The COD removal in chemical laboratory wastewater by using sugarcane bagasse-activated carbon

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Abstract

Chemical oxygen demand (COD) has been the crucially problematic parameter in chemical laboratory wastewater. This study was conducted to investigate the COD adsorption onto activated carbon prepared from sugarcane bagasse in batch process. The effects of adsorption such as contact time (5-240 min) and adsorbent dose (0.5-5.0 g) were evaluated. The adsorption reached the equilibrium at 120 min and the percentage of adsorption increased with increasing adsorbent dose. The equilibrium adsorption data were analyzed using Langmuir and Freundlich adsorption isothermat 30 ^oC. It was found that the adsorption correlated well with the Langmuir model and the maximum monolayer adsorption capacity was 29.15 mg/g. The kinetic data followed pseudo-second order model. The study revealed that the activated carbon prepared from sugarcane bagasse can be used as an adsorbent for the removal of COD in chemical laboratory wastewater.

Keywords: removal, kinetic, isotherm, COD, activated carbon

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Introduction

The increasing contamination of urban and industrial wastewater by chemicals is a growing environmental problem. Waste chemicals from academic laboratories are generated fundamentally by small amounts of different wastes. The complex organic and inorganic composition of laboratory wastewaters can make them difficult to treat. As a result, the treatment has been typically via chemical action or incineration (National Research Council, 1995; Benatti *et al*., 2003). Several treatment technologies have been developed for wastewater such as chemical coagulation-flocculation, biological process, membrane-based separation process and adsorption. Adsorption is an innovative and economical alternative due to its performance and ease of operation (Ali, 2012; Bennani *et al*., 2015).

Activated carbon is used as adsorbent for wastewater treatment because of its high adsorption capacity, large surface area, microporous structure (Low *et al*., 2011). However, commercially available activated carbon is expensive. Recently, this has prompted a growing research interest in the activated carbon from a range of residues–mainly industrial or agricultural by-products (Martin *et al*., 2003). The use of wastes for producing activated carbon have both economic and environmental impacts as it helps converting unnecessary, low-value waste material into a valuable adsorbent (Abdel-Ghani *et al*., 2015). Activated carbons are manufactured from a variety of materials such as Malaysia bamboo (Ahmad and Hameed, 2009), date pith (El-Naas *et al*., 2010), Lawsoniainermis wood (Omri *et al*., 2012), sugarcane bagasse-based activated carbon by microwave-induced KOH activation (Azmi *et al*., 2015), coconut shell (Zhu and Kolar, 2016) and olive cake (Abdel-Ghani *et al*., 2016), etc. This study proposes the removal of COD in chemical laboratory wastewater onto low-cost activated carbon prepared from sugarcane bagasse by using H_3PO_4 as the activating agent. The experimental conditions for adsorption such as contact time (5-240 min) and adsorbent dose (0.5-5.0 g) were investigated. The experimental data were analyzed by isotherm and kinetic equations.

Methodology

1. Preparation of activated carbon from sugarcane bagasse

Sugarcane bagasse was obtained from a local shop in Lopburi city. It was cut into small pieces with the size of 1-2 cm and washed several times with tap water to remove surface impurities followed by distilled water. Then it was dried in a hot air oven. The dried sugarcane bagasse (SB) was soaked in 1.0 mol/L phosphoric acid (H_3PO_4) using SB to H_3PO_4 ratio at 1:10 (g/ml) for 24 hr. The H_3PO_4 -treated SB was dried at temperature 120 °C. The char of SB was carbonized at temperature 500 °C for 1 hr. The acid activated carbon product was washed by double distilled water until its residual solution reached the level of pH 7. It was dried in a hot air oven at 100 °C for 24 hr. The dried adsorbent was powdered and sieved to particle size of 150-300 μm and stored in a desiccator for further use.

2. Batch adsorption process

Adsorption studies of COD in chemical laboratory wastewater onto activated carbon were performed in batch method. The effects of the adsorption system such as contact time (5-240 min) and adsorbent dose (0.5-5.0 g) were investigated.

