

Comparison of adsorption behaviour of coconut coir activated carbon and commercial activated carbon for textile dye

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Abstract

The objective of the study was to prepare activated carbon from coconut coir and compare its adsorption behaviour for textile dye with that of a commercial activated carbon. The coconut coir activated carbon (CCAC) and commercial activated carbon (CAC) were characterised in terms of ash content, bulk density, pH, pH_{ZPC} , surface area, micropore area, micropore volume, average pore diameter, surface morphology and surface functional groups. Adsorption of a textile dye, Acid Red 18 (AR 18), by CCAC and CAC was examined. Batch adsorption test showed that extent of dye adsorption was dependent on dye concentration, contact time and pH. Equilibrium adsorption was attained in 240 min and maximum adsorption occurred at pH 2. Adsorption by CCAC and CAC followed pseudo-second-order kinetics and equilibrium adsorption data were described by the Freundlich and Langmuir isotherm models. CCAC showed higher adsorption capacity for the dye [25.7 (Freundlich) and 48.5 (Langmuir)] compared to that [12.0 (Freundlich) and 37.3 (Langmuir)] of CAC. CCAC is a suitable substitute for CAC in the removal of acid dyes from aqueous solution

Keywords: Acid Red 18, activated carbon, adsorption, coconut coir, Freundlich isotherm, Langmuir isotherm.

1 Introduction

In order to colour their products, industries such as food, paper, carpet, rubber, cosmetic and plastic use dyes. Commercially, there are more than 100,000 available dyes with a world wide production of more than 7×10^5 metric tons per year. It is estimated that 10-15% of the dye is lost to waste streams during the



dyeing process in the textile industry [1, 2]. Due to synthetic origin and complex aromatic molecular structure, dyes are more stable and difficult to biodegrade [3]. Dyes can accumulate in sediment and soil at locations of wastewater discharge, and due to leaching from the soil groundwater systems are also affected [4]. Some dyes are mutagenic and carcinogenic and can cause severe damage to humans such as dysfunction of the kidney, reproductive system, liver, brain and central nervous system [5].

Dye waste treatment has been the target of concern not only because of the toxicity of the dyes but also due to their visibility [6]. Treatment methods such as chemical oxidation, ion exchange, evaporation, reverse osmosis and chemical precipitation have the disadvantages of high capital and operational cost and disposal of the residual sludge [7]. Adsorption by activated carbon is a promising technique for dye waste treatment. However, use of coal-based commercial activated carbon is limited because of its relatively high price and its feedstock is nonrenewable. Low-cost, renewable, and easily available plant-based materials need to be used as a source in the production of activated carbon.

In recent years, plant-based material such as silk cotton hull, coconut tree sawdust, banana pith, maize cob and sago waste [5] corncob wastes [8], coir pith [9], sawdust [10], rice husk [11], bagasse [12, 13], peach stone [14], seed shell [15] and sunflower seed hull [16] have been used as sources in the production of activated carbon for the treatment of textile dye waste. Coconut coir is an agricultural solid waste. In Malaysia, coconut is the fourth most important industrial crop in terms of total planted area. Coconut coir is available free of cost in large quantities from the coconut oil and desiccated product industry. Preparation of activated carbon from this agricultural solid waste would not only be economical but also solve part of solid waste disposal problem.

In this study, activated carbon was prepared from coconut coir and adsorption of a textile dye, Acid Red 18 (AR 18), from aqueous solution by the coconut coir activated carbon and a commercial activated carbon was examined.

2 Materials and methods

2.1 Preparation of activated carbon

Coconut coir activated carbon (CCAC) was prepared according to a method used by Santhy and Selvapathy [9] for preparing coir pith activated carbon. Washed and dried coconut coir was treated with concentrated sulphuric acid and kept in a hot-air oven at $105\pm 5^\circ\text{C}$ for 24 h. Thereafter, the char was washed with water followed by washing with 2% sodium bicarbonate solution until effervescence had ceased and then kept in a 2% sodium bicarbonate solution overnight. The char was separated and washed with water until free from bicarbonate and dried at $105\pm 5^\circ\text{C}$ for 24 h. It was then subjected to activation at 900°C for 30 min in an atmosphere of nitrogen. The activated carbon obtained was repeatedly washed with distilled water and soaked in 10% hydrochloric acid to remove calcium oxide, followed by repeated washing with water to remove free acid and drying



at $105 \pm 5^\circ\text{C}$ for 24 h. The CCAC was ground to a size of 200-500 μm and used in adsorption test.

