RESEARCH PAPER



Removal of Colour and COD in Biologically pre-treated Leachate using Activated Carbon from Corn Cobs

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ABSTRACT

Activated carbon was prepared from corn cob agricultural waste with different impregnation ratios and pyrolysis times. The optimal adsorbent prepared using at 4:1 ZnCl₂:corn cob char ratio at a temperature of 800 °C for 180 min provided the maximum Brunauer-Emmett-Teller (BET) surface area, total pore volume and average pore width, with values of 912.47 m²/g, 0.52 cm³/g and 22.61 Å, respectively. ZnCl₂ was effective in creating well-developed pores on the surface of the activated carbon. The removal efficiency and adsorption capacity of the colour and the chemical oxygen demand (COD) of the biologically pre-treated leachate were examined utilizing the best corn cob activated carbon (CCAC) with varying CCAC dosages, contact times and initial pH values. The greatest colour and COD removal effectiveness were 88.6±0.2% and 83.7±0.4%, respectively, at the optimum CCAC dosage of 12 g for 40 min with an initial pH value of 10. In addition, maximum adsorption capacities were achieved for colour and COD of 10.3±0.02 mg/g and 12.6±0.05 mg/g, respectively, under the same conditions. The kinetics of colour and COD adsorption fitted very well with pseudo-second-order kinetic model. The CCAC performs well as an adsorbent for removing colour and COD in biologically pre-treated leachate.

Keywords: Refractory organic compound; Landfill leachate; Adsorption

INTRODUCTION

Municipal landfill leachate, a dark brown liquid generated from excess water, percolates through the waste layers in landfills while carrying a heterogeneous mixture of organic and inorganic loads (Azmi et al., 2015; Naveen & Malik, 2019). These materials can seep into soil, groundwater and surface water, causing many environmental impacts (Taylor & Allen, 2006). Landfill leachate is commonly characterized by high colour strengths, high BOD values and COD values of 2,200-9,259 Pt-Co (Azmi et al., 2015; Ghani et al., 2017), 188-2,000 mg/L and 2401-12,610 mg/L (Azmi et al., 2015; Ghani et al., 2017; Hassan et al., 2017; Montero et al., 2019), respectively. The major problems associated with coloured effluent include poor light transparency, reduced photosynthesis and damage to the aesthetic nature of water surfaces. In addition, the main heavy metals present in landfill leachate are Zn, Cu, Pb and Cd (Salem et al., 2014; Erabee et al., 2018; Montero et al., 2019). Furthermore, the old landfill release stabilized leachate with low BOD/COD ratio, which is difficult to be further biologically degraded. Stabilized leachate classically contains high levels of refractory organic compounds such as humic and fluvic substances. These impurities causing colour are usually expressed in terms of colour and COD (Shehzad et al., 2015; Ghani et al., 2017; Ramli et al., 2021).

The production of corn (Zea mays) encompasses a large agricultural area in northern

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Thailand. Corn waste, including stems, leaves and corn cobs, has not been optimally utilized causing air pollution every year. High carbon, celluloses and hemicelluloses contents are present in corn cobs at 42.10% 40.0% and 41.4%, respectively, giving the cobs a strong and ridged structure. Their advantages consist of their reasonable hardness, low ash content, and low cost (Biswas et al., 2017). Therefore, to increase the economic value of corn cobs, corn cobs, as a biomass and agricultural waste product, can be applied as an attractive raw activated carbon material through an activation process. Chemical activation is always preferred over physical activation due to the low temperatures and shorter times required to obtain the activated carbon as well as the energy savings. The adsorbent properties of activated carbon are essentially attributed to its large surface area, highly porous structure and favourable pore size (Song et al., 2013; Kaźmierczak et al., 2013; Milenković et al., 2013; Louis, 2015; Buah et al., 2016). The popular activators used to prepare activated carbon from corn cobs are ZnCl₂ (Duan et al., 2019; Yaseen et al., 2021), H₃PO₄ (Sych et al., 2012; El-Sayed et al, 2014; Louis, 2015; Armonio et al., 2019) and KOH (Bagheri & Abedi, 2011; Song et al., 2013; Kaźmierczak et al., 2013). A ZnCl₂ solution was previously used as an activating reagent, and Duan et al. (Duan et al., 2019) studied the preparation of activated carbon from corn cobs using ZnCl₂. The BET surface area of the adsorbent was between 556-1,270 m²/g, and the highest total pore volume was 0.67 cm³/g.

