Thai Environmental Engineering Journal Vol. 38 No. 1 (2024) : 47-57
www.eeat.or.th

Removal of Dichloroacetonitrile in Synthetic and Tap Water by Napier grass-derived Adsorbent

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Article History; *Received: 12 October 2023, Accepted: 25 April 2024, Published: 30 April 2024*

Abstract

The objectives of this study are to investigate the characteristics of Napier grass-derived adsorbent and its efficiency on DCAN removal in synthetic water and tap water. Napier grass is one of the materials that contains a high amount of cellulose content. Thus, it can be utilized as an alternative and potential sustainable resource of raw material to produce biosorbent. Napier grass-derived adsorbent was produced by carbonized at 600 °C under Liquefied Petroleum Gas (LPG) for 1 hour. The characteristics of Napier grass-derived adsorbent were investigated by using the Brunauer Emmett-Teller (BET) method and the surface charges by using Point of Zero Charge (PZC) method. The results showed that BET surface area was 182.53 m^2/g, average pore diameter was 2.9579 nm., and PZC was approximately 7 both in synthetic water and tap water. Napier grass-derived adsorbent was proved to provide high efficiency to remove DCAN from water source. The removal efficiency was increased with increasing adsorbent. The optimal dosage of Napier grass-derived adsorbent was 2.0 g/L both in synthetic water and tap water with more than 90% removal efficiency. Adsorption kinetics were conducted, it was found that the adsorption of DCAN by using Napier grass-derived adsorbent was fitted to pseudo-second order which can be indicated that the mechanism of adsorption was chemisorption. The adsorption was reaching equilibrium after 50 minutes both in synthetic water and tap water. In addition, the adsorption isotherm was conducted and found that physical adsorption was the major adsorption mechanism of DCAN in Napier grass-derived adsorbent.

Keywords : adsorption; dichloroacetonitriles; haloacetronitrile; low-cost adsorbent; napier grass

Introduction

Haloacetonitriles (HANs) is the regulated disinfection by-product (DBPs) which are classified as nitrogenous disinfection by-products [1]. It has been reported as a stronger cytotoxicity and genetic toxicity [2]. Dichloroacetonitrile (DCAN) is a type of haloacetonitriles (HANs) which mostly detected in tap water [3]. Tap water in Bangkok has been found to contain DCAN in concentrations of 2.5 to 27 μg/L [4]. In addition, it was found that the water distribution networks of Khon Kaen Municipality have been detected HANs (DCAN, TCAN and DBAN) up to 30 μg/L [5].

DCAN is a by-product of the chlorination of humic substances, algae and amino acids contained in drinking water and pulp bleaching processes. It is formed during the chlorination process of water and wastewater treatment with the occurrence of humic substance as a precursor. DCAN affects animal, aquatic, and plant life; and conformance with environmental and public health regulations [6]. So, the WHO guideline value for DCAN in drinking water is set at 0.02 mg/L or 20 μg/L. Therefore, it is crucial to control DCAN formation in a water treatment system. Various physical or chemical methods were used to remove DCAN from aqueous solution to reach a standard concentration such as precipitation, photocatalysis and adsorption [7-9]. Adsorption technique is deserving as promising technique to remove DCAN from water due to its low consumption of energy, simple operation, high efficiency, low cost as well as the wide suitability for purified water [10].

Activated carbon is a well-known and efficient adsorbent that is commonly used in the environmental aspects. Nowadays, low-cost materials are increasingly utilized as low-cost adsorbent due to the low cost and related to the waste reduction issue. Several low-cost materials were utilized as low-cost adsorbent such as pig bone, cotton, canvas fabric, corn etc.

In Thailand, Napier grass has been promoted for planting to be use as alternative animal feeding. It was attended because of its fast growth without much nutrients supply, good disease resistance, adaptability, high production yield and easy propagation. Napier grass is also considered as a cheap cellulosic resource [11]. Importantly, it contains a high amount of cellulose content about 35–50% [12]. Thus, this material has been the principal reason for supplement as an alternative and potential sustainable resource of raw material to produce biosorbent. However, the condition for producing biosorbent from Napier grass is not well determined. In addition, the adsorption efficiency and adsorption mechanism of Napier grass adsorbent on DBPs rarely conducted. So, the Napier grass was utilized as raw material for producing Napier grass-derived adsorbent. Thus, the purposes of this research are to investigate the characteristics of Napier grass-derived adsorbent and its efficiency on DCAN removal.