A commercial activated carbon (CAC) was obtained from the Calgon Carbon Corporation, Pittsburgh, PA. It was ground to a size of 200-500 μm and used in adsorption tests.

2.2 Textile dye

A textile dye, Acid Red 18 (AR 18) was obtained in powdered form from Euro Chemo-Pharma Sdn. Bhd., Prai Industrial Estate, Penang, Malaysia.

2.3 Adsorption test

Batch adsorption test was carried out by shaking 100 mL of dye solution of desired concentration with 2 g/L of activated carbon in a conical flask at room temperature (22°C) using an orbital shaker at 150 rpm. After a predetermined contact time, the flask was removed from the orbital shaker and the supernatant was filtered through 0.45 μm membrane filter, and the residual dye concentration was determined spectrophotometrically by measuring the absorbance at the wavelength of maximum absorbance (508 nm) against a standard curve. The effect of contact time (15–300 min), dye concentration (40–100 mg/L), pH (2–8) and carbon dosage (1–8 g/L) on adsorption were determined. The adsorption isotherms for CCAC and CAC were determined by batch equilibrium test using the optimum contact time and pH for dye adsorption by the activated carbons.

3 Results and discussion

3.1 Characterisation of activated carbon

Various physical and chemical characteristics of CCAC and CAC are listed in table 1. CCAC possesses higher surface and micropore area, micropore volume and average pore diameter, and lower pH_{ZPC} and pH than those of CAC.

Table 1: Physical and chemical characteristics of CCAC and CAC.

Parameter	CCAC	CAC
Surface area (m^2/g)	826	626
Micropore area (m^2/g)	551	509
Micropore volume (mL/g)	0.25	0.23
Average pore diameter (\AA)	24	15.35
Ash content (%)	14	22
Bulk density (g/mL)	0.31	0.52
pH_{ZPC}	5.3	7.2
pH	4.8	5.6

3.2 Scanning electron micrograph

Scanning electron micrographs of CCAC and CAC at 200X magnification are shown in fig. 1. CCAC contains more macro- and micropores than the CAC.



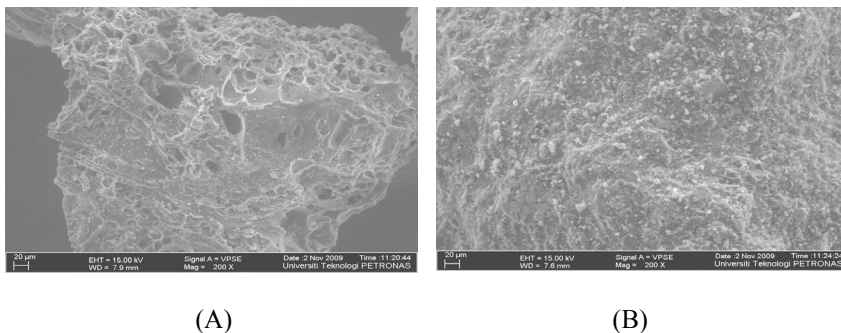


Figure 1: Scanning electron micrograph of (A) CCAC and (B) CAC.

3.3 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra recorded in the region of 500-4000 cm^{-1} for CCAC and CAC are shown in fig. 2. The band at 3407 cm^{-1} corresponds to stretching vibration of OH^- . Two weak bands at 2923-2852 cm^{-1} and at 2921-2850 cm^{-1} for CCAC and CAC, respectively indicate aliphatic group stretching vibration [17]. Large peaks observed at 2360 cm^{-1} and 2341 cm^{-1} for CCAC and CAC, respectively indicate antisymmetric stretching of CO_2 [18]. The peaks observed at approximately 1658 cm^{-1} and 1656 cm^{-1} for CCAC and CAC, respectively can be assigned to symmetric and asymmetric stretching vibration of $\text{C}=\text{C}$ group. The peaks at 1581 cm^{-1} and 1571 cm^{-1} for CCAC and CAC, respectively are due to aromatic rings of $\text{C}=\text{C}$. The intensity for CCAC was found to be greater than CAC at the peak 1402 cm^{-1} , indicating the presence of pyrones and aromatic groups in CCAC. The small peaks in the region of 1100-1200 cm^{-1} for both

