order kinetics was used to describe the kinetic behaviour of the ion exchange, whether the adsorption type was physisorption or chemisorption. Intra-particle diffusion was the model that was accessed to determine the rate-controlling process.

### 2.6.1. Pseudo-first-order kinetics

The equation is expressed in Eq. (11) as presented by Lagergren [32]:

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad (11)$$

where  $q_e$  is the amount of COD, colour and  $\text{NH}_3\text{-N}$  adsorbed at equilibrium and  $q_t$  is the amount of COD, colour and  $\text{NH}_3\text{-N}$  adsorbed on ion exchange resin at time  $t$ .  $K_1$  is the rate constant (1/min). The linear form of Lagergren first-order-rate equation is as presented in Eq. (12) [31]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (12)$$

### 2.6.2. Pseudo-second-order kinetics

The model forecasts the performance over the entire adsorption spectrum and pseudo-second-order equations based on adsorption by equilibrium is expressed in Eq. (13) [32]:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad (13)$$

where  $q_e$  is the amount of COD, colour and  $\text{NH}_3\text{-N}$  adsorbed onto ion exchange resin at equilibrium (mg/g),  $K_2$  is the rate constant of pseudo-second-order sorption (g/h mg).  $q_t$  is the amount of adsorbate adsorbed per unit weight of the resin at a time,  $t$  (mg/g); incorporating Eq. (13) for boundary conditions  $t$  and  $q_i = 0$ ,  $t = t$ , and  $q_i = q_t$  gives the following Eq. (14):

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (14)$$

The linearised form of the pseudo-second-order model is given by the equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (15)$$

### 2.6.3. Intra-particle diffusion

The model states that the overall adsorption process may be controlled either by one or more steps such as external diffusion, pore diffusion, surface diffusion, or by a combination of more than one step. It is expressed in Eq. (16):

$$q_t = k_{\text{pi}} t^{1/2} + C_i \quad (16)$$

where  $k_{\text{pi}}$  is the intra-particle diffusion rate constant (mg/g min<sup>0.5</sup>),  $t^{1/2}$  is the time for half adsorption of COD, colour and  $\text{NH}_3\text{-N}$ .  $C_i$  is the intercept called the Weber–Morris diffusion constant [33,34].

## 2.7. Thermodynamics

The model is used to estimate the nature of the sorption process. At the temperature of 30°C, 40°C, 50°C, 60°C, and 70°C, the thermodynamics parameter for COD, colour, and NH<sub>3</sub>-N adsorption on to cation and anion exchange resin was estimated based on Gibbs free energy  $\Delta G$  equation (Eq. (17)), enthalpy  $\Delta H$ , and entropy  $\Delta S$ . The change in Gibbs energy during the adsorption process is expressed by Van't Hoff as shown in Eqs. (18) and (19):

$$\Delta G = -RT \ln K_0 \quad (17)$$

$$\ln K_0 = \left( \frac{\Delta S}{R} - \frac{\Delta H}{RT} \right) \quad (18)$$

$$\Delta G = (\Delta H - T\Delta S) \quad (19)$$

where  $R$  is the gas constant (8.314 J/mol K),  $T$  is the absolute temperature,  $K_0$  is the adsorption equilibrium constant [35].

## 3. Results and discussion

### 3.1. Characterisation of CPW

CPW is characterised by low pH (3.5–4.2), this could be as a result of high production of volatile fatty acid during acidification caused by high organic matter compounds [36], it can also be caused by the formation of acetic acid from the fermentation of sugar. High conductivity value of 221–354  $\mu\text{S}/\text{cm}$ ; COD 2,309–7,328 mg/L; colour 2,512–5,342 mg/L and NH<sub>3</sub>-N (124.67–197.67) indicated the presence of tannin, pectin, protein, and sugar [37]. The result shows similarity with other studies both in Malaysia [38] and other parts of the world [39]. From the characterisation result in Table 2, The parameters analysed did not comply with the Malaysian regulation limits for Environmental Quality (Industrial Effluents) 2009 Department of Environmental Malaysia, 2018 Standard B.