Methodology

Synthesis of the Napier grass-derived adsorbent

Dry Napier grass was used as raw materials for preparation of Napier grass-derived adsorbent. Napier grass was carbonized at 600 °C under Liquefied Petroleum Gas (LPG) for 1 hour with the pilot furnace which fed raw Napier grass 1 kg. The details of pilot furnace was proposed by the study of Sriboonnak (2019) [13]. The size of Napier grass-derived adsorbent was sieved by 60-100 mesh sieve size to obtains the particle size of Napier grass char in the range of 100-250 µm.

Characterization of Napier grass-derived adsorbent

The characteristics of Napier grass-derived adsorbent were analyzed. The specific surface area was determined by using The Brunauer Emmett-Teller (BET) method with the nitrogen adsorption isotherm at temperature 77 kelvin using the Automatic Surface Analyzer Instrument (Quanta Chrome, model autosorb 1) and the surface charges were investigated by using Point of zero charge (PZC) method.

The PZC experiment was conducted with the initial solution from synthetic water and tap water. The pH of initial solution was adjusted to a range of 1 – 14 by using 0.1 and 0.5 M of NaOH and HCl. After that, the Napier grass-derived adsorbent was added into a flask that contained the initial solution. Then, it was shaken at 200 rpm under room temperature for 48 hr and measured pH every 24 hr. Finally, the initial and final pH were plotted together. The result of PZC from synthetic water and tap water was compared.

Removal of DCAN by Napier grass-derived adsorbent

In the DCAN removal experiment, two sources of water sample were used during the experiment including synthetic water and tap water. Synthetic water was prepared by dissolved potassium dihydrogen phosphate and dipotassium hydrogen phosphate in milli-Q water. While tap water was taken from the laboratory room at department of Environmental Engineering, Faculty of Engineering, Chiang Mai university. DCAN was purchased from Sigma-Aldrich®, Laboratory grade.

The DCAN removal experiment was conducted with 100 mL of DCAN solutions at initial concentration 50 µg/L. The prepared solution was added to the volumetric flask containing Napier grass-derived adsorbent in the varied dose of 0.25 to 3.0 g/L. Then, it was shaken at 200 rpm under room temperature for 24 hr. After that, the samples were filtered through a 0.20 µm nylon syringe filter. DCAN concentrations were analyzed by Gas

Chromatography (GC). Then, compared results between synthetic water and tap water.

Adsorption Kinetics

The adsorption kinetics experiment was investigated by using 2.0 g of Napier grass-derived adsorbent in 100 mL of water sample containing 50 μg/L of DCAN. The adsorption kinetic was conducted by shaking at 200 rpm under room temperature for 24 hours. The water samples were collected at various times including 0.5, 1, 3, 5, 10, 20, 30, 40, 50, 60, 180, 360, 720, 900, 1080, and 1440 minutes. The collected water samples were filtered through a 0.20 μm nylon syringe filter and DCAN concentrations were analyzed by Gas Chromatography (GC). Then, compared results between synthetic water and tap water.

The pseudo-first order and pseudo-second order were investigated by plotting graph of a linear equations in Equation 1 and Equation 2, respectively.

$$\log (Q_e - Q_t) = \log Q_e - [(k_1/2.303)*t] \quad (1)$$

$$t/Q_t = [1/(k_2 Q_e^2)] + (t/Q_e) \quad (2)$$

Adsorption Isotherm

The adsorption isotherm experiment was conducted by using 2.0 g of Napier grass-derived adsorbent in 100 mL of water sample. Water sample was varied the DCAN concentration at 25, 50, 75, 100 and 125 ug/L. The adsorption kinetic was conducted by shaking at 200 rpm under room temperature for 50 minutes. The linear and Freundlich isotherm equation are shown in Equation 3 and 4, respectively.

$$1/q_e = 1/q_m + 1/(b q_m C_e) \quad (3)$$

$$q = K_f C_e{}^\wedge{}^{(1/n)} \quad (4)$$

Results and Discussions

Characteristics of Napier grass-derived Adsorbent

BET surface area of Napier grass-derived adsorbent was 182.53 m^2/g and average pore diameter was 2.9579 nm. The results of BET surface area and average pore diameter were compared with the low-cost adsorbent for calico fabric as shown in Table 1.