Corncob-derived activated carbon has been used as a physicochemical treatment to remove biologically resistant organic and inorganic compounds in wastewater since several of these compounds are not eliminated by conventional biological treatment processes. Previous research has demonstrated that activated carbon obtained from corn cobs has a high heavy metal removal efficiency (Buah et al., 2016; Christica et al., 2018; Wang et al., 2018; Duan et al., 2019) and a high removal efficiency of dyes in wastewater (Louis, 2015). In addition, activated carbon derived from other precursors can effectively adsorb various pollutants in landfill leachate (Azmi et al., 2017; Shehzad et al., 2015; Ghani et al., 2017; Erabee et al., 2018). Banana (Ghani et al., 2017) and sugarcane bagasse (Azmi et al., 2015) have been used to prepare activated carbon for landfill leachate treatments with high colour removal percentages of 91.2% and 87.3%, respectively, and COD values of 83.0% and 77.8%, respectively. In the present work, the adsorption efficiencies and capacities of the colour and COD in biologically pre-treated leachate by CCAC were investigated.

MATERIALS AND METHODS

The corn cob samples used in this experiment as the precursors for CCAC preparation were collected locally from Phayao province, Thailand. The corn cobs were cut into small sizes and sieved to a particle size of 4 mm. Then, the samples were washed several times with distilled water and dried to constant weight in a hot air oven at 105 °C for 4 h. Corn cob chars derived from the carbonization process were obtained in a furnace under a pyrolysis temperature of 600 °C for 2 h. Then, they were soaked in 0.5 M ZnCl₂ solution as the activating agent with ZnCl₂:char waste ratio of 1:1, 2:1 and 4:1. After soaking, the samples were activated in a furnace under heated temperatures of 800 °C for 60 and 180 min. The produced CCAC was washed with distilled water until the pH of the filtrate reached 6.5-7.5. The final products were dried in a hot air oven at 105 °C for 2 h, then sieved to a particle size of 1 mm and stored in a desiccator.

CCAC samples prepared under all considered conditions were taken for morphology analyses of the surface area and porosity, including the BET surface area, cumulative pore volume and average pore size. The surface area and porosity analyses were performed with a Micromeritics Model ASAP 2020 under N_2 adsorption analysis. The porosity of the CCAC was also detected by Scanning electron microscopy (SEM) performed with a JEOL JSM-5910LV. In addition, identification of the functional groups on the CCAC surface before and after adsorption was carried out by Fourier transform infrared spectroscopy (FTIR) using a Thermo Scientific spectrometer (model: Nicolet iS5). Discs were prepared by mixing 0.1 g of CCAC with 100 mg of KBr (Merck, for spectroscopy) in an agate mortar and then pressing the sample pellets under a pressure of 7 tons/cm² for 30 min. The FTIR spectra were recorded between 4,000 and 400 cm⁻¹ (Azmi et al., 2015; Ghani et al., 2017). Furthermore, measurements of the pH_{pzc} values on the surface of the CCAC were conducted using 100 ml deionized water in Erlenmeyer flasks with 0.1 mg of CCAC. The pH values of various flasks were set between 1 and 11 by adding 0.1 N HCl or 0.1 N NaOH. Then, the samples were shaken at 120 ppm for 24 h, after which the final pH values of the solutions were measured. The pH_{pzc} is the point at which the pH_{final} vs pH_{initial} curve intersects the pH_{initial} - pH_{final} line (El-Sayed et al., 2014).