### 3.2. Adsorption study

#### 3.2.1. Effect of dosage

The effect of resin dosage is the most critical parameter to consider in the adsorption process since it determines the ability of the adsorbent to remove the adsorbate. Fig. 1 shows the results for removing COD, colour, and NH<sub>3</sub>-N in CPW using both cation (a) and anion (b) exchange resin. At room temperature, default wastewater pH, a fixed contact time of 90 min, and shaking speed 200 rpm obtained from preliminary experiments, the resin doses were varied. From the result, the optimum dose was obtained at 35 g of cation exchange resin, whereby the highest removal of COD and colour was 29.19% and 24.97%, respectively. The reduction of NH<sub>3</sub>-N concentration in CPW increased to an optimum of 70.54% with the increase of adsorbent dose; this could be because of the availability of more exchangeable media sites.

Moreover, the reduction of COD and colour can be hypothesised to be physisorption [40]. In the case of removal

Table 2  
Characteristics of raw coffee effluent over 12 months

Parameter	Min	Max	Standard <sup>a</sup>
pH	3.5	4.2	5.5–9.0
Residual conductivity ( $\mu\text{S}/\text{cm}$ )	221	354	–
Temperature (°C)	29.0	34.0	40
Colour (pt.co)	2,512	5,342	200
BOD <sub>5</sub> (mg L <sup>-1</sup> )	1,136	3,200	50
COD (mg L <sup>-1</sup> )	2,309	7,328	200
Turbidity (NTU)	147	179	–
TDS (mg L <sup>-1</sup> )	124.67	197.67	50
NH <sub>3</sub> -N (mg L <sup>-1</sup> )	137	478	100

COD: Chemical oxygen demand; BOD: Biological oxygen demand; TDS: total dissolved solids.

<sup>a</sup>Environmental quality regulation 209 under the laws of Malaysia Environmental Quality Act (MEQA)1974(MDC,1997).

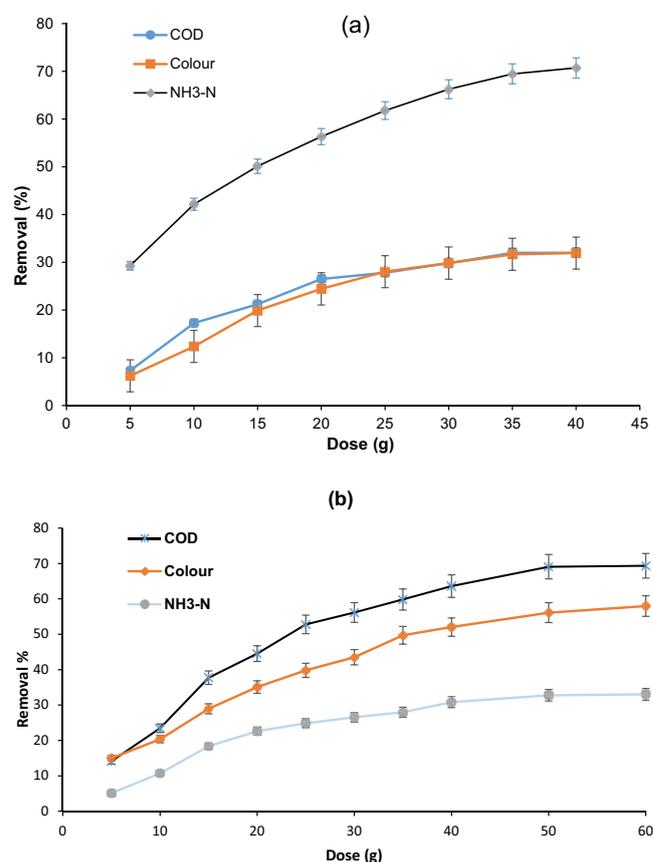


Fig. 1. Effect of resin dosage on the removal of chemical oxygen demand, colour, and NH<sub>3</sub>-N by cation exchange resin (a) (at 90 min, 200 rpm) and anion exchange resin (b) (at 120 min, 250 rpm).

by anion resin, the pH was adjusted to neutral as obtained from preliminary studies; it was also observed that pollutant removal increase with an increase in dosage. The highest reduction of 61.18% of COD, 55.41% of colour, 26.8% of NH<sub>3</sub>-N was achieved at 45 g of anion resin dosage.