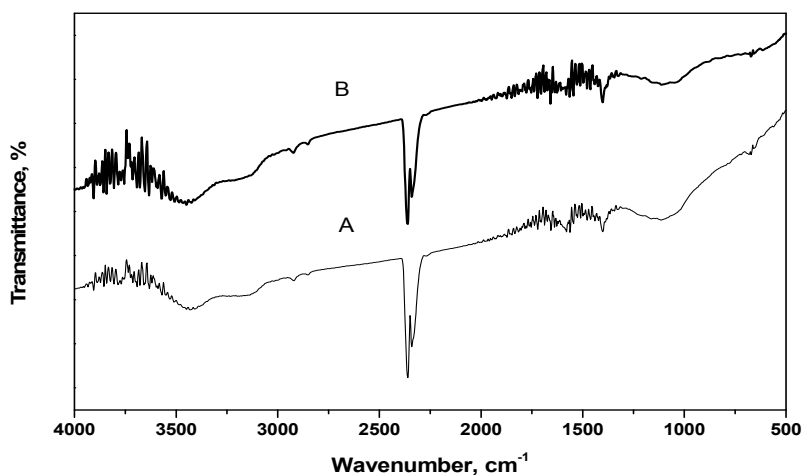


Figure 2: FTIR spectra of (A) CCAC and (B) CAC.

CCAC and CAC can be assigned to the C-O stretching vibrations of carboxylic and phenolic groups [19]. The peaks in the region of $700\text{-}610\text{ cm}^{-1}$ are due to symmetric and asymmetric stretching of SO_2 and symmetric stretching vibration of S-O groups, confirming the presence of surface SO_2 complexes [17] in both CCAC and CAC.

3.4 Adsorption test

3.4.1 Effect of contact time and dye concentration on adsorption

The effect of contact time and dye concentration on adsorption of AR 18 by CCAC is shown in fig. 3. The extent of dye adsorption increased as the initial dye concentration decreased and as the contact time increased. Equilibrium adsorption was attained in 240 min. Similar equilibrium contact time of 240 min also has been reported by Thinakaran *et al.* [15] for the adsorption of Acid Red 114 from aqueous solution using activated carbons prepared from seed shells.

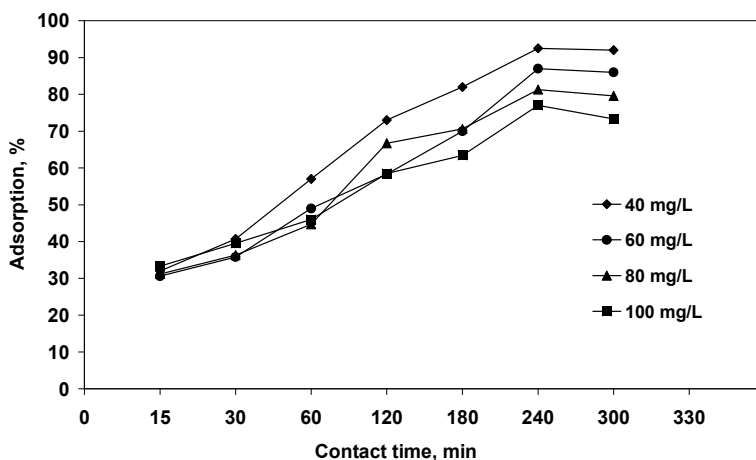


Figure 3: Effect of contact time and dye concentration on adsorption of AR 18 by CCAC.

3.4.2 Effect of pH on dye adsorption

The effect of pH on the adsorption of AR 18 by CCAC was studied by varying the pH of the dye solution in the range 2-8, with 2 g/L carbon dose and initial dye concentration of 80 mg/L, fig. 4. It is observed that maximum adsorption (91%) occurred at acidic pH 2. Similar observation has been reported by Thinakaran *et al.* [16] for adsorption of Acid Violet 17 by activated carbon prepared from sunflower seed hull. As the pH_{ZPC} of CCAC is 5.3, the positive surface charge on the carbon surface increases in the acidic pH range and this would attract the negatively charged functional groups on the dye. pH 2 was selected as optimum pH value for adsorption and all subsequent adsorption tests were conducted at pH 2.

