Reduction of Organics in Dairy Wastewater by Adsorption on a Prepared Charcoal from Iraqi Sugarcane

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Abstract. The prepared charcoal from Iraqi sugarcane was used to reduce the high organic content in dairy wastewater. The Iraqi sugarcane was washed and cut to the size of 1 to 1.5 cm length, then placed in a stainless-steel reactor in an electrical furnace. After 2 hours at 400°C the produced charcoal was collected and weighted. The prepared charcoal with particle size less than 500 µm has 213.52 m²/g surface area and 1.2824 mL/g pore volume. The performance of organics adsorption on the surface of the prepared charcoal was studied. The amount of organic reduction, expressed as dropping in chemical oxygen demand (COD), was measured initially (6948 mg/L) and at equilibrium to identify the adsorption isotherm. Adsorption isotherms of organics was consistent with Freundlich adsorption isotherm. The kinetics results of the adsorption show the process follow the pseudo-second order kinetic in different operating temperatures (15, 25, 35, and 45°C). The obtained thermodynamic parameters (∆G, ∆H and ∆S) were valuable to prove the spontaneity of the adsorption process.

Keywords: Dairy, wastewater, adsorption, charcoal, sugarcane, COD.

1. Introduction

The dairy is one of the main industries in food manufacturing. The dairy industry produces about 2.5 liter of wastewater effluent of richly with organic material per each liter of milk processed [1]. Both of the cheese and ice cream factories producing very large amount of the rich-organics stream. The organic materials in the produced wastewater from the dairy industry definitely containing protein (most of them are amino acid), fats, protein carbohydrate [2]. Also, direct discharging of the dairy wastewater into the surface water streams resulting an environmentally shock load, caused by reduction of dissolved oxygen that consumed in the converting reaction of the lactose into lactic [3]. The fairly high concentration of organics in dairy waste makes its consequences in higher biological oxygen demand (BOD) as well as chemical oxygen demand (COD). The COD of the dairy waste stream widely vary between 60 to 80000 mg/L depending on the final product [1], [4].

Several handling techniques used to treat the dairy waste streams. The treatment methods are classified as physical, chemical and biological. The selection of the treatment procedures is depending on the location of the treatment plant and the required level of the purification[5]. Sometimes, the dairy wastewater stream needs to pre-treatment by equalization, neutralization and separation/clarification. The main techniques used to treatment the dairy wastewater are: biological methods, activated sludge process, aerobic process and anaerobic digestion [5], [6]. Other techniques are usually used for treatment dairy effluents, such as osmosis membranes [7], [8], ultrafiltration [9], electrochemical treatment [10], [11], electrocoagulation [12] and adsorption [13], [14].
The aim of the research is trying to reduce the organic content of the dairy wastewater (got from the cheese industry) and to absorb the organics materials by the charcoal prepared from the Iraqi sugarcane. The wastewater was selected for containing a high amount of organic matter (and high COD). Also, it will be one of the objectives of the study to estimate and discussed the equilibrium isotherms and kinetics model of the process of removal by adsorption and perform a thermodynamic analysis for the process.

2. Experimental work
2.1 Charcoal preparation

Sugarcane was used to prepare the charcoal. Firstly, the sugarcane was washed with distilled water several times to remove the dirty and soil and then dried at 100 °C for 96 h. The dried sugarcane was cut to pieces with a size between 1 and 1.5 cm, then mounted to a stainless-steel reactor with 3 cm in diameter and 15 cm length that was closed in one end and the other end had a removable cover containing a 1 mm hole in the middle of it for escaping pyrolysis gases. The reactor was heated at a rate of 10 °C/min in an electrical furnace at 400°C for 2 hours. Then, allowed to cool to the room temperature.

The produced charcoal was crushed by disk mill and then sieved. Carbon material of particle size less than 500 µm was characterized by measuring surface area, and pore volume, before used in reduction of the organic from dairy wastewater.

2.2 Adsorption of organic

Batch adsorption experiments were carried out by using 0.5 g of charcoal per half litre of the dairy wastewater and its diluted solutions. The solutions were putted on a shaker at a uniform speed of 300 rpm at 25 °C for 40 hours to reach the equilibrium state. The amount of the equilibrium COD (CODₐ) was reported by averaging the COD value after treatment of three samples and then the amount of adsorbed organic per weight of charcoal adsorbent (adsorption capacity) at equilibrium (qₑ, mg/g) was calculated from Eq. (1).

$$ qₑ = \left( CODᵢ - CODₑ \right) \times \frac{V}{m} \tag{1} $$

Where $qₑ$ is the adsorption capacity of the adsorbent (mg/g), $CODᵢ$ and $CODₑ$ in (mg/L) refer to initial and final (equilibrium) concentrations of organics in the adsorption solution, $V$ (L) is the volume of adsorption solution and $m$ (g) is the weight of charcoal used.

The experimental setup consists of a half-litre three-necked flask placed on a temperature controlled magnetic heating mantel. A water-cooled condenser placed in the main vertical neck to ensure that no water loss due to evaporation from the mixture. The thermometer held in the side neck to measure the adsorption temperature and the third neck plugged with the rubber stopper as a sampling point.