Additionally, it was observed that less dosage of cation was required to remove the pollutant as compared with anion exchange resin dosage used to remove negatively charged species. This could be due to fact that the concentration of ammonium in water was far less than that of COD and colour as shown in the characterization studies in Table 1.

### 3.2.2. Effect of contact time

The removal percentage of COD, colour and  $\text{NH}_3\text{-N}$  increased with an increase in the contact time until it reached the optimum of 120 min in the case of treatment via cation resin as illustrated in (Fig. 2a); this can be attributed to the saturation of exchangeable sites. Additionally, maximum COD and colour removal were achieved at 90 min. In the case of treatment via anion resin, the removal percentage of pollutants also increased with the increase in contact time until it reached a maximum of 180 min, as shown in Fig. 2b. The result further show that removal by anion resin takes more time in comparison with cation resin; this could be attributed to a few numbers of cations present in coffee wastewater making it faster for cation to exchange.

### 3.2.3. Effect of shaking speed

The effect of shaking speed was examined by varying the speed of the orbital shaker from 50 to 400 rpm using the optimum resin dose and contact time obtained above. The result indicated that pollutant removal increased

steadily until it reached 300 rpm before stabilizing in the case of treatment via cation exchange resin as presented in Fig. 3a, and 200 rpm in the case of treatment via anion exchange resin as illustrated in Fig. 3b. Therefore, shaking speed has a considerable effect on pollutant removal in the treatment process.

### 3.2.4. Effect of wastewater pH

The pH of a solution plays a significant role in the removal of adsorbate during wastewater treatment. The influence of pH on the treatment process was investigated at different pH conditions (3–11). As presented in Figs. 4a and b, the removal of COD, colour decreased with an increase in pH until it reached neutral pH 6. This could be attributed to the water losing its acidity. Likewise,  $\text{NH}_3\text{-N}$  removal decreased with an increase in pH, possibly because of the unavailability of enough  $\text{H}^+$  in the solution for exchange. High acidity resulted from the increased alkalinity removal and the inter-exchange between positive  $\text{H}^+$  ions and the negative ions from weak organic compounds. In the case of treatment via anion resin, the reverse was the case. An increase in pH increases the negatively charged species, thus removing negatively charged organic compounds. However, it was found that the removal of COD and colour increased with increasing pH until it reached its maximum at pH 8.0. Over the

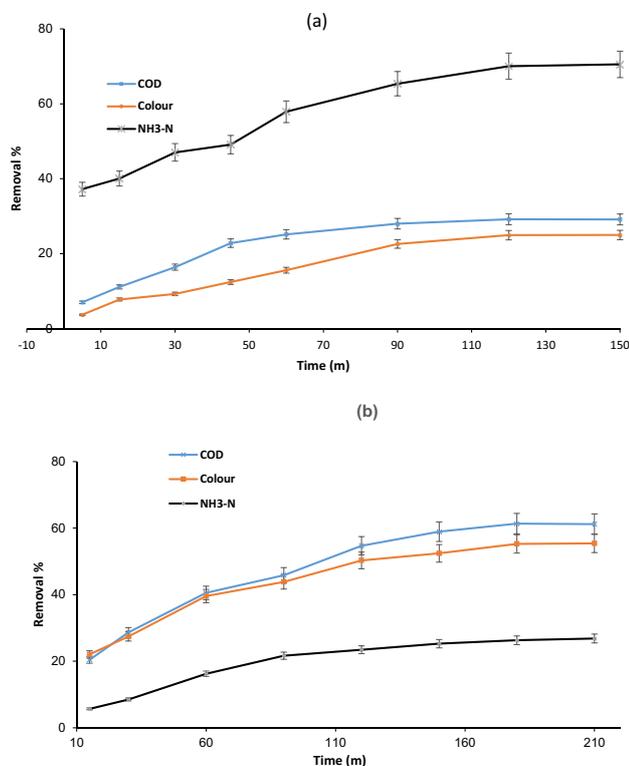


Fig. 2. Effect of contact time on the removal of chemical oxygen demand, colour, and  $\text{NH}_3\text{-N}$  by cation exchange resin (a) (using 35 g, 200 rpm) and anion exchange resin (b) (using 45 g, 250 rpm).

