An Investigation on Organic Matter Removal from Wastewater by Local Groundnut Shell Derived Adsorbent from Salgar Budruk-Kinetic, Isotherm and Parameter Studies

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Abstract: Removal of organic matter is normally done by activated sludge process in conventional plants. Studies have revealed that these plants are not effective and there is need for advanced treatment method for tackling the problem. The present work includes review of some investigations on various advanced methods for COD removal. Also experimental results of batch and column experiments for COD removal by using groundnut shell adsorbent are reported in the present paper. The parameters affecting the adsorption were studied and optimum values of these parameters were estimated. For the initial 0.5 to 1.5 grams of adsorbent, comparatively steep drop in concentration is observed. The central part of the curve indicates almost linear drop in COD with increase in adsorbent dosage. At lower pH, the H+ ions compete with adsorbate for the sites. At higher pH, there can be formation of complex ions or there can be hydroxides formation and subsequent precipitation also.

Keywords: Chemical oxygen demand, dissolved oxygen, concentration, isotherm, kinetics.

1. INTRODUCTION

The treatment was distillery wastewater is important aspect of sustainable growth of agro economy. The distilleries provides value addition to the sugar industry wastewater. The wastewater contains high amount of organic matter. This organic matter consumes dissolved oxygen (DO). The permissible minimum dissolve oxygen is 5 mg/l and desirable is 10 mg/l. The water with low DO smells very bad and not suitable for use. Removal of organic matter is normally done by activated sludge process in conventional plants. Studies have revealed that these plants are not effective and there is need for advanced treatment method for tackling the problem. The present work includes review of some investigations on various advanced methods for COD removal. Also experimental results of batch and column experiments for COD removal by using groundnut shell adsorbent are reported in the present paper.

2. LITERATURE REVIEW

The chemical oxygen demand and biological oxygen demand are important indicators of the dissolved oxygen content of the wastewater. Various studies have been reported on removal of the organic matter and subsequent effect on dissolved oxygen[1-5]. Various investigations on effect of organic matter on river and reservoirs indicate that the organic matter with high COD is reaching alarming level in the country. A review on modelling of packed beds for wastewater treatment was presented by Kulkarni [6]. According to him, various models like Thomas model, Yoon Nelson model and Modified Dose model are used for describing breakthrough curves. Amale et al. used wood charcoal as an adsorbent in a fixed bed for removal of organic matter from effluent[8]. They observed decrease in exhaustion time with initial concentration. With increase in bed height, the exhaustion time delayed. Dairy wastewater treatment by anaerobic fixed bed reactors was carried out by Nikolaeva et al.[8]. They used hybrid material composed of waste tyre rubber and zeolite. They observed that increase in the hydraulic retention time (HRT) brought about an improvement in the effluent quality. Kulkarni and Goswami used bagasse flyash as an adsorbent for organic matter removal from wastewater[9]. They carried out investigation in batch and column modes with satisfactory results. Electrocoagulation was used for organic matter removal by Khandegar and Saroh[10]. They
obtained COD removal efficiency was 84.6 % and 76.9 % at initial pH (7.2). Many investigations have been carried out for COD removal by using various advanced biological treatments[11-14]. These treatment includes both, aerobic and anaerobic methods. Advanced methods including membrane separations such as pervaporation, reverse osmosis, electrodialysis are also used in few investigations[15-19]. These methods are costly but yield very high quality water. Also chemical treatments using various coagulants and flocculants have been used in various investigations[20-23].

3. METHODOLOGY

Batch experiments were carried out with 150 ml of the sample volume. The effluent from the distillery was treated by using groundnut shell adsorbent. The adsorbent was prepared by thermal and chemical activation. The analysis of the sample was done for COD and colour. COD was measured by using usual method involving potassium dichromate and COD digestion apparatus (Spectralab SL 159). Absorbance was analysed by using U.V. spectrophotometer (Elico). The column operation was carried out with 1:1 mix adsorbent. The filter used was sand. The column was 5 cm in diameter and 15 cm in height. The volumetric flow rate was 20 ml/min.

