Adsorption Isotherm studies for COD-BOD Removal from Dairy Waste Water Using Freshly Prepared Adsorbent

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Abstract
Dairy industry is a major source of waste water generation with the major pollutants as organic components like dissolved sugars, carbohydrates, proteins and fat, Suspended Solid, Total Dissolved Solid, Sulfur, Phosphorous and Nitrogen. So the dairy wastewater is considered as high concentration of organic matter, high COD and high BOD. An experimental study was carried out for the treatment of dairy waste water using low cost adsorbents coconut shell activated carbon. The adsorbent was used for treatment of dairy waste water with different dosages and contact time. The results of COD and BOD removal is up to 76 % and 82 % for coconut shell activated carbon at dosage of 150 mg and at contact time 120min. The results were validated using Langmuir and Freundlich equations.
Keywords: Dairy waste water, COD, BOD, Isotherms.

1. INTRODUCTION

Industrialization is an essential part for economic growth of country. Due to industrialization, pollution is the major problem throughout the world, (1). Among various industries, the food industries are one of the highest consumers of water and are one of the biggest producers of effluent. The dairy industry is an example of food industries. India is the largest producer of milk and dairy products in world and ranked first among the milk producing countries. Every year, the growth rate of dairy industry is expected to 4-5%. It produces various milk products like milk powder, butter milk, curd, cheese, pasteurized milk etc. In dairy industries, large amount of fresh water is used throughout all the steps of processing starting from milk receiving station to packaging station for example collecting, cooling, heating, sanitary, processing, utilities and service section during processing of milk and milk products, (2). It is estimated that dairy industries generate 2.5 to 10 L of wastewater for the processing of 1 L of milk, (3). The waste water from dairy industry contains large quantities of milk constituents such as casein, lactose, fat, inorganic salt, besides detergents and sanitizers used for washing, (4). Dairy waste water is identified having high COD, BOD due to high organic contents having 1/3 dissolved, 1/3 colloidal, and 1/3 suspended substances, and TDS, TSS contents, (5). Due to the presence of high pollutants in dairy waste water, the milk-processing industries discharging untreated or partially treated waste water cause serious environmental problems, (6). Effluent production and disposal remain a big issue for the dairy industry. As per the CPCB and WHO, the permeable level of effluent is mentioned in Table I.

TABLE I. Minimum standards maintained for discharge of effluents from the dairy industry

Parameter	**Maximum Value (mg/L)**	**World Bank Report CPCB, India**
pH	6-9	6.5-8.5
BOD5	50	100
COD	250	-
TSS	50	150
Oil & Grease	10	10
Total Nitrogen	10	-
Total Phosphorus	2	-
Temperature Increase	< = 30 C	-
Coliform Bacteria	400 Most Probable Number / 100 mL	-

Hence, Suitable disposal of effluents in wastewater has been a major challenging issue for the dairy industry in India. In this work, the adsorption method is used for removal of the effluent from the dairy waste water. The adsorbent manufactured from Coconut shell is designed for reduction of tastes, odors and dissolved organic chemicals from industrial water supplies, (7). Coconut shell based activated carbon can act as a good adsorbent for waste water treatment because its adsorption capacity depends upon the pore size, surface area micropore volume of the activated carbon.

2. MATERIALS AND METHOD

2.1 Synthetic dairy waste water Preparation:

The synthetic dairy waste water was prepared by mixing different chemicals in 1 L of tap water, (8 and 9). The ratio is given in Table II.

TABLE II. Quantity of chemicals added in 1L tap water for preparation of synthetic dairy waste water

Sl No.	**Name of Chemicals**	**Quantity (gm)**
1	Milk powder	5
2	Glucose	2
3	Sodium Nitrate	1
4	Potassium Phosphate	1
5	Calcium Chloride	1

After mixing the chemicals, the mixture was kept for 24 hrs for fermentation. The synthetic dairy waste water of 10 L was prepared to carry out the experimental work.

2.2 Coconut Shell Granular Activated Carbon (CGAC) preparation

The granular activated carbon was prepared from coconut shell. Coconut shell was collected from temple side of GIET University, Gunupur and Gunupur locality. It was dried for 15 days in sunlight. After drying, the coconut shell was separated from other materials like coconut fibre or sand, cleaned and prepared to be placed in the furnace. Then, it was heated in furnace at 400^0C for 2 hrs.