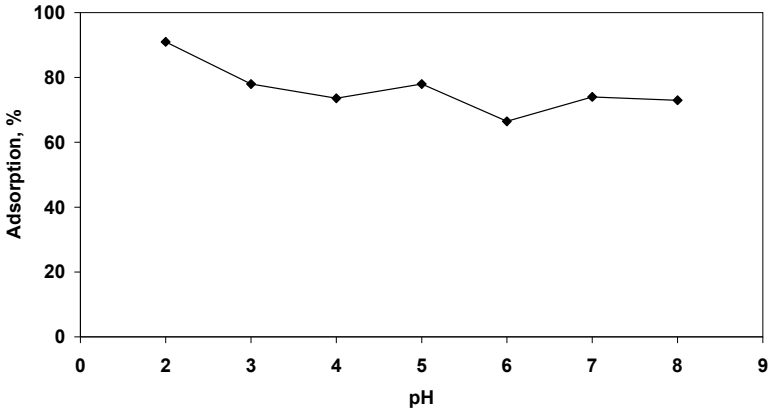


Figure 4: Effect of pH on adsorption of AR 18 by CCAC.

3.4.3 Effect of carbon dose on dye adsorption

Adsorption of AR 18 by CCAC from a 120 mg/L dye solution was studied by varying the carbon dose over a range of 1–8 g/L, employing a pH of 2 and a contact time of 240 min. As shown in fig. 5, the maximum adsorption (99.5%) occurred at 4 g/L of carbon dose.

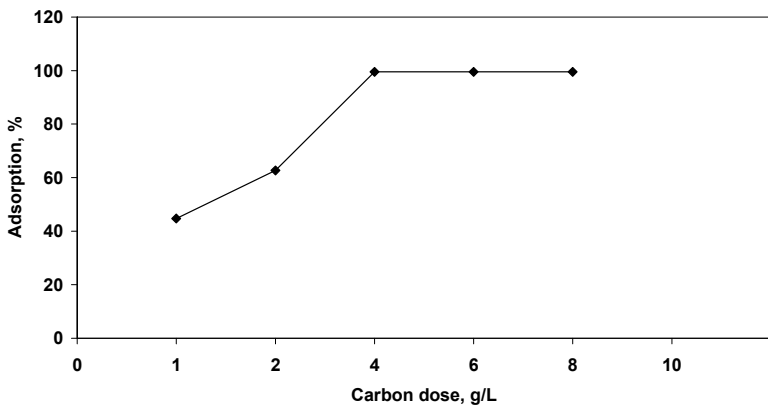


Figure 5: Effect of carbon dose on adsorption of AR 18 by CCAC.

3.5 Adsorption isotherm

In adsorption in a solid-liquid system, the distribution ratio of the solute between the liquid and the solid phase is a measure of the position of equilibrium. The preferred form of depicting this distribution is to express the quantity q_e as a

function of C_e at a fixed temperature, the quantity q_e being the amount of solute adsorbed per unit weight of the solid adsorbent, and C_e the concentration of solute remaining in the solution at equilibrium. An expression of this type is termed an *adsorption isotherm* [20].

The Langmuir adsorption isotherm is

$$q_e = \frac{Q^{\circ} b C_e}{1 + b C_e} \quad (1)$$

where, Q° is the amount of solute adsorbed per unit weight of adsorbent in forming a monolayer on the surface (monolayer adsorption capacity) and b is a constant related to the energy of adsorption.

The Freundlich adsorption isotherm is

$$q_e = K_f C_e^{1/n} \quad (2)$$

where, K_f is the Freundlich constant (adsorption capacity) and $1/n$ represents the adsorption intensity or surface heterogeneity.

Adsorption isotherms for AR 18 onto CCAC and CAC were determined by batch equilibrium test employing the optimum contact time 240 min and optimum pH 2 for both activated carbons. The isotherm data were fitted to the linear forms of the Langmuir equation, fig. 6 and the Freundlich equation, fig. 7, and values of the constants were determined, Table 2. The values of Q° and K_f indicate that CCAC exhibited higher adsorption capacity for AR 18 than CAC.