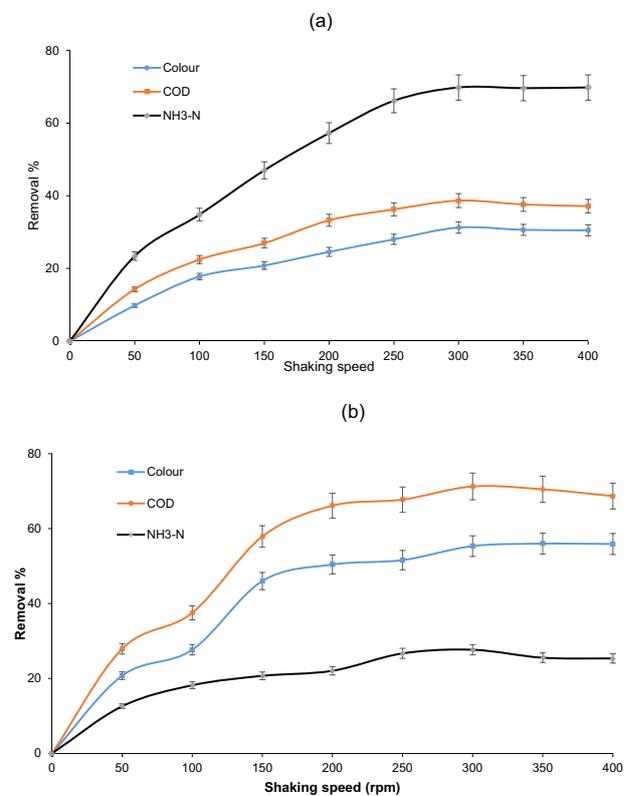


Fig. 3. Effect of shaking speed on the removal of chemical oxygen demand, colour, and  $\text{NH}_3\text{-N}$  by cation exchange resin (a) (using 35 g for 120 min), and anion exchange resin (b) (using 45 g for 180 m).

pH 8, the removal of COD and colour decreased with further increasing of pH. This might be due to the repulsive reaction between active site of anionic resin and organic pollutants [10]. The minimum reduction was observed in the case of  $\text{NH}_3\text{-N}$  removal, which could be due to the volatilization of  $\text{NH}_3$  at high pH.

### 3.2.5. Effect of temperature

The effect of temperature on the removal of COD, colour, and  $\text{NH}_3\text{-N}$  was studied by varying the temperature from room temperature to  $80^\circ\text{C}$ . As illustrated in Fig. 5, there is very little influence of temperature on the removal of COD, colour and  $\text{NH}_3\text{-N}$  in both treatments using cation and anion exchange resin; this shows that the reaction is endothermic and is similar to other studies [41]. Therefore subsequent experiments were carried out at room temperature ( $30^\circ\text{C} \pm 1^\circ\text{C}$ ).

### 3.3. Equilibrium studies

For surface modelling, BET, Langmuir and Freundlich adsorption isotherm models were used to describe the sorption equilibrium parameters in this study as earlier stated. These models are helpful in explaining the ion-exchange behaviour of metals on resins [42,43].

#### 3.3.1. Cation resin surface modelling plots

From the result in Table 3, the Langmuir correlation coefficient  $R^2$  values for COD, colour and  $\text{NH}_3\text{-N}$  are 0.706, 0.6085 and 0.9904, respectively, which is higher than the Freundlich and BET models; hence, the Langmuir model fits well with the data [42].