The chemical reaction carried out as shown in equation 1.

$$\text{Cocunut shell} \xrightarrow{400^0\text{C}} \text{Carbon} + \text{Ash} + \text{Volatile gases} \quad [1]$$

After that, it was allowed to cool in a desiccator for 20 min. Then it was ground and sieved to get a particle size of 1mm. Then it was acid washed using Hydrochloric acid to activate its surface. The activation was carried out as shown in equation 2.

$$\text{Carbon} \xrightarrow{\text{HCl}} \text{Activated Carbon} + \text{HCl} \quad [2]$$

Its activated characteristic was checked. Fig. 1 shows the preparation process of CGAC.

Figure 1. Preparation of CGAC

Coconut shell-based activated carbons are the less dust, predominantly micro porous. So the CGAC is well-suited for organic chemical adsorption. This activated carbon has the highest hardness compared to other types of activated carbons, which makes it the ideal carbon for water purification.

2.3 Experimental Set up

The set up was done in the laboratory. The freshly prepared CGAC was used in this experiment. The absorption column was designed using cylindrical glass pipe. The diameter and height of the glass pipe was 3 cm and 50cm, respectively. 5 different fixed beds were designed with various dosage of CGAC like 30 mg, 60 mg, 90 mg, 120 mg and 150 mg was packed in 5 different glass bars. The particle size for CGAC was taken as 1 mm. The treated water was collected from the bottom of the cylindrical pipe. The contact time was maintained for 30 min, 60 min, 90 min and 120 min, respectively.

2.4 Experimental Procedure

The synthetic dairy waste water was pre-treated before the analysis of COD and BOD. The waste water was first filtered using filter paper to separate the suspended solid in it. The COD and BOD value of the filtered synthetic dairy waste water was analyzed before passing through the bed. Then it was allowed to flow through the beds from the top through various bed heights at various contact time. After a fixed contact time, it was collected from the bottom of the column and taken for further COD and BOD analysis.

2.4.1 Analytical method for COD measurement

The COD test was carried out using a standard procedure. 50 mL of samples were carried out in 6 flasks, out of which 1 flask having the untreated water and rest 5 flasks having treated water by CGAC. Potassium dichromate solution was added to each flask with stirring gently. Solutions were heated in water bath at 100^0C for 1 hr. Then samples were removed and allowed to cool till room temperature. Then potassium iodide & sulphuric acid were added to the samples. The samples were titrated with sodium thiosulphate solution. The COD values were determined.

2.4.2 Analytical method for BOD

The BOD tests were done using BOD bottles and BOD incubator. The samples were taken in 6 BOD bottles, out of which 1 bottle was filled with untreated water and rest 5 bottles were filled with treated water by CGAC. The bottles were kept in the incubator maintaining temperature 20^0C for 5 days. After 5 days, BOD values were observed.

3. RESULTS AND DISCUSSION

3.1 Analysis

The above experiment has been done to observe the efficiency of CGAC which can be used as an effective adsorbent in treating dairy wastewater. The COD and BOD of the Dairy waste water before treatment were obtained as 735 mg/L and 439 mg/L, respectively. With increase in dosage of adsorbents and contact time, the COD decreases. It is due to the oxidation of organic compounds. The results of COD removal using freshly prepared CGAC were reported in Table III.

TABLE III. Experiential value of removal of COD from dairy waste water at different dosage and contact time

Dosage	**Contact time (min)**				
(mg)	0	30	60	90	120
30	735	547	532	514	502
60	735	430	399	375	362
90	735	387	354	340	312
120	735	302	285	267	245
150	735	266	208	197	176

The figure 2 shows the effect of COD removal on contact time at various dosages of adsorbents.

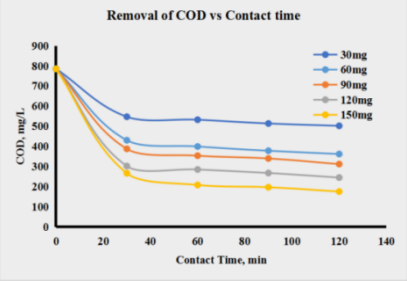

Figure 2. Variation of COD at different dosages and contact time

With increase in dosage of adsorbents and contact time, the BOD decreases. It is due to increase in dissolved oxygen and decrease in decomposition of organic compounds. The result of BOD removal using freshly prepared CGAC were reported in Table IV.

TABLE IV. Experiential value of % removal of BOD from dairy waste water at different dosage and contact time

Dosage	**Contact time (min)**				
(mg)	0	30	60	90	120
30	439	339	320	315	303
60	439	299	275	268	257
90	439	197	183	173	160

120	439	167	148	139	118
150	439	100	82	76	65

The figure 3 shows the effect of COD removal on contact time at various dosages of adsorbents.