The untreated chemical laboratory wastewater was obtained from chemical laboratory of Thepsatri Rajabhat University (Lopburi) and the pH of wastewater was adjusted to 6.5-7 by using 1 mol/L HCl and 1 mol/L NaOH. After adjusting the pH, the precipitate formed and the clear wastewater obtained was the treated wastewater. The treated wastewater having the COD value of 1128.01 mg/L was used for adsorption study in batch experiments. In the experiments, 100 ml of treated wastewater and known amounts of the adsorbent were added to each 250-ml flask. The flasks were agitated at a constant speed of 200 rpm at any time in an isothermal shaker at 30±1 °C. Then the suspended matters in each sample were filtered and supernatant was measured for COD by closed reflux colorimetric method using double beam UV/Vis spectrophotometer (Analytik Jena, Specord 210 plus). The percentage of adsorption (%) and the capacity of adsorption (q_t) were calculated as follows:

$$\%\ \text{adsorption} = \frac{(C_o - C_t)}{C_o} \times 100 \qquad (1)$$

$$q_t = \frac{V(C_o - C_t)}{W} \qquad (2)$$

when q_t (mg/g) is the amount adsorbed at any time, C_o (mg/L) is the initial COD concentration, C_t (mg/L) is the concentration of COD at any time, V(L) is the total volume of solution and W (g) is the mass of adsorbent.

Adsorption isotherm

The Langmuir isotherm in a linear form is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} Ce + \frac{1}{K_L q_m} \qquad (3)$$

where C_e (mg/L) is the concentration of COD at equilibrium time, q_e (mg/g) is the amount adsorbed at equilibrium, K_L is the Langmuir constant and q_{max} (mg/g) is the maximum adsorption capacity.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter, R_L which is defined by

$$R_L = 1/(1 + K_L C_o) \qquad (4)$$

The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm in a linear form is represented as follows:

$$\log q_e = \log K_F + 1/n \log C_e \qquad (5)$$

where K_F (L/g) is the adsorption capacity and 1/n is the adsorption intensity.

Adsorption kinetic

The pseudo-first order kinetic in a linear form is written as follows:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (6)$$

The pseudo-second order kinetic in a linear form is written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (7)$$

where k_1 and k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) is the rate constant of pseudo-first and pseudo-second order

The intra-particle diffusion model is expressed as:

$$q_t = k_{id} (t)^{1/2} + C \qquad (8)$$

k_{id} is the intra-particle diffusion rate constant (mg/g $min^{1/2}$) and C is the intercept:

Results and discussion

Effect of contact time

The effect of contact time was investigated by shaking 100 ml COD wastewater with 1.0 g of activated carbon at varying time. The results of adsorption capacity at any time were presented in (Figure 1). As seen in (Figure 1), the uptake of COD occurred rapidly at the first 15 min of the contact period and thereafter it became slower and constant at equilibrium. The results showed that the contact time of adsorption reached equilibrium at 120 min. The adsorption capacity increased from 7.85 to 20.12 mg/g with an increase in the contact time from 5 to 120 min. It was seen that the adsorption increased with the increase of contact time up to 120 min. Further increase in contact time did not enhance the adsorption. Initially, the rate of adsorption was rapid due to the adsorption of dye molecules onto the exterior surface. Thereafter, the molecules enter into pores, interior surface, with a relatively slow process (Ahmad and Kumar, 2010). The initial faster rates of adsorption may be attributed to the presence of large number of binding sites for adsorption and the slower adsorption rates for further contact time is due to the saturation of the binding sites and attainment of equilibrium (Palanisamy *et al*., 2013). Similar observation for the adsorption of COD on zeolite, activated carbon and composite material was reported (Halim *et al*., 2010).