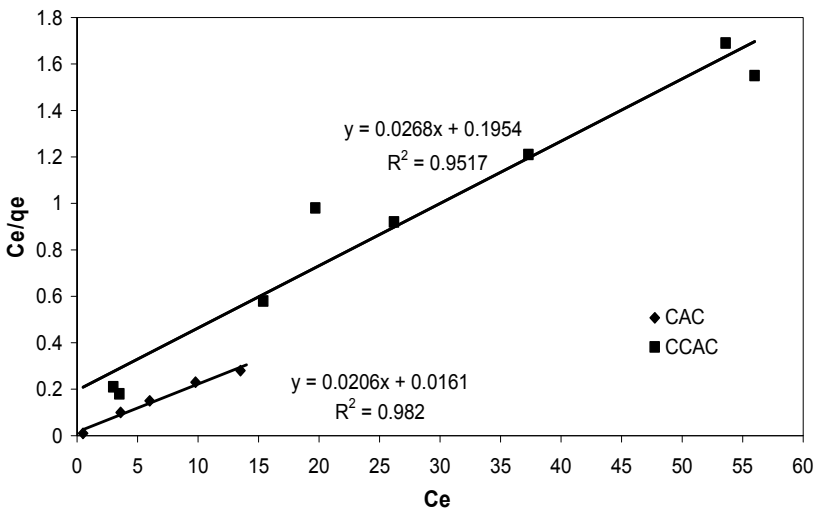


Figure 6: Langmuir adsorption isotherm of AR 18 adsorption.

Table 2: Langmuir and Freundlich constants for AR 18 adsorption by CCAC and CAC.

Activated carbon	Langmuir isotherm constant		Freundlich isotherm constant	
	Q^s (mg/g)	b (L/g)	K_f	$1/n$
CCAC	48.5	1.27	25.7	0.2
CAC	37.3	0.13	12.0	0.2

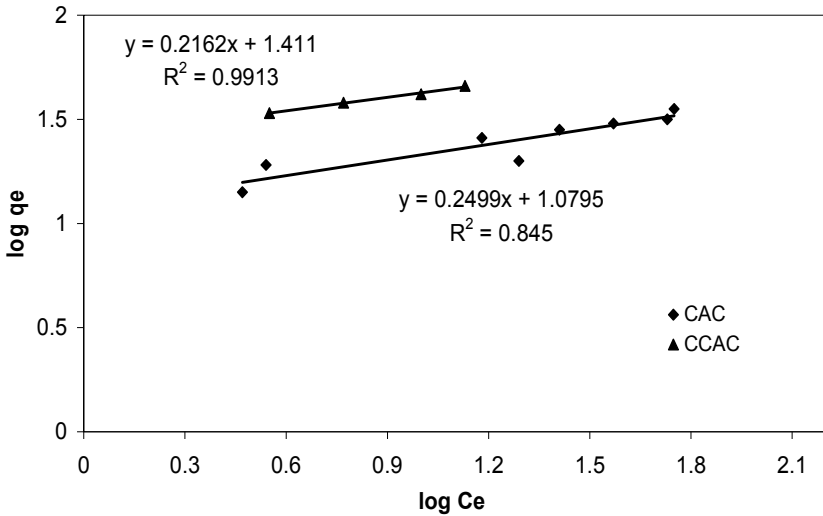


Figure 7: Freundlich adsorption isotherm of AR 18 adsorption.

3.6 Adsorption kinetics

A kinetic study for adsorption of AR 18 by CCAC and CAC was carried out by using two models i.e. the pseudo-first-order and pseudo-second-order.

The linear form of the pseudo-first-order model is

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

The linear form of the pseudo-second-order model is

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{t}{q_e} \right) \tag{4}$$

where, q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and any time t , respectively; k_1 is the equilibrium rate constant of pseudo-first-order kinetics (min^{-1}); and k_2 is the equilibrium rate constant of pseudo-second-order kinetics ($\text{g/mg}\cdot\text{min}$).