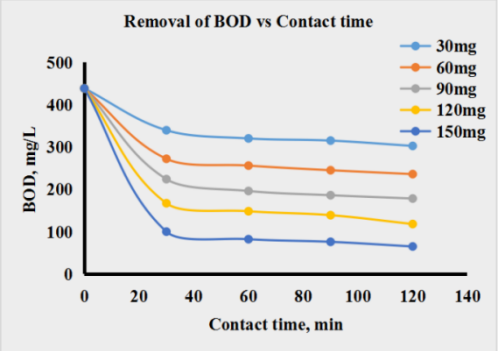

Figure 3. Variation of BOD at different dosages and contact time

It was observed that, by increasing the dosage of CGAC in the bed, the removal efficiency of COD and BOD increases.

3.2 Adsorption Isotherms

Adsorption isotherm is the representation of the amount of effluents adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the solution at constant temperature. Different adsorption isotherms are proposed by different scientists for the representation of adsorption data like, Langmuir isotherm and Freundlich isotherm.

The Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad [3]$$

Where C_e = Equilibrium concentration in mg/L

q_e = Amount of effluents adsorbed at equilibrium time (mg/g)

Q_0, b = Langmuir constants.

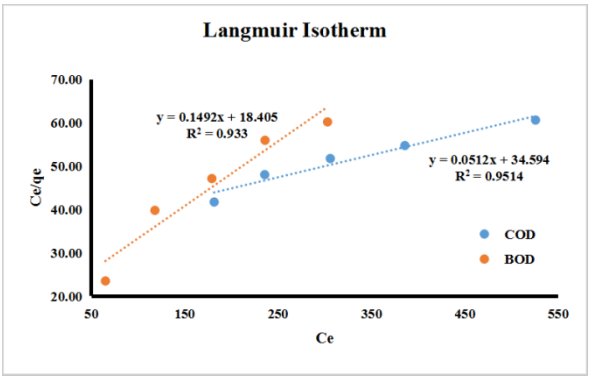

Figure 5. Langmuir isotherm

The values of the Langmuir constants are calculated from the intercept and slope of the plot of C_e/q_e versus C_e.

The Freundlich isotherm is expressed as:

$$\log q_e = \log K_f + \frac{\log C_e}{n} \qquad [4]$$

Where C_e = Equilibrium concentration in mg/L

q_e = Amount of effluents adsorbed at equilibrium time (mg/L)

K_f, n = Freundlich constants.

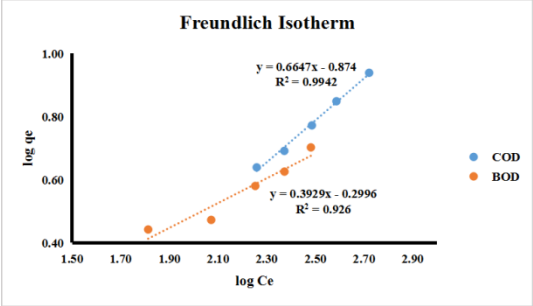

Figure 6. Freundlich isotherm

The values of the Freundlich constants are calculated from the intercept and slope of the plot of log q_e versus log C_e.

The correlation coefficients were calculated through Langmuir isotherm for COD removal as 0.9514 and for BOD removal as 0.933. The correlation coefficients were calculated through Freundlich isotherm for COD removal as 0.9942 and for BOD removal as 0.926. The analysis suggested that the Langmuir isotherm proved better fit to the adsorption data for COD removal, but Freundlich isotherm proved better fit to the adsorption data for BOD removal.

4. CONCLUSION

According to the guidelines of WHO and EPA, it has been observed that adsorption is an effective, efficient and commonly used method of water treatment providing risk free treated water. CGAC has the highest hardness compared to other types of activated carbons, which makes it as the ideal carbon for water purification. The concept of using coconut shell has proved to optimize the quantity of waste in dairy wastewater and CGAC is an effective, Economical & a sustainable adsorbent to treat the dairy wastewater. It is observed from the result that by increasing the dosage of adsorbent in the adsorption column and the contact time, the removal efficiency of BOD and COD is gradually increasing. Langmuir isotherm fitted best for COD removal and Freundlich isotherm fitted best for BOD removal.

The experiment can be carried out in continuous manner for industrial application with slight change in the experimental setup, for future progress.

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