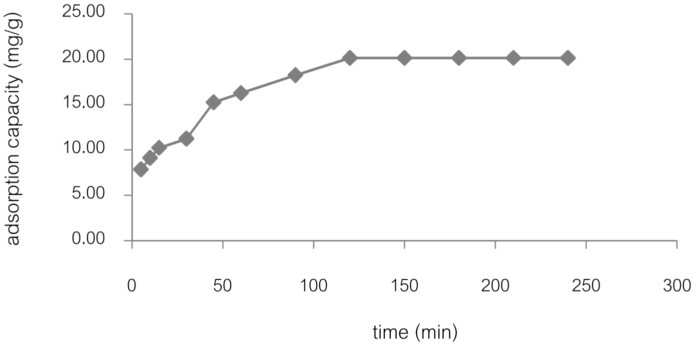


Figure 1 The effect of contact time of COD adsorption.

Effect of adsorbent dose

The effect of adsorbent dose at a contact time of 120 min was investigated by varying the amount of activated carbon from 0.5 to 5.0 g in 100 ml COD wastewater. (Figure 2) showed the adsorption percentage versus the adsorbent doses. The percentage of adsorption increased from 8.92 to 16.71 32.48 45.47 54.41 and 56.40 as the adsorbent dose increased from 0.5 to 1.0 2.0 3.0 4.0 and 5.0 g, respectively. The percentage of adsorption increased with increase in adsorbent dosage (g) due to increase binding sites at higher amount of adsorbent (Fytianos *et al*., 2000). Increased adsorbent dose implied a greater surface area of adsorbent and, consequently, a great number of possible binding sites. At higher dose, the change of adsorption was little because of the presence of higher amount of adsorbent in COD wastewater resulting in reduced distance between the adsorbent particles, thus making some binding sites unoccupied (Ahmed *et al*., 2016). Therefore, at the adsorbent dose over 5.0 g, the percentage of adsorption would reach a plateau. Similar observation has been reported for the adsorption of methylene blue on montmorillonite clay (Almeida, *et al*., 2009).

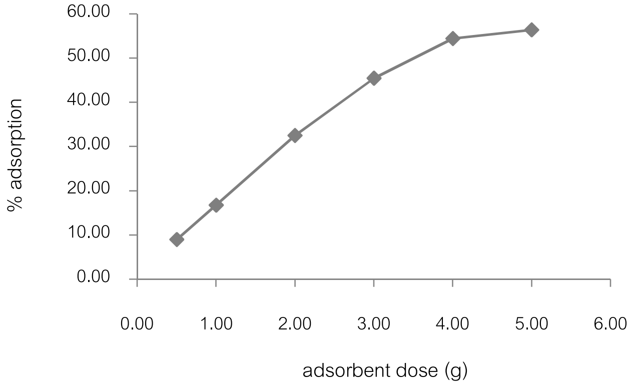
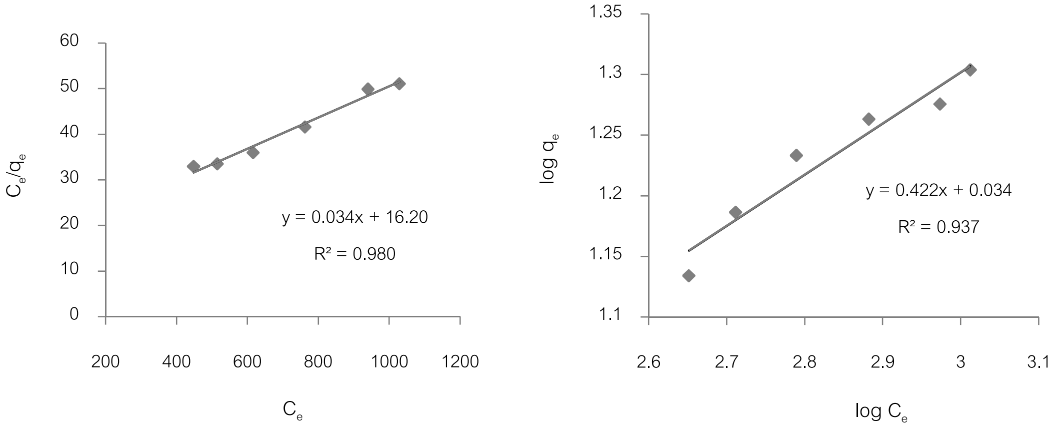


Figure 2 The effect of an adsorbent doses on COD adsorption.