The optimal CCAC obtained by chemical activation was used to study the pollutant removal and adsorption capacity of colour and COD in biologically pre-treated leachate. The wastewater samples were collected from a sanitary landfill in Phayao province, Thailand. Before treatment, the samples were filtered with a 0.45 µ glass fibre filter (GF/C Whatman) to remove suspended solids. All experiments were conducted at the laboratory scale under a batch process and were duplicated. The effects of the CCAC dosages (2, 4, 6, 8, 10 and 12 g), contact times (5, 10, 20, 40 and 80 min), initial pH values of the wastewater (2, 4, 6, 8 and 10) on the removal efficiency and adsorption capacity of pollutants were investigated. Leachate samples of 250 ml were used in the experiments and the pH of the leachate was adjusted with NaOH and H_2SO_4 . The temperature of wastewater was kept at 30 °C with shaking at 120 rpm. The characteristics of the leachate wastewater and treated wastewater were analysed following standard methods for the examination of water and wastewater (APHA, AWWA & WEF, 2017). An atomic adsorption spectrophotometer (Shimadzu, AA-6880) was used to The colour concentration was analysed by a UV-visible measure heavy metals. spectrophotometer (Thermo Scientific, Genesys 10S). The removal efficiency and adsorption capacity of the pollutants were deduced using Equation (1) and (2), respectively:

Removal efficiency (%) =
$$\frac{C_0 - C_t}{C_0} \times 100$$
 (1)

$$q_e = \frac{C_0 - C_t}{M} \times V \tag{2}$$

where $q_e (mg/g)$ is the adsorption capacity at equilibrium. $C_0 (mg/L)$ is the initial concentration of pollutants, $C_t (mg/L)$ is the final concentration of pollutants at any time t (min) and V (L) and M (g)represent the volume of treated solution and the dry mass of utilized CCAC, respectively. (Azmi et al., 2015; Ghosh et al., 2020). The adsorption kinetics of colour and COD onto CCAC were studied using three models including pseudo-first-order kinetic model, pseudo-second-order kinetic model and intraparticle diffusion model which can be expressed in linear form as Equation (3), (4) and (5), respectively:

$$log(q_e - q_t) = logq_{ecal} - \frac{k_l}{2.303}t$$
(3)

$$\frac{t}{q_t} = \frac{l}{k2^2 qecal^2} + \frac{l}{q_e} t \tag{4}$$

$$q_t = k_t t^{1/2} + C \tag{5}$$

Where $q_t (mg/g)$ is the adsorption capacity at any time t (min), $k_1 (min^{-1})$, $k_2 (g/mg.min)$ and k_i $(mg/g.min^{1/2})$ are the rate constant for pseudo-first-order kinetic model, pseudo-second-order kinetic model and intraparticle diffusion model, respectively and C (mg/g) is the intercept and it gives an idea of the thickness of the boundary layer (Nethaji et al., 2013; Yaseen et al., 2021).

RESULTS AND DISCUSSION

Table 1 shows the characteristics of the municipal landfill leachate and biologically pretreated leachate obtained from a landfill located in Phayao province, Thailand. The leachate had a high colour and COD concentration. COD concentrations below 4,000 mg/L, colour concentrations ranges of 1,500-7,000 Pt-Co and low BOD:COD ratios (<0.1) characterize stabilized leachate (Azmi et al., 2015; Shehzad et al., 2015; Ghani et al., 2017). According to Shehzad et al. (Shehzad et al., 2015), most organic compounds present in stabilized municipal landfill leachate containing refractory compounds, such as humic acid and fulvic acid, are not biodegradable. Furthermore, heavy metals as Zn, Cu, Pb, and Cd can also be found in the leachate according to previous studies (Salem et al., 2014; Erabee et al., 2018; Montero et al., 2019). In addition, the remaining high colour and COD concentrations in biologically pretreated leachate demonstrate that the conventional biological treatment technology is ineffective in removing these refractory substances. Therefore, physicochemical processes such as activated carbon adsorption are alternatives for treatment of biologically pre-treated leachate.

Parameters	Landfill leachate	Biologically pre-treated leachate		
Temperature (°C)	32-34	29-31		
pH	7.5-8.5	7.4-7.6		
Conductivity (µs/cm)	560-623	125-153		
Suspended Solids (mg/L)	204-424	146-178		
Colour (Pt-Co)	1,764-2,845	382-694		
BOD (mg/L)	90-180	105-140		
COD (mg/L)	906-1,986	373-872		
TKN (mg/L)	0.09-0.20	0.01-0.03		
Zn (mg/L)	0.069-0.092	0.039-0.077		
Cu (mg/L)	0.942-1.641	0.646-1.052		
Pb (mg/L)	0.084-0.101	0.072-0.093		
Cd (mg/L)	0.001-0.005	0.001-0.003		