From the results in Table 1, it was found that the surface area of Napier grass-derived adsorbent was lower than calico fabric-derived adsorbent due to the production of calico fabric-derived adsorbent used higher temperature (880 ^oC) than the production of Napier grass-derived adsorbent (600 ^oC). From the results, it can be confirmed that the production of adsorbent at higher temperatures results in surface area increasing and lower pore diameter. However, production of adsorbent at higher temperatures requires higher operation cost.

The surface charges of Napier grass-derived adsorbent in synthetic water and tap water were studied through point of zero charge (PZC) by varied pH of solution. The results are shown in Figure 1 and Figure 2, respectively.

From the results, it was found that the point at which the total charge is equal to zero was approximately 7 both in synthetic water and tap water. If the pH value in solution was lower than pH value at PZC, the carbon surface has a net positive charge. On the other hand, if the pH value in solution higher than pH value at PZC, the carbon surface has a net negative charge [15].

The DCAN removal efficiency by Napier grass-derived adsorbent

The DCAN removal efficiency by Napier grass-derived adsorbent was investigated under synthetic and tap water. The results are shown in Figure 3 and Figure 4, respectively.

From the obtained results, it was found that DCAN was highly adsorbed by Napier grass-derived adsorbent. The DCAN species can absorb on the adsorbent surface and inside the pore volume [15]. The DCAN removal efficiency was increased with increasing of Napier grass-derived adsorbent dosage both in synthetic water and tap water. The highest DCAN removal efficiency was found at Napier grass-derived adsorbent dosage 3.0 g/L for both synthetic water (100%) and tap water (100%), respectively. When considered the DCAN removal efficiency from Napier grass-derived adsorbent dosage at 2.0 g/L, it found that the removal efficiency was higher than 95% and close to removal efficiency from 3.0 g/L dosage. Therefore, the optimal dosage of Napier grass-derived adsorbent should be 2.0 g/L due to provide higher efficiency and use less adsorbent.

Table 1 The comparison of BET surface area and average pore diameter

Materials	S_{BET} [a] (m^2/g)	pore diameter (nm)
Napier grass-derived Adsorbent	182.53	2.958
Calico fabric-derived Adsorbent[b]	262.51	1.514

[a] The Brunauer-Emmett-Teller (BET) surface area

[b] Yimyam, (2023) [14]

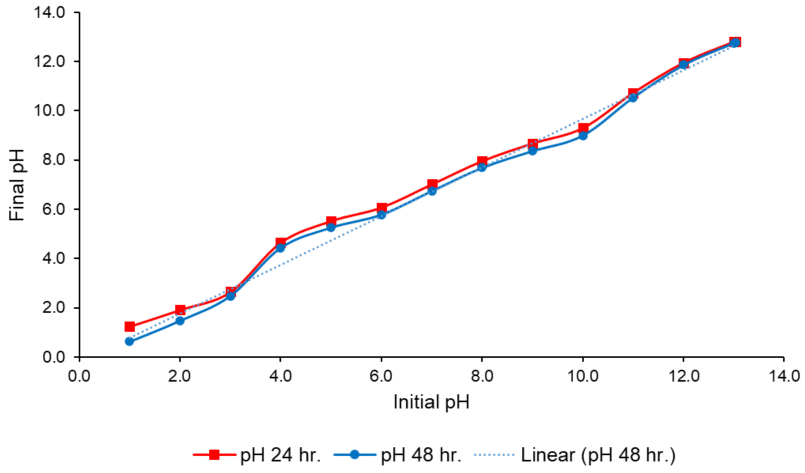


Figure 1 Point of zero charge (PZC) of Napier grass-derived adsorbent in synthetic water

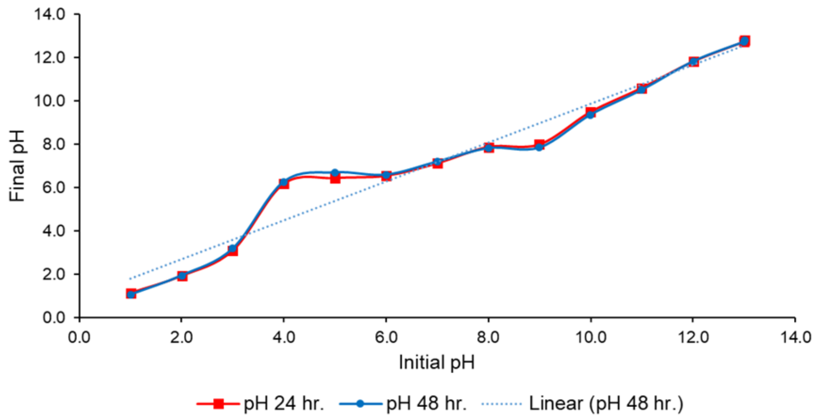


Figure 2 Point of zero charge (PZC) of Napier grass-derived adsorbent in tap water