It was observed that adsorption capacity increased with a decrease in dosage. The COD and colour adsorption capacities on the cation resin were relatively low, having 3.15 and 1.25 mg/g; the adsorption capacity of 5.11 for  $\text{NH}_3\text{-N}$ , though is considered low but is similar to other studies on removal of  $\text{NH}_3\text{-N}$  from wastewater [44]. The low adsorption capacity could likely be due to the presence of other competing cations. The Langmuir isotherm dimensionless factor  $R_{LL}$  defined as in Eq. (9), it was deduced that the adsorption of COD, colour and  $\text{NH}_3\text{-N}$  onto cation resin is favourable,  $R_{LL}$  are determined to be 0.5476, 0.25168, and 0.6996, respectively.

#### 3.3.2. Anion resin surface modelling plots

Similarly, from the result in Table 4, Langmuir correlation coefficient  $R^2$  values for COD, colour, and  $\text{NH}_3\text{-N}$  onto anion resin were 0.9041, 0.9447, and 0.7932, respectively. Although the  $R^2$  values are closely related, they are higher than Freundlich and BET models; consequently, the data better fit the Langmuir model than the other two [42].

It was also observed that adsorption capacity increase proportionally as the resin dosage was decreased. The maximum capacities for COD and colour adsorption on the anion resin were relatively high, having 49.26 and 20.70 mg/g; the adsorption capacity of 0.54 for  $\text{NH}_3\text{-N}$  show that there was limited ion exchange. The Langmuir isotherm dimensionless factor  $R_{LL}$  defined in Eq. (9) for COD, colour, and  $\text{NH}_3\text{-N}$

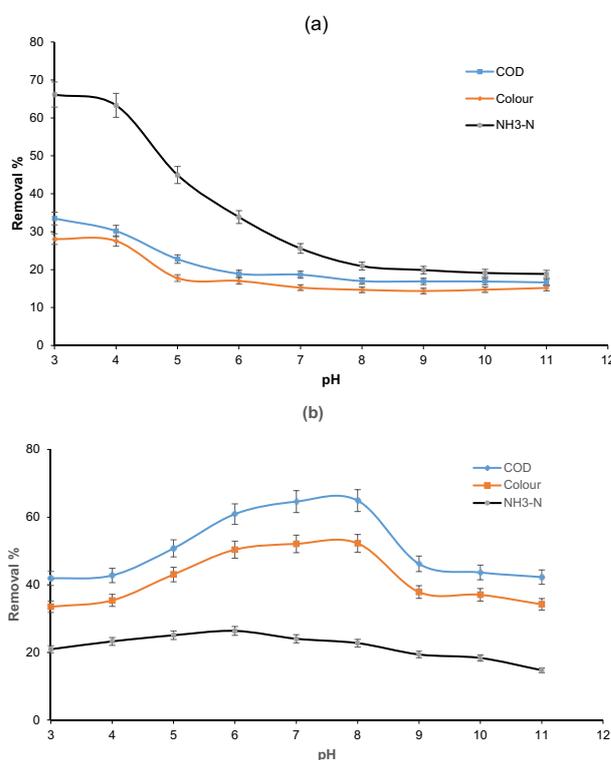


Fig. 4. Effect of pH on the removal of chemical oxygen demand, colour, and  $\text{NH}_3\text{-N}$  by cation exchange resin (a) (using 35 g, at 120 min and 300 rpm), and anion exchange resin (b) (using 45 g at 180 min, using 200 rpm).

adsorption onto cation resin is favourable,  $R_{LL}$  is determined to be 0.7436, 0.685, and 0.0004, respectively.

Therefore, COD and colour ion exchange isotherms for the cation resin were not described well by the models tested, while the  $\text{NH}_3\text{-N}$  isotherm was represented quite well in the case of treatment with cation resin. Conversely, for the anion exchange isotherms, the COD and colour data were described well, while that for the  $\text{NH}_3\text{-N}$  ion exchange was not. The result is similar to the one in the study by Yang et al. [45] when bromate was removed from water by ion exchange.