4. RESULT AND DISCUSSION

4.1. Effect of Adsorbent Dose on COD and Percent Removal

Effect of adsorbent dose on COD and percent removal is shown in fig.1A,B. Initial experiments were carried out for contact time of 3 hours. There was almost linear decrease in the percentage removal for part of the curve. The curve becomes flat of dosage more than 4 grams per 150 ml. For the initial 0.5 to 1.5 grams of adsorbent, comparatively steep drop in concentration is observed. The central part of the curve indicates almost linear drop in COD with increase in adsorbent dosage. Overall curve, when approximated as a straightline was having R^2 value above 0.9, which can be considered satisfactory. For 4 gram of the adsorbent maximum 70 percent removal was obtained. The further increase in dosage does not have any significant effect on removal percentage. The reason can insufficient contact due to dense slurry formation. For initial concentration of 1205 mg/l, final minimum concentration was 350 mg/l. For higher initial concentration (6050 mg/l), maximum removal was 68 percent for 10 grams of adsorbent. The removal flowed better fit to a straightline (Fig. 1B).
4.2. Effect of pH

Fig. 2 depicts effect of pH on COD removal. The COD removal was highest for pH value between 5 to 6. At lower pH, the $H^+$ ions compete with adsorbate for the sites. At higher pH, there can be formation of complex ions or there can be hydroxides formation and subsequent precipitation also.

![Fig2. Effect of pH](image1.png)

4.3. Effect of Contact Time

Effect of contact time on COD removal is shown in fig.3. The middle portion of the curve is linear. The linearized line for COD and removal curves has $R^2$ values more than 0.9. After 150 minutes of contact time, the percentage removal was stable at 64% with negligible rise for next time intervals. This is indication of equilibrium. So optimum contact time was 150 minutes.

![Fig3. Effect of contact time](image2.png)

4.4. Effect of Initial Concentration

Effect of initial concentration on COD removal and COD is shown in fig.4. For initial COD upto 2000 mg/l there was steep rise in the COD followed by equation $y = 0.0223x + 6.3$ with $R^2 = 0.9852$. For further increase in initial COD the rise in removal becomes flat. There is no appreciable rise in removal or reduction in COD. The later part of the line follows the equation $y = 0.0025x + 46.667$ with $R^2 = 0.9868$. It can be seen that the slope decreased by 9 times for later part of the line. The reason can be exhaustion of adsorbent capacity and hindrance by the adsorbates for each other’s movement, affecting the reach of adsorbate to the adsorbent.

![Fig4. Effect of initial concentration](image3.png)
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4.5. Freundlich Isotherm

Freundlich equation is given by

\[ \frac{X}{M} = K C^{1/n} \]

where \(X\) is adsorbate adsorbed, \(M\) amount of adsorbent, \(C\) equilibrium concentration and \(K, 1/n\) are constants.

The data was plotted to fit in Freundlich equation. Fig. 5 indicates Freundlich isotherm equation. The data followed the equation with \(R^2\) value 0.9009. \(1/n\) value was found to be 0.0104.

![Freundlich Isotherm](image)

Fig5. Freundlich isotherm

4.6. Continuous Operation

The colour removal was significant for 120 minutes. The colour removal dropped thereafter. Initial 120 minutes of flat rise in the COD is followed by steep rise in COD. First 150 minutes of the column operation were found to follow the equation, \(1.0804x + 187\) with \(R^2 = 0.906\). The later portion of the curve followed, \(y = 19.6x - 3456\) with \(R^2 = 0.9434\). It can be said that the curve can be divided into two linear portions flowing separate straight line equation. Fig.6 depicts colour and COD variations for continuous column. Fig. 7 shows absorption at various time intervals. It was seen that unlike COD, this plot doesn’t show any particular trend. Initial decrease in absorptivity is followed by increase and again decrease. This indicates that COD and colour are not related linearly. There are other pollutants, which are imparting colour and having some interactions with the adsorbent.

![Continuous column operation](image)

Fig6. Continuous column operation
4.7. Kinetics of COD Removal

Removal curve can be expresses as

\[ A_s = K t^m \]

Where \( A_s \) = percent removal, \( t \), time and \( K \), the rate constant.

The plot of percentage removal verses time indicated satisfactory fit for first order kinetics with \( R^2 \) value above 0.9.

Here, \( y=1.6806x-0.7972 \) with \( R^2 = 0.9833 \)

The value of \( m \) was observed to be 1.68.

5. CONCLUSION

The parameters affecting the adsorption were studied and optimum values of these parameters were estimated. The present work includes review of some investigations on various advanced methods for COD removal. Also experimental results of batch and column experiments for COD removal by using groundnut shell adsorbent are reported in the present paper. The data followed the equation with \( R^2 \) value 0.9009. \( 1/n \) value was found to be 0.0104. For the initial 0.5 to 1.5 grams of adsorbent, comparatively steep drop in concentration is observed. The central part of the curve indicates almost linear drop in COD with increase in adsorbent dosage. At lower pH, the \( H^+ \) ions compete with adsorbate for the sites. At higher pH, there can be formation of complex ions or there can be hydroxides formation and subsequent precipitation also.

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