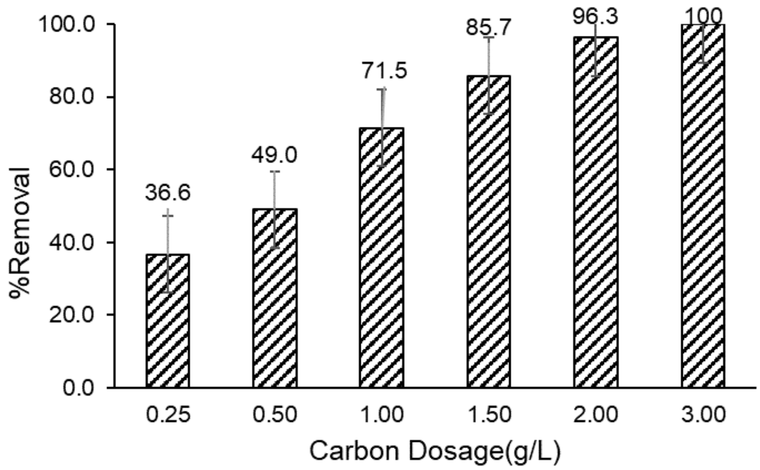


Figure 3 Removal efficiency of DCAN in synthetic water

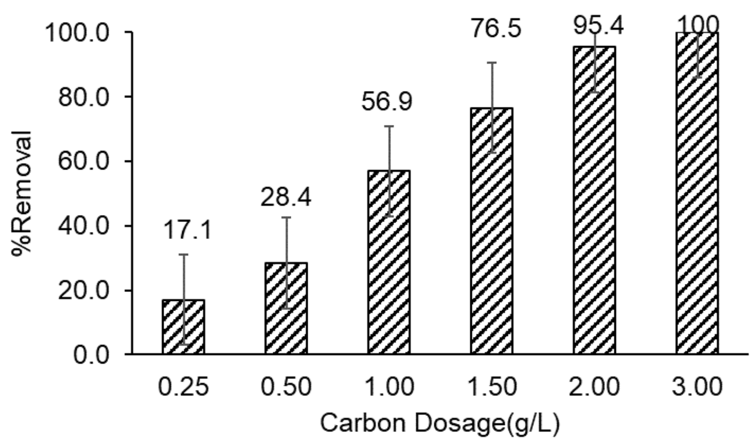


Figure 4 Removal efficiency of DCAN in tap water

When compared the results of synthetic and tap water, the DCAN removal efficiency in tap water was lower than those in synthetic water at the same Napier grass-derived adsorbent dosage. The decrease of removal efficiency might be affected from the presence of organic and inorganic matter in tap water. The organic and inorganic matter presence in tap water can be absorbed by Napier grass-derived adsorbent. Thus, it can reduce the removal efficiency of DCAN.

Kinetic adsorption of Napier grass-derived adsorbent

Kinetic adsorption of DCAN by Napier grass-derived adsorbent in synthetic water and tap water were studied. The kinetic curve for DCAN adsorption on Napier grass-derived adsorbent in synthetic and tap water are shown in Figure 5 and Figure 6, respectively.

The results from adsorption kinetic showed that the adsorption rate was fast in the beginning and then slowed down before reaching equilibrium condition. The adsorption rate was related to the adsorption capacity of adsorbent. The quick adsorption rate in the beginning step might be due to the high number of active sites on the adsorbent surface in the beginning of adsorption experiment [16]. The equilibrium time for DCAN adsorption by Napier grass-derived adsorbent in synthetic water and tap water was 50 minutes. The equilibrium time for DCAN adsorption was the same as DCAN adsorption using adsorbent from calico fabric materials [14]. The quickly of reaching equilibrium related to the molecular surface, it can be stated that the molecular surface of Napier grass-derived adsorbent was the same as adsorbent from calico fabric materials.

The kinetics model was investigated by plotting graphs of linear equations of pseudo-first order and pseudo-second order in Equation 1 and Equation 2, respectively. The plotting of pseudo-first order and pseudo-second order of synthetic water are shown in Figure 7 and Figure 8, respectively.