Half-litre of the dairy wastewater of 6948 mg/L placed in the three-neck flask and cooled (via ice-water bath) or heated to the desired temperature (15, 25, 35, and 45°C) and the stirrer speed kept at 300 rpm for constant mixing. After reaching the required temperature, half gram of the prepared charcoal was added to the solution. At each interval up to 2 hours, four samples of 3 ml of the mixture taken and placed in the centrifuge separator with 2000 rpm for ten minutes to ensure separation of the charcoal particles and to be suitable for COD measuring.

2.3 COD measurement

Two mL of the collected samples were digested with an oxidizing agent (K₂Cr₂O₇) for 120 min at 150°C in (Lovibond COD reactor RD 125). Digested samples cooled down to room temperature then analysed in a photometer (MD 200 COD VARIO Photometer). The percentage of COD reduction from the treated solution by the adsorption over the prepared charcoal was reported, for each interval, by averaging the evaluated values obtained by Eq. (2).

$$ COD\text{ reduction } % = \frac{CODᵢₐₗₐₜ − CODₑ}{CODᵢₐₗₐₜ} \times 100 \tag{2} $$
Where \( \text{COD}_{\text{initial}} \) is the initial value of COD concentration in mg/L (6948 mg/L) at zero time, while \( \text{COD}_t \) is the value of COD concentration in mg/L after \( t \) time of adsorption.

### 2.4 Adsorption isotherms, models and regression technique

The adsorption isotherms demonstrate the interaction between the adsorbates and adsorbents. Most popular two-parameter isotherms were selected to describe the adsorption of organic on the prepared charcoal. These isotherms models are Langmuir and Freundlich [15]. The Langmuir adsorption isotherm [16] is based on monolayer adsorption on active surface sites and can be expressed as a simple model represented in Eq. (3). While, the Freundlich adsorption isotherm [17], which is assumed the adsorption process is heterogeneous on multilayer (\( n \)) as represented in Eq. (4).

\[
q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}
\]  
(3)

\[
q_e = K_F C_e^n
\]  
(4)

Where \( q_e \) adsorption capacity mg adsorbate per g adsorbent, \( C_e \) is concentration at equilibrium mg/L, \( q_{\text{max}} \) is the maximum adsorption capacity in forming complete monolayer on the surface mg/g, \( K_L \) is Langmuir coefficient related to the affinity between the adsorbate and adsorbent (L/mg), \( K_F \) is the Freundlich coefficient and \( n \) is the number of multilayer.

Adsorption–reaction models [18] were used to described the adsorption capacity variation with time. These models are; Pseudo-first order (Eq. 5) [19], and pseudo-second order (Eq.6) [20].

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  
(5)

\[
t = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]  
(6)

Where \( q_e \) and \( q_t \) (in mg/g) are the adsorption capacity at equilibrium and any time (t), respectively. \( k_1 \) (1/min), and \( k_2 \) (g/mg.min) are the adsorption rate constants for pseudo-first order, and pseudo-second order kinetic models, respectively.

All isothermal and kinetics models were solved numerically by maximized the correlation coefficient \( R^2 \) and minimised of the Chi-squared statistic \( \chi^2 \) (Eq. 7 and 8, respectively). A genetic algorithm of optimisation that written in Python [21] to solve this maximization-minimisation problem simultaneously.

\[
\chi^2 = \sum_{i=1}^{n} \left( \frac{q_{\exp} - q_{\text{cal}}}{q_{\text{cal}}} \right)^2
\]  
(7)

\[
R^2 = \frac{\sum_{i=1}^{n} \left( q_{\text{cal}} - q_{\exp} \right)^2}{\sum_{i=1}^{n} \left( q_{\exp} \right)^2} - \frac{\sum_{i=1}^{n} \left( q_{\text{cal}} - q_{\exp} \right)^2}{\sum_{i=1}^{n} \left( q_{\text{cal}} - q_{\exp} \right)^2}
\]  
(8)

Where \( q_{\exp} \) and \( q_{\text{cal}} \) (in mg/g) are the experimental value and calculated value (from model) of the adsorption capacity, respectively, \( i \) the current number of the experiment, and \( n \) is the total number of the adsorption experiments.
2.5 Thermodynamic analysis

Thermodynamic behaviour of the organic adsorption on the prepared charcoal was examined to determine thermodynamic parameters of the adsorption process. The change in Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$), were calculated by classical thermodynamic relations (Eq. (9) and Eq. (10)) based on the distribution coefficient ($K_d$) for the adsorption of organics on the surface of the adsorbent (Eq. 11) [22].

\[
\Delta G = \Delta H - T \Delta S
\]

\[
\Delta G = -RT \ln(K_d)
\]

\[
K_d = \frac{q_e}{C_e} \left( \frac{m}{V} \right)
\]

Where R is the gas constant (8.314 J/mol K) and T (K) is the absolute temperature of the adsorption process.