Plots of $\log (q_e - q_t)$ versus t and of t/q_t versus t are presented in fig. 8 and 9, respectively, while table 3 lists the values of k_1 , k_2 , q_e and R^2 for the two models. Comparatively higher values of R^2 for the pseudo-second-order kinetic model than those for the pseudo-first-order kinetic model, and the close values of q_e , calc and q_e , exp indicate that the pseudo-second-order kinetic model gave better fit to the experimental data for both activated carbons. Similar observations have been reported for the adsorption of Acid Violet 17 onto activated carbon prepared from sunflower seed hull [16] and acid dyes onto activated carbon cloth [21].

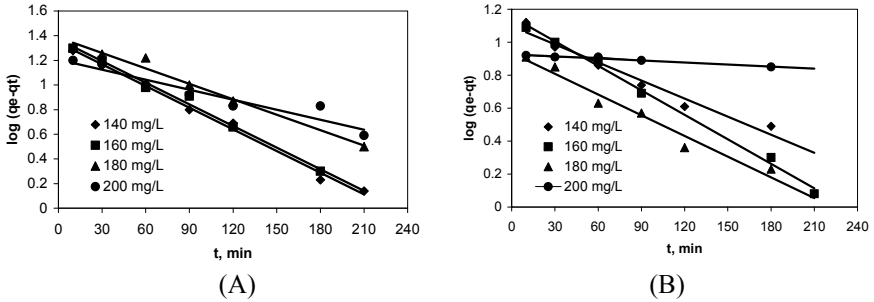


Figure 8: Pseudo-first-order kinetics of AR 18 adsorption by (A) CCAC and (B) CAC.

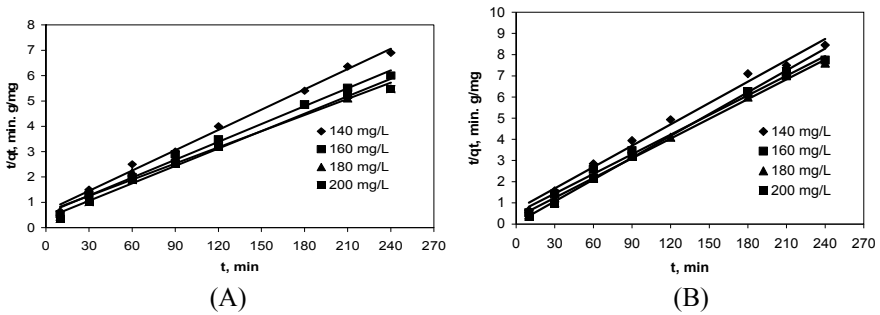


Figure 9: Pseudo-second-order kinetics of AR 18 adsorption by (A) CCAC and (B) CAC.

4 Conclusions

The adsorption capacity of coconut coir activated carbon for Acid Red 18 was higher than that of a commercial activated carbon, with the adsorption kinetics for both activated carbons following the pseudo-second-order model. Coconut coir activated carbon is a suitable substitute for commercial activated carbon in the adsorption of acid dyes from aqueous solution.



Table 3: Pseudo-first-order and pseudo-second-order kinetic rate constants and experimental and calculated q_e values of AR 18 adsorption by CCAC and CAC.

Activated carbon a_{nd} initial dye concentration	q_e , exp (mg/g)	Pseudo-first order model			Pseudo-second-order model		
		$k_1 \times 10^{-3}$ (min ⁻¹)	q_e , cal (mg/g)	R ²	$k^2 \times 10^3$ (g/mg min)	q_e , cal (mg/g)	R ²
CCAC							
140 mg/L	34.7	13	22.0	0.9939	1.1	37.4	0.9944
160 mg/L	38.9	13	23.4	0.9904	1.0	42.5	0.9936
180 mg/L	43.7	9.6	24.2	0.9793	0.7	46.9	0.9809
200 mg/L	43.9	6.2	16.0	0.9135	1.4	43.6	0.9853
CAC							
140 mg/L	28.4	8.5	12.5	0.9635	1.7	29.7	0.9904
160 mg/L	31.0	11	14.2	0.9943	1.9	32.3	0.9957
180 mg/L	31.3	9.6	8.5	0.9644	3.2	32.1	0.9974
200 mg/L	36.0	9.2	9.2	0.9692	31.0	29.0	0.9996

Acknowledgements

The authors are thankful to the management and authorities of the Universiti Teknologi PETRONAS (UTP) and the Civil Engineering Department, UTP for providing facilities for this research.

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