From the linear plot with the pseudo-first order and pseudo-second order equation is shown in Figure 7, the obtained correlation coefficient (R^2) was 0.9458 and 0.9900, respectively. While the obtained result in Figure 8 showed that the correlation coefficient (R^2) was 0.9195 and 0.9851, respectively. Thus, it can conclude that the adsorption of DCAN by using Napier grass-derived adsorbent was fitted with pseudo-second order both in synthetic and tap water. It can be described that the adsorption mechanism on Napier grass-derived adsorbent is caused by chemical forces (Chemisorption) and depends on the sharing or exchange of electrons [17]. The results were well related to the results of DCAN removal by using adsorbent produced from calico fabric which reported that it was fitted to pseudo-second order model with higher correlation coefficients (R^2 = 0.9890) [14].

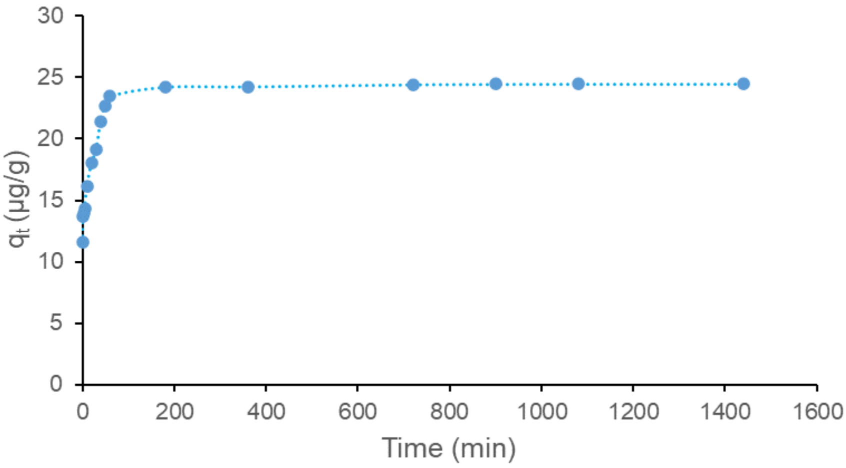


Figure 5 Adsorption kinetic of DCAN on Napier grass-derived adsorbent in synthetic water

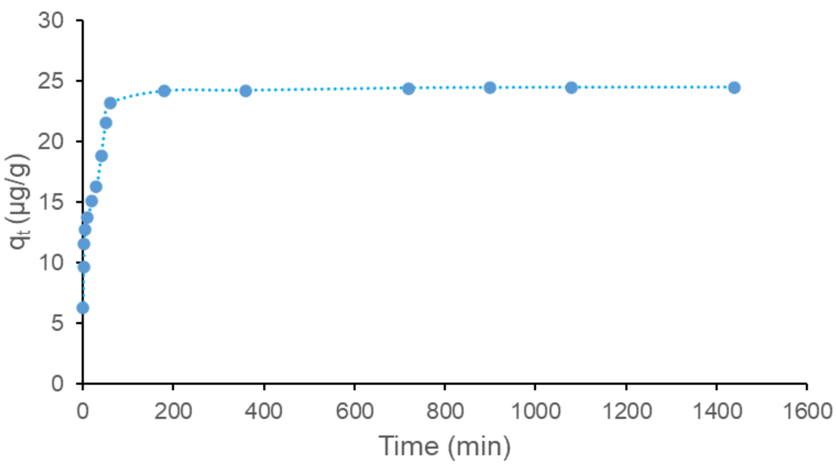


Figure 6 Adsorption kinetic of DCAN on Napier grass-derived adsorbent in tap water