3. Results and discussion

The produced charcoal with size less than 500 µm was 12.2 g for each 100 g of green sugarcane. The organics amount versus different initial concentration of COD (raw dairy wastewater and the diluted solutions) represented in Fig.1. With dilution of the raw dairy wastewater the produced equilibrium concentration of the organics decreased from 2830 to 154 mg/L, and the adsorption quantity of organics on the prepared charcoal decreasing from 4118 to 1004 mg/g.

![Figure 1](image)

**Figure 1:** Effect of the equilibrium COD concentration on the adsorption capacities and adsorption equilibrium isotherms

The isotherm constants were determined using the nonlinear regression analysis, as shown in Fig.1. The different isotherm parameters along with correlation coefficient values ($R^2$) are given in Table 1. The results show that the prepared charcoal has maximum adsorption capacity with 334.0 mg of organics per each gram of the prepared charcoal. The high values of the $R^2$ value (0.9604) indicate that the Freundlich isotherm model best fits the adsorption equilibrium data and the organics adsorbed in multilayer with n equal to 1.92.
Table 1: Adsorption isotherm models constants and correlation coefficients ($R^2$) for the reduction of COD on the papered charcoal

| Isotherm model | Model parameters | Parameter value | $R^2$ |
|---------------|------------------|----------------|-------|
| Langmuir     | $q_{max}$ mg/g   | 334.0          | 0.7169 |
|              | $K_L$ l/mg       | 0.0025         |       |
| Freundlich   | $K_F$ mg$^{1-n}$/g | 69.16          | 0.9604 |
|              | $n_r$ -          | 1.92           |       |

The reduction of COD of the dairy wastewater was growing with time at all adsorption temperatures, as shown in Fig. 2. Organic removal (measure as COD reduction) higher in lower temperature, as adsorption process temperature increased the amount of the removal decreases.

![Figure 2: Effect of time on the organic removal (COD reduction) via adsorption on the prepared charcoal](image)

The removal of organics increasing sharply in the first 15 minutes, then increasing gradually up to 45 minutes. After about 60 minutes, no valid change was detected. Because of the emptiness of the pores of the prepared charcoal at the beginning, the high speed of the transfer organics from liquid bulk to the charcoal surface occurred due to the excessive difference in concentration. With progress over time, more organics adsorbed on the surface and the organics concentration difference becomes low, causing lowering in the mass transfer rate of organics from the bulk to the charcoal surface.

The kinetic analysis results of the adsorption of the organics from dairy wastewater on the prepared charcoal are summarized in Table 2. The obtained values of the $R^2$ indicate a well fit of the pseudo-second-order model (Eq. 6) with the experimental data. The $R^2$ values for ranging for the pseudo-second-order model 0.994 to 0.9998, which indicate highly and precisely explanation of the experimental adsorption data with the pseudo-second-order model. While, the very low values of $R^2$ of the pseudo-first-order model indicated bad representation of the experimental data. The pseudo-second order equation is typically described the adsorption of the organics from aqueous on different adsorbents. [23]–[26]
The thermodynamic analysis results (Table 3) of the COD reduction (organics removal) from dairy wastewater shows the process is endothermic with positive value of $\Delta H$ (1385.7 J/mol). This mean as the process temperature decreases, the organics adsorption increases. This observation was obviously appearing in Fig. 2. Also, the decreasing values of $\Delta G$ with the temperature mark that the adsorption process preferred lowing in temperature. Nevertheless, the negative values $\Delta G$ and the positive value of $\Delta S$ (7.74 J/mol K) realizing the spontaneity of the organic adsorption process on the prepared charcoal from Iraqi sugarcane.

### Table 3: Adsorption thermodynamic parameters and correlation coefficients ($R^2$) for the reduction of COD on the papered charcoal

| Temperature, °C (K) | $K_d$ | $\Delta G$, J/mol | $\Delta H$, J/mol | $\Delta S$, J/mol K | $R^2$ |
|---------------------|------|-------------------|------------------|---------------------|-------|
| 15 (288)            | 1.418 | -835.5            |                  |                     |       |
| 25 (298)            | 1.455 | -929.3            |                  |                     |       |
| 35 (308)            | 1.477 | -998.7            | 1385.7           | 7.74                | 0.9836|
| 45 (318)            | 1.498 | -1069.1           |                  |                     |       |

### 4. Conclusion

Organics high contents in dairy wastewater (COD= 6948 mg/L) can be reduced sufficiently by using charcoal prepared from the sugarcane. Freundlich adsorption isotherm described the adsorption of organics on the charcoal surface with a 334.0 mg/g maximum adsorption capacity. An average of about 60% of the organics (represented as COD) removed within 45 to 60 minutes of treatment and in the temperature range between 15 to 25 °C. The kinetics of the adsorption of the organics on the charcoal followed the pseudo-second-order model for all temperature range (15 to 45 °C) and the values of the adsorption rate constant lower obviously with the temperature of the treatment. Finally, thermodynamic parameters ($\Delta G$, $\Delta H$ and $\Delta S$) values showed that the adsorption process is endothermic with a positive value of $\Delta H$ (1385.7 J/mol) and the negative values $\Delta G$ and the positive value of $\Delta S$ (7.74 J/mol K) realizing the spontaneity of the organic adsorption process on the prepared charcoal from Iraqi sugarcane.

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