#### 3.3.3. Kinetic study via cation exchange resin

To determine the adsorption kinetics of COD, colour and  $\text{NH}_3\text{-N}$  onto cation and anion exchange resin, linear plots of  $t/q_t$  and  $\log(q_e - q_t)$  were plotted against time ( $t$ ) for pseudo-first-order and pseudo-second-order models, respectively. Additionally,  $q_t$  was plotted against  $t^{0.5}$  for intra-particle diffusion, while the values of  $K_1$ ,  $K_2$ ,  $K_3$ ,  $R^2$ , and the calculated  $q_e$  are presented in Tables 5 and 6.

It can be deduced from Table 5 that the determined correlation coefficient ( $R^2$ ) for the pseudo-second kinetic model and intra-particle diffusion model was greater than 0.9 and close to unity for all parameters, which was not the case of a first-order kinetic model. The high correlation coefficient ( $R^2$ ) values suggested that the model accurately

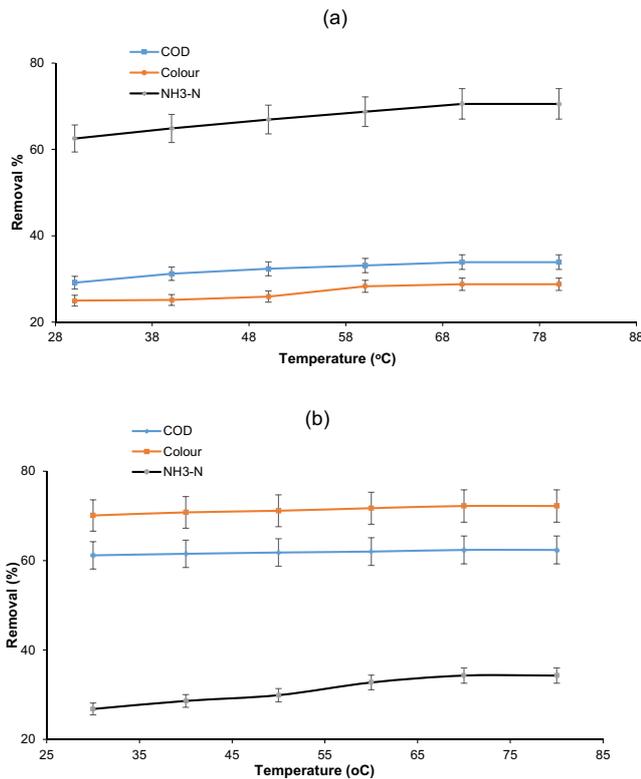


Fig. 5. Effect of temperature on the removal of chemical oxygen demand, colour, and NH<sub>3</sub>-N by cation exchange resin (a) using 35 g, at 120 min and 300 rpm, and anion exchange resin (b) using 45 g at 180 min, using 200 rpm.

described the parameter. Also, the equilibrium sorption capacities ( $q_e$ ) estimated from pseudo-second-order models were found to be in line with the experimental values in terms of COD, colour and NH<sub>3</sub>-N adsorption. Hence, the

pseudo-second-order kinetic model's sorption reaction was more favourable than the first-order kinetics, suggesting that the reaction was a chemisorption process. This result is similar to other studies [34,46,47].

### 3.3.4. Kinetic study via anion exchange resin

Table 6 summarises the parameters of the kinetic studies. Similarly, the result suggests that the pseudo-second-order models and intra-particle diffusion model describe the model well. The calculated  $q_e$  values were found to agree with the experimental  $q_e$  values. Moreover, the  $R^2$  values obtained from the pseudo-second-order model for COD, colour, and NH<sub>3</sub>-N adsorption onto anion resin were relatively high in comparison with the pseudo-first-order model; thus, the result demonstrated agreement with the pseudo-second-order model and intra-particle diffusion model on the experimental data. Consequently, indicating that the mechanism of adsorption can either be chemisorption or intra-particle diffusion. The result is similar to other works of literature [48–50].