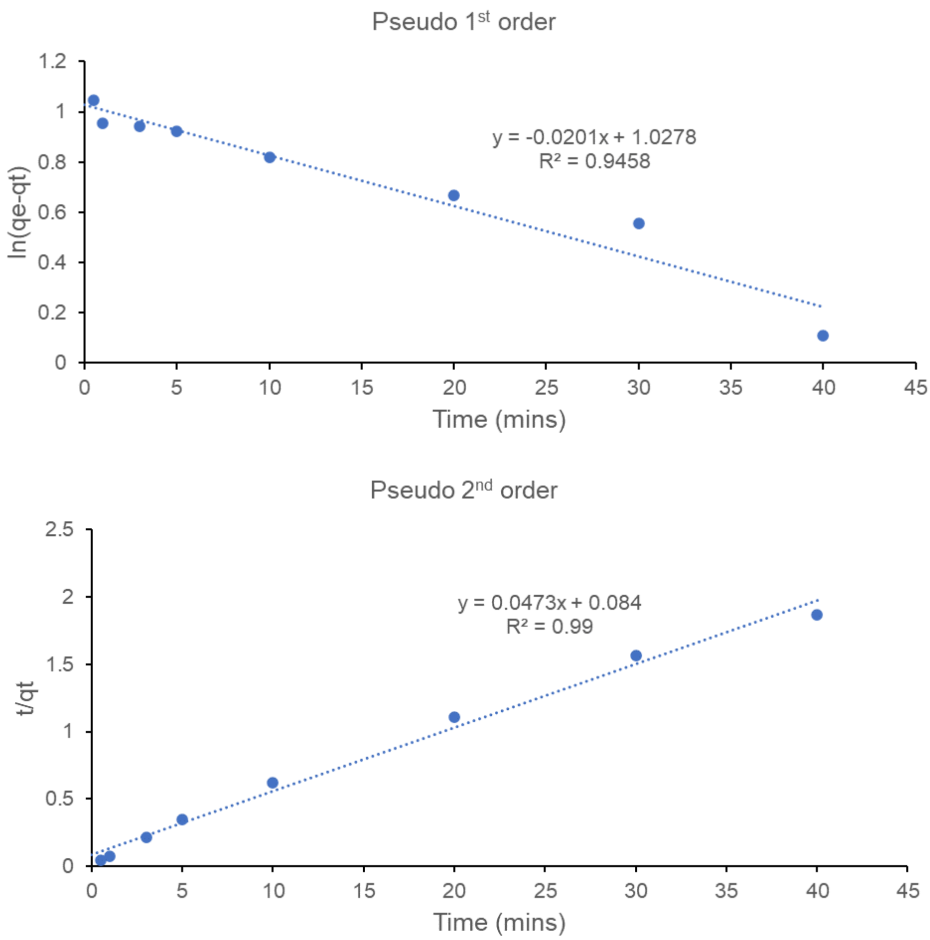


Figure 7 Linear equations of pseudo-first order and pseudo-second order of Napier grass-derived adsorbent in synthetic water