Table 2 shows the surface characteristics of the CCAC obtained under different preparation conditions. The BET surface area and pore volume increases with increasing impregnation ratio, heating temperatures and time, according to Sych et al. (Sych et al., 1012) and Song et al. (Song et al., 2013). The optimized production condition of CCAC is 4:1 ZnCl₂:corn cob biochar at a pyrolysis temperature of 800 °C for 180 min under condition set 6, providing a BET surface area, total pore volume and average pore width of 912.47 m²/g, 0.52 cm³/g and 22.61 Å, respectively. The properties of the adsorbent in the present study were obtained following the study of Duan et al. (Duan et al., 2019). The BET surface area of the CCAC

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obtained in this research was higher than that reported in a previous study; Yaseen et al. (Yaseen et al., 2021) obtained a BET surface area of 257 m²/g from an impregnation ratio of 1:1 ZnCl₂:char at 550 °C for 2 h. Furthermore, a ZnCl₂ solution is a better activator than HCl in terms of obtaining hinger BET surface areas (Wang et al., 2018), which ranges from 500-2,000 m²/g for commercially available activated carbon (Kumar & Jena, 2015). The different results resulted from the variable conditions in the preparation of the activated carbon, such as the types and ratio of the activator, heating temperature and duration.

Table 2. Surface characteristics of different CCAC samples						
Conditions	ZnCl ₂ :corn cob biochar (w/w)	Temperature (°C)	Time (min)	BET surface area (m²/g)	Total pore volume (cm ^{3/} g)	Average pore diameter (Å)
1	1:1	800	60	503.69	0.28	21.77
2	1:1	800	180	649.36	0.38	23.20
3	2:1	800	60	549.41	0.32	23.20
4	2:1	800	180	699.53	0.40	22.69
5	4:1	800	60	606.24	0.35	22.99
6	4:1	800	180	912.47	0.52	22.61

The nitrogen adsorption-desorption isotherm of CCAC under optimal conditions is shown in Fig. 1. It can be classified as mixed type based on the International Union of Pure and Applied Chemistry (IUPAC) classification (Sing et al., 1985). The isotherm initially rapidly increases at low relative pressures, characterizing type I and corresponding to adsorption in the micropores. It is of type IV at intermediate and high relative pressures, when it is characterized by simultaneous pressure of mesopores according to the studies of Synch et al. (Sych et al., 2012) and Sun and Webley (Sun & Webley, 2010). The pore size distribution of the CCAC displayed in Fig. 2 indicates that the pore size is concentrated at 18.6 Å (1.86 nm) in the micropore structure (IUPAC, 1972).



Fig. 1. Nitrogen adsorption-desorption isotherms of the optimal CCAC



Fig. 2. Pore size distribution of the optimal CCAC

The surface morphologies of CCAC prepared under optimum conditions were observed using a scanning electron microscope. SEM images at scales of 100 μ m and 50 μ m are presented in Fig. 3 (a) and (b), respectively. ZnCl₂ is effective in creating well-developed surface pores on activated carbon. The honeycomb-shaped holes are arranged well and regularly, leading to a large surface area and porous structure (Njoku & Hameed, 2011).



Fig. 3. SEM images of the optimal CCAC: (a) scale: 100 μ m, (b) scale: 50 μ m

The FTIR spectra of the optimally prepared CCAC obtained before and after the adsorption treatment are shown in Fig. 4. Fig. 4 (a) illustrates that the functional groups present on the CCAC before adsorption in the observed bands ranging from 3200-3650 cm⁻¹ were associated with the stretching vibrations of hydroxyl groups (OH) of alcohol and phenol (Sych et al., 2012; Louis, 2015; Wang et al., 2018; Yaseen et al., 2021). The peak centred at 2299-2395 cm⁻¹ was assigned to the stretching vibrations of amino groups (Ching et al., 2011). A band appeared at approximately 1,690-1,710 cm⁻¹ and was attributed to the stretching vibration of COO in the carboxyl group (Yaseen et al., 2021; Sych et al., 2012). Carbonyl groups (C=O) were also detected at wavenumber 1610 (Sun & Webley, 2010). However, the peaks were located at 1570 cm⁻¹ and 1500 cm⁻¹, and these peaks were attributed to the masses of C=C carbons in alkenes and aromatics, respectively (Song et al., 2013; Louis, 2015; Yaseen et al., 2021). The three next peaks, which occured at 1112, 1065 and 1010 cm^{-1} , illustrated the presence of C-O groups (Song et al., 2013; Yaseen et al., 2021). These results indicated that the CCAC included carbon-oxygen surface groups, which influence adsorption processes. After adsorption, as shown in Fig. 4 (b), many peaks were found to have shifted in position, such as that of the OH groups (from 3650 cm⁻¹ to 3640 cm⁻¹). These functional group changes in the spectrum reveal the possible involvement of functional group interactions via oxygen for binding the pollutants in leachate to the CCAC (Azmi et al., 2015).