### 3.4. Thermodynamics

The thermodynamic parameters were calculated by plotting the  $\ln K_0$  vs.  $1/T$  graph for COD, colour, and NH<sub>3</sub>-N adsorption on both ion exchange resin. The values of enthalpy  $\Delta H$  and entropy  $\Delta S$  were obtained from the slope and intercept and given in Tables 7 and 8. The result showed that the positive value of enthalpy change  $\Delta H$  shows that the adsorption COD, colour, and NH<sub>3</sub>-N is endothermic. The negative value of  $\Delta G$  decreases with an increase in temperature, indicating that the reaction is spontaneous and demonstrating that the higher temperatures facilitate the adsorption. The obtained positive values of  $\Delta S$  showed the affinity of cation and anion exchange resin to remove COD, colour and NH<sub>3</sub>-N the increasing

Table 3 Isotherm equation parameters for COD, colour, and NH<sub>3</sub>-N adsorption onto cation exchange resin

Parameters	Langmuir model				Freundlich model			BET model		
	$R^2$	$K_L$	$R_L$	$q_e$	$R^2$	$K_f$	$1/n$	$R^2$	$K_{BET}$	$q_e$ (mg/g)
COD	0.706	0.00023	0.5476	3.1506	0.6897	5.5E-07	0.494218	0.679	-1.6524	0.14901
Colour	0.6085	0.0009	0.25168	1.25471	0.5908	0.00042	0.862515	0.7676	1.26194	-0.1194
NH <sub>3</sub> -N	0.9904	0.00107	0.69958	5.10986	0.9879	0.00164	0.783883	0.9673	5.88748	0.77065

COD: Chemical oxygen demand.

Table 4 Isotherms equation parameters for COD, colour and NH<sub>3</sub>-N adsorption onto anion exchange resin

Parameters	Langmuir model				Freundlich model			BET model		
	$R^2$	$K_L$	$R_L$	$q_m$	$R^2$	$K_f$	$n$	$R^2$	$K_{BET}$	$q_e$ (mg/g)
COD	0.9041	1E-04	0.74357	49.2611	0.8859	0.00467	0.40263	0.8248	-2.799	2.2007
Colour	0.9447	0.0001	0.68348	20.7039	0.9086	4.1E-09	0.357334	0.8985	-3.198	1.47645
NH <sub>3</sub> -N	0.7932	7.07263	0.0004	0.54048	0.5742	3.3E-05	0.61185	0.6648	-0.514	0.02476

Table 5  
Kinetic parameters for adsorption of COD, colour, and NH<sub>3</sub>-N onto cation exchange resin

Response	Pseudo-first-order				Pseudo-second-order			Intra-particle diffusion		
	$q_{e,exp}$	$R^2$	$K_1$	$q_e$	$R^2$	$K_2$	$q_e$	$R^2$	$K_{IPD}$	$q_e$
COD	2.98	0.6446	0.0307	3.059	0.9903	0.0106	3.5790	0.9609	0.0658	3.9122
Colour	1.82	0.8014	0.0487	4.480	0.9044	0.0056	2.6695	0.9609	0.0658	3.9122
NH <sub>3</sub> -N	0.69	0.955	0.022	1.968	0.9854	0.0712	0.7540	0.9609	0.0658	3.9122

Table 6  
Kinetic parameters for adsorption of COD, NH<sub>3</sub>-N onto anion exchange resin

Response	Pseudo-first-order				Pseudo-second-order			Intra-particle diffusion		
	$q_{e,exp}$	$R^2$	$K_1$	$q_e$	$R^2$	$K_2$	$q_e$	$R^2$	$K_{IPD}$	$q_e$
COD	5.11	0.949	0.020	5.517	0.993	0.00324	6.46412	0.925	0.087	55.38
Colour	3.02	0.845	0.027	4.346	0.996	0.00309	3.57654	0.925	0.087	55.38
NH <sub>3</sub> -N	0.23	0.977	0.021	0.289	0.992	0.07124	0.32052	0.925	0.087	55.38