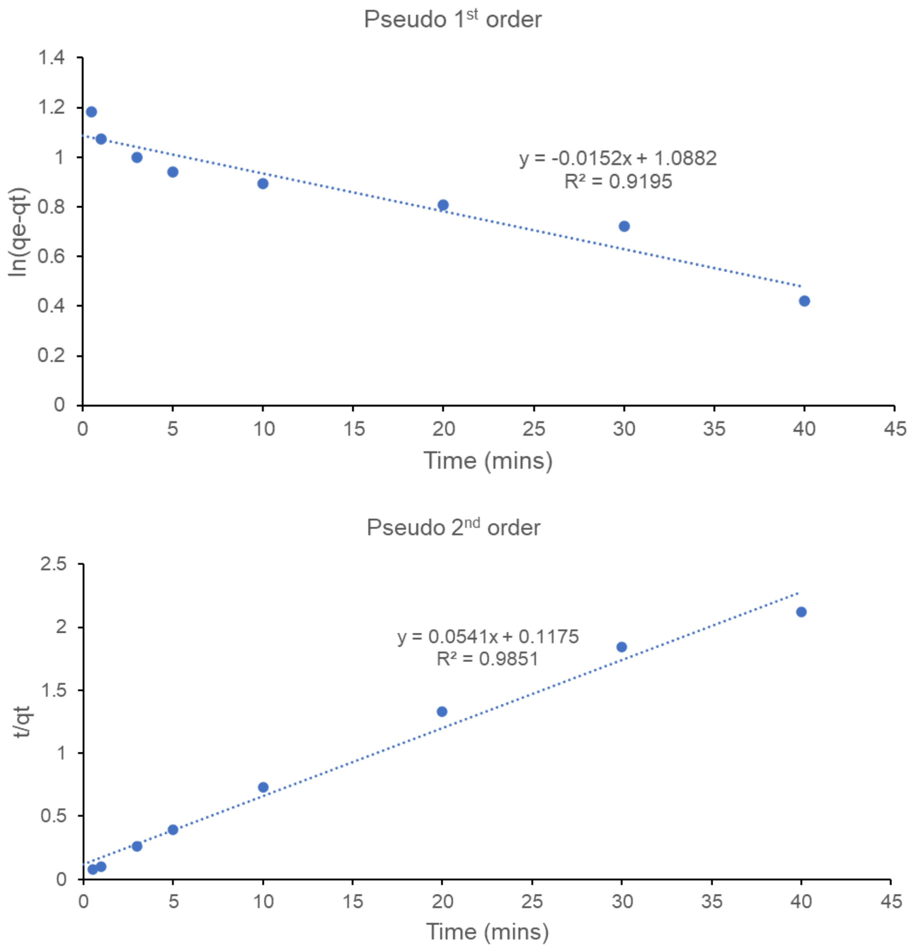


Figure 8 Linear equations of pseudo-first order and pseudo-second order of Napier grass-derived adsorbent in tap water

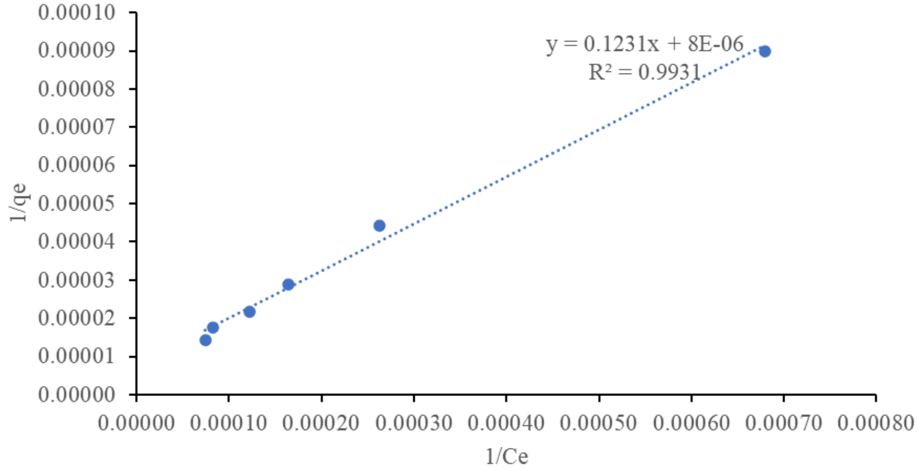
Adsorption isotherm of Napier grass-derived adsorbent

Adsorption isotherm of DCAN by Napier grass-derived adsorbent in synthetic water and tap water were studied. The linear isotherm curve and freundlich isotherm curve for DCAN adsorption on Napier grass-derived adsorbent in synthetic and tap water are shown in Figure 9 and Figure 10, respectively.

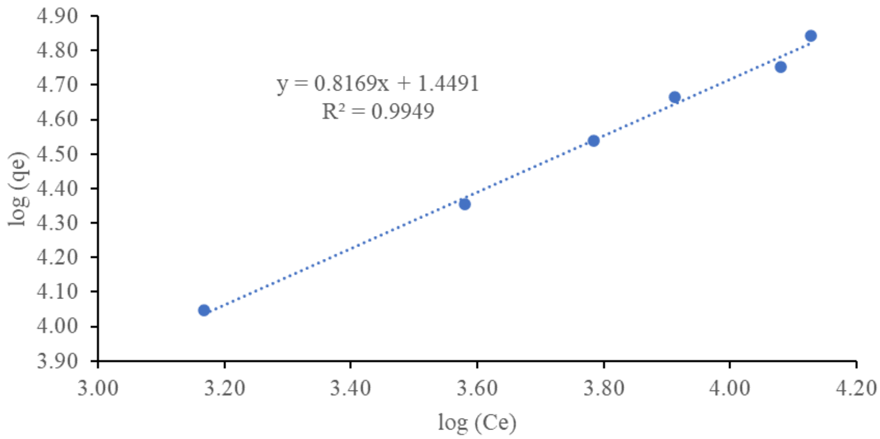
From the results of linear adsorption isotherm, the amount of DCAN adsorbed on adsorbent in synthesis water and tap water were 129.87 and 178.57 ug/g, respectively. On the other hand, the results of freundlich isotherm showed that the Kf constant of DCAN adsorbed on adsorbent in synthesis water and tap water were 7.94 and 2.32 ug/g, respectively.

When comparing the R^2 value of linear and freundlich isotherm it was found that the R^2 of freundlich isotherm was higher that R^2 of linear isotherm in synthesis water. It can be indicated that the adsorption isotherm was related to freundlich isotherm. Thus, the adsorption mechanism of DCAN in synthesis water was physical adsorption and adsorb with multiple layers on adsorbent.