Fig. 4. FTIR spectra of the optimal CCAC (a) before adsorption and (b) after adsorption

The removal efficiency and adsorption capacity of the colour and COD of biologically pretreated leachate were examined utilizing the best CCAC. A total of 250 ml of wastewater was generated for the investigation with varying CCAC dosages of 2, 4, 6, 8, 10, and 12 g. Fig. 5 shows the increase in the colour and COD removal efficiency with increasing CCAC dosage, indicating the influence of the adsorbent surface area on the adsorption process under the conditions applied herein. With an increasing adsorbent dosage, the surface area of the adsorbent increases, and more adsorption sites become available. The greatest colour and COD removal effectiveness were $78.1\pm0.7\%$ and $74.4\pm0.5\%$, respectively, and were obtained at the optimum CCAC dosage of 12 g. Previous studies have found similar results (El-sayed et al., 2014; Rattanapan et al., 2017; Duan et al., 2019; Ghosh et al., 2020; Yaseen et al., 2021). In contrast, as demonstrated in Fig. 6, the adsorption capacity trend decreased with an increasing CCAC dosage. The decreasing adsorption density observed as the adsorbent dosage increased could be due to unsaturation sites arising during the adsorption process (Ghani et al., 2017; Ching et al., 2011; Rattanapan et al., 2017; Ghosh et al., 2020). Another factor could be the overlapping or aggregation of adsorption sites, resulting in a reduction in the total adsorbent surface area available to the adsorbate and a lengthening of the diffusion channel. (Ching et al., 2011)



Fig. 5. The effect of the CCAC dosage on the removal efficiency



The adsorption treatment was repeated using varied contact times of 5, 10, 20, 40, and 80 min at the optimum CCAC dosage of 12 g. The colour and COD treatments showed similar in removal efficiency and adsorption capacity trends, as shown in Fig. 7 and Fig 8, respectively. In the case of colour removal, adsorption increased rapidly in the first 10 min of contact and then decreased until equilibrium was reached (Njoku & Hameed, 2011; Ching et al., 2011; Elsayed et al., 2014; Buah et al., 2016). Because of the analyte's desorption from the adsorbent, the colour adsorption decreases after 10 min. (Yaseen et al., 2021). The maximum percent removal and adsorption capacity were measured at 10 min, with values of $86\pm0.5\%$ and 10 ± 0.06 mg/g, respectively. For the COD treatment, the optimal removal of $74.4\pm0.5\%$ and optimal adsorption capacity of 11.3 ± 0.12 mg/g were achieved at 40 min. The elimination percentage and adsorption capacity were quickly raised from 5 to 20 min and thereafter remained constant. Apparent adsorption equilibrium occurred at 40 min due to active site saturation on the adsorbent surface and slow pore diffusion (Njoku & Hameed, 2011; Rattanapan et al., 2017).