Adsorption Isotherm

The linear plots of Langmuir and Freundlich isotherm models for COD adsorption onto the activated carbon were shown in (Figure 3 (a-b)), respectively. The calculated isotherm constants and their corresponding correlation coefficients (R^2) were presented in (Table 1). As seen in (Figure 3) and (Table 1), the results showed that the equilibrium adsorption data were fitted to Langmuir and Freundlich isotherm model with the correlation coefficients of 0.98 and 0.93 respectively. The best fit of experimental data with the Langmuir isotherm indicated the homogeneous nature by the monolayer coverage on surface and the maximum sorption capacity (q_{max}) of COD was found to be 29.15 mg/g.



a. Langmuir isotherm

b. Freundlich isotherm

Figure 3 The linear plots of Langmuir and Freundlich isotherm for COD adsorption.

Table 1 Langmuir and Freundlich isotherm constants of COD adsorption.

Langmuir isotherm				Freundlich isotherm		
q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	K_F (L/g)	1/n	R^2
29.15	0.002	0.31	0.98	0.03	0.42	0.94

Adsorption kinetic

From the effect study of contact time, the kinetic parameters of COD adsorption on to activated carbon were calculated using pseudo-first order, pseudo-second order and the intra-particle diffusion models, the parameters were represented in (Table 2).

Table 2 Kinetics parameters of COD adsorption for activated carbon.

kinetics	parameters
q_e, exp (mg/g)	20.12
Pseudo–first order	
q_e (mg/g)	14.24
k_1 (min^{-1})	0.002
R^2	0.98
Pseudo–second order	
q_e (mg/g)	21.83
k_2 (g.mg^{-1}.min^{-1})	0.003
R^2	0.99
Intra-particle Diffusion	
k_{id} (mg/g min$^{1/2}$)	1.49
C (mg/g)	4.35
R^2	0.97

As seen in Table 2, the correlation coefficient (R^2) of pseudo-first order and pseudo-second order models onto COD adsorption were 0.98 and 0.99 respectively. The equilibrium adsorption capacity values (q_e, cal) calculated from pseudo-first order and pseudo-second order were 14.24 and 21.83 mg/g, respectively. Based on the correlation coefficient, the kinetic data were fitted better with pseudo-second order model. Therefore, the kinetic of COD adsorption onto activated carbon could be explained by pseudo-second order model. The pseudo-second kinetic model is based on the assumption that the reaction is chemisorption involving valence force or exchange of electron between adsorbent and adsorbate (Ibrahim *et al.*, 2006).

The intra-particle diffusion model describes the diffusion mechanisms and rate controlling steps that affect the adsorption process (Zhang *et al.*, 2015). In this study, the plot of q_t against $t^{1/2}$ showed two separate linear portions. The first linear portion was attributed to intra-particle diffusion and the second linear portion was ascribed to equilibrium. The fact that portion of external surface of an adsorption was absent, implied that it was relatively very fast and the stage of intra-particle diffusion is rapidly attained and continued to equilibrium (Omri *et al.*, 2012). The k_{id} value, the intra-particle diffusion rate constant, obtained from the slope of the first linear portion was 1.49 mg/g min$^{1/2}$. While, the intercept (C) was 4.35 mg/g revealing the thickness of boundary layer. The straight line of the plot did not pass through the origin, indicated that the intra-particle diffusion was not only-rate controlling step. (Nethaji *et al.*, 2013).

Conclusion

In this study, the adsorption of COD in chemical laboratory wastewater onto activated carbon prepared from sugarcane bagasse was carried out at 30 ºC in batch process. The COD adsorption reached equilibrium at 120 min. The percentage of adsorption increased with the increase in adsorbent dosage. However, at the activated carbon dose above 5 g, the percentage of adsorption reached a plateau. The adsorption equilibrium data were well fitted by the Langmuir equation. The maximum adsorption capacity of COD on activated carbon was 29.15 mg/g. The kinetic model of COD adsorption was best described by pseudo-second order model. The results showed that the activated carbon prepared from sugarcane bagasse can be used as an adsorbent for the COD adsorption in chemical laboratory wastewater.

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