Interestingly, the adsorption isotherm of DCAN in tap water was linear isotherm based on the higher R^2 values obtained. It can be indicated that DCAN was absorbed on adsorbent surface with only one layer. It might be due to the contaminant particle in tap water that need to conduct further research to clarify this assumption.

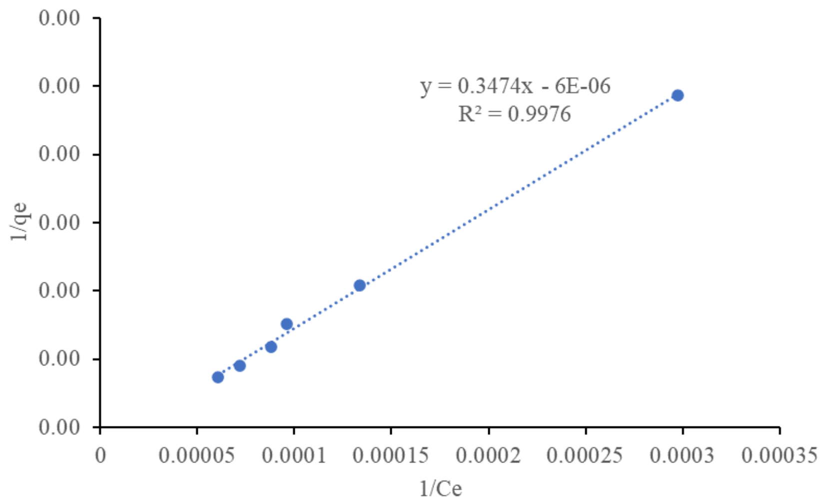


(a)

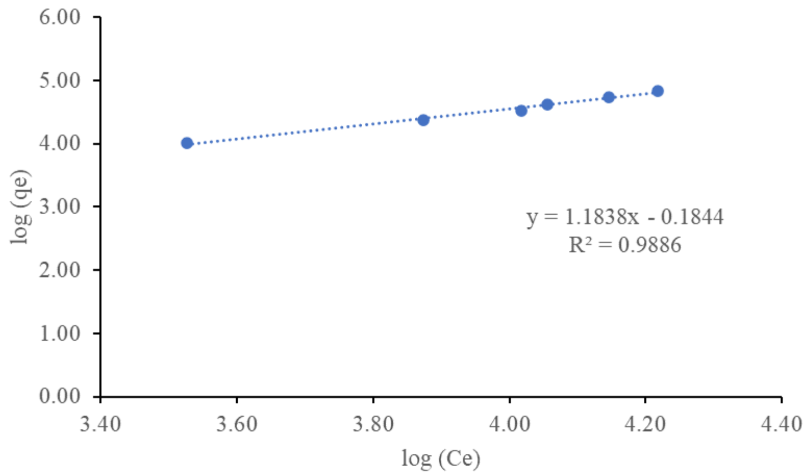


(b)

Figure 9 (a) linear isotherm curve and (b) freundlich isotherm curve for DCAN adsorption on Napier grass-derived adsorbent in synthetic



(a)



(b)

Figure 10 (a) linear isotherm curve and (b) freundlich isotherm curve for DCAN adsorption on Napier grass-derived adsorbent in synthetic

Conclusion

BET surface area of Napier grass-derived adsorbent was 182.53 m^2/g and average pore diameter was 2.9579 nm. Napier grass-derived adsorbent in synthesis water and tap water had point of zero charge (PZC) was 7. Napier grass-derived adsorbent at the optimal dosage (2.0 g/L) had a high removal efficiency of DCAN both in synthetic water and tap water (96.3% and 95.4%, respectively). The presence of organic and inorganic matter in tap water seems to affect the DCAN removal efficiency. Kinetic adsorption of Napier grass-derived adsorbent in synthetic water and tap water were fit to the pseudo-second order. In addition, the adsorption isotherm results indicated that the adsorption mechanism of DCAN on Napier grass-derived adsorbent was physical adsorption. With the highest DCAN removal percentage by using Napier grass-derived adsorbent, it indicated that Napier grass-derived adsorbent is high potential to use as low-cost adsorbent for remove DBPs from water. However, the column experiment condition also needs to be clarified before utilized in the real situation.

Acknowledgement

This research was partially funded by the Graduate School of Chiang Mai University.

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