Fig. 7. The effect of the contact time on the removal efficiency



Fig. 8. The effect of the contact time on the adsorption capacity

The effects of the initial pH values of the leachate wastewaters on colour and COD adsorption were studied using different pH levels ranging from 2 to 10 at the optimum CCAC dosage of 12 g. The results indicate that increasing the initial pH of wastewater enhances the colour and COD removal, as presented in Fig. 9 and Fig. 10. The optimum pH of 10 provided the highest colour and COD removal efficiencies of 88.6±0.2% and 83.7±0.4%, respectively (Fig. 9). Furthermore, the adsorption capacity of both the colour and COD also obtained similar percent removal trends with maximum of 10.3±0.02 mg/g and 12.6±0.05 mg/g, respectively (Fig. 10). The same behaviour has been observed by other researchers (Ching et al., 2011; El-sayed et al., 2014; Yaseen et al., 2021). The pH_{pzc} value is determined by the combined action of all the functional groups of activated carbon. The surface charge of CCAC is neutral at a pH_{pzc} value of 6.2. At pH values below pH_{pzc}, the CCAC surface is positively charged, while at pH values above pH_{pzc}, the surface is negatively charged. (Elsayed et al., 2014). At an increased initial pH, the CCAC has a greater adsorption potential for colour and COD adsorption. This can be explained by the attraction force at the surface between positive sites of various components that are cationic of the colour and COD in leachate, such as lignin, humic acid, fulvic acid, and dissolved organic compounds (Ghani et al., 2017), and the anionic sites of the activated carbon. In addition, pollutants in leachate with positive charges can also react with and adhere to functional groups such as hydroxyl and carbonyl groups on adsorption surfaces (Ching et al., 2011). Furthermore, a simultaneous chemical reaction has been observed between organic constituents in solution and functional groups on the adsorbent surface (Ghani et al., 2017).



Fig. 9. The effect of the initial pH on the removal efficiency



Fig. 10. The effect of the initial pH on the adsorption capacity

The adsorption kinetics of colour and COD onto CCAC were predicted by pseudo-firstorder kinetic model, pseudo-second-order kinetic model and intraparticle diffusion model. The linear plot for pseudo-first-order, pseudo-second-order and intraparticle diffusion equation are shown in Fig. 11, Fig. 12 and Fig. 13, respectively. The parameters obtained from these models are presented in Table. 3. It was observed that the intraparticle plot does not pass through the origin which indicate that intraparticle diffusion is not the sole process involved in adsorption (Fig. 13). Both colour and COD adsorption fitted very well with pseudo-second-order kinetic model with R^2 values close to unity. In addition, the experimental q_e values were closer to the q_e values to the pseudo-second-order kinetic model. Overall, it implied that the adsorption of colour and COD onto CCAC were a chemisorption process involving valence force through sharing or exchange of electrons between adsorbate and adsorbent species (Aziz et al, 2011; Nethaji et al., 2013; Yaseen et al., 2021).



Fig. 11. Pseudo-first-order kinetic model for colour and COD adsorption



Fig. 12. Pseudo-second-order kinetic model for colour and COD adsorption



Fig. 13. Intraparticle diffusion model for colour and COD adsorption

Adsorbates	Pseudo-first-order kinetic			Pseudo-second-order kinetic		Intraparticle diffusion model			
	q _{ecal} (mg/g)	k ₁ (min ⁻¹)	\mathbb{R}^2	q _{ecal} (mg/g)	k ₂ (g/mg.min)	R ²	k _i (mg/g.min ^{1/2})	C (mg/g)	\mathbb{R}^2
Colour	3.53	0.1379	0.9235	10.92	0.2446	0.9988	0.8657	6.49	0.8290
COD	10.23	0.1356	0.9872	14.68	0.1196	0.9954	1.8964	3.61	0.9889

Table 3. Kinetic model parameters for colour and COD adsorption onto CCAC

CONCLUSION

The physicochemical process of obtained CCAC by chemical activation was used to investigate the removal percentage and adsorption capacity of colour and COD of biologically pre-treated leachate. The optimized production condition of the CCAC provided a maximum BET surface area, total pore volume and average pore width of 912.47 m²/g, 0.52 cm³/g and 22.61 Å, respectively. SEM images indicated that ZnCl₂ was effective in creating well-developed pores on the surface of the activated carbon. The FTIR spectra of the CCAC before adsorption illustrated that the CCAC included carbon-oxygen surface groups, which influenced the adsorption processes. Changes in the positions of functional groups after adsorption revealed the possible involvement of functional group interactions via oxygen for the binding of pollutants in the leachate to the CCAC. At the optimum CCAC dosage of 12 g

and contact time of 40 min with an initial pH value of 10, The greatest colour and COD removal efficiency were 88.6 \pm 0.2% and 83.7 \pm 0.4%, respectively. Whereas, the maximum adsorption capacities of the colour and COD were 10.3 \pm 0.02 mg/g and 12.6 \pm 0.05 mg/g, respectively. The kinetics of colour and COD adsorption onto the CCAC followed the pseudo-second-order kinetic model. The CCAC is an effective adsorbent for removing colour and COD in biologically pre-treated leachate.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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