Table 7  
Thermodynamic equilibrium parameters for adsorption of COD, colour and NH<sub>3</sub>-N on cation resins at different temperature

COD				Colour				NH <sub>3</sub> -N			
$T$	$\Delta H$	$\Delta S$	$\Delta G$	$T$	$\Delta H$	$\Delta S$	$\Delta G$	$T$	$\Delta H$	$\Delta S$	$\Delta G$
303.15	15.516	0.061	-33.914	303.15	4.9310	0.0748	-27.615	303.15	1.6121	0.0241	-8.9212
313.15	15.516	0.061	-34.521	313.15	4.9310	0.0748	-28.363	313.15	1.6121	0.0241	-9.1623
323.15	15.516	0.061	-35.128	323.15	4.9310	0.0748	-29.111	323.15	1.6121	0.0241	-9.4034
333.15	15.516	0.061	-35.735	333.15	4.9310	0.0748	-29.859	333.15	1.6121	0.0241	-9.6445
343.15	15.516	0.061	-36.342	343.15	4.9310	0.0748	-30.608	343.15	1.6121	0.0241	-9.8856

Table 8  
Thermodynamic equilibrium parameters for adsorption of COD, colour and NH<sub>3</sub>-N on anion resins at different temperature

COD				Colour				NH <sub>3</sub> -N			
$T$	$\Delta H$	$\Delta S$	$\Delta G$	$T$	$\Delta H$	$\Delta S$	$\Delta G$	$T$	$\Delta H$	$\Delta S$	$\Delta G$
303.15	-3.827	0.042	-16.431	303.15	-10.983	0.0599	-29.12	303.15	-7.544	0.0316	-17.12
313.15	-3.827	0.042	-16.846	313.15	-10.983	0.0599	-29.72	313.15	-7.544	0.0316	-17.44
323.15	-3.827	0.042	-17.262	323.15	-10.983	0.0599	-30.33	323.15	-7.544	0.0316	-17.75
333.15	-3.827	0.042	-17.678	333.15	-10.983	0.0599	-30.93	333.15	-7.544	0.0316	-18.07
343.15	-3.827	0.042	-18.093	343.15	-10.983	0.0599	-31.52	343.15	-7.544	0.0316	-18.39

COD: chemical oxygen demand.

randomness. The positive value of  $\Delta H$  indicated the endothermic nature of the adsorption process. This result agrees with other studies [34]. Contrarily, in other studies, adsorption of molecular phenol species on N-butylimidazolium functionalized strongly basic anion exchange resin with Cl<sup>-</sup> anion (MCl) was found to be exothermic under acidic pH [41].

#### 4. Conclusion

In this study, COD, colour, and NH<sub>3</sub>-N were reduced from CPW by strong acid cation exchange resin and strong

base anion exchange resin. We found that the treatment process was potentially affected by pH, temperature, contact time, ion exchanger doses, and shaking speed. The highest removal percentage of COD, colour, and NH<sub>3</sub>-N achieved with the cation exchange resin was 29.19%, 24.97%, and 70.54%, respectively. The COD, colour, and NH<sub>3</sub>-N removal were 61.18%, 55.41%, and 26.8% using anion exchange resin, respectively. Based on the obtained results, for cation exchange resin, the COD and colour isotherm were not described well by the Langmuir model none of the models tested did. For the anion exchange resin, COD and colour

isotherm data were also described well by the Langmuir model, the sorption equilibrium data best fitted with the Langmuir isotherm model. The adsorption kinetics followed the pseudo-second-order and intra-particle diffusion for the COD colour and  $\text{NH}_3\text{-N}$  removal from CPW using cationic and anionic resins. From the thermodynamic properties analyses, it was found that the adsorption process was spontaneous. The enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were positive, which indicates that the removal of COD, colour, and  $\text{NH}_3\text{-N}$  was endothermic. The findings of the present study revealed that the ion exchange resins could remove some of the contaminants; however, it did not demonstrate that these contaminants have been removed to the point that direct discharge would be safe. Therefore, a series treatment of cation followed by anion resin or vice versa is recommended for future study.

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