

Dr. Sunil J. Kulkarni

Chemical Engineering Department, Datta Meghe College of Engineering, Airoli, Navi Mumbai, 400708, Maharashtra, India

*Corresponding Author: Dr. Sunil J. Kulkarni, Chemical Engineering Department, Datta Meghe College of Engineering, Airoli, Navi Mumbai, 400708, Maharashtra, India

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 resluts 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 asepct 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 permissiblem 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 resluts 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 resrviors indicate that the orgaic 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].Accrding 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 varried out for COD removal by using various advanced biological treatment[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 carrid out with 150 ml of the saple 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 usind usual method involving potassium dischromate and COD digestion apparatus(Spectralab SL 159). Absorbance was nalysed by using U.V. spectrophotometer(Elico). The column operation was carreid ou with 1:1 mix adsorbent. The fillter 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 almot 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 R² 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 doent 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 minimium concentration was 350 mg/l. For higher initial concentration(6050 mg/l), maximum removal was 68 percent for 10 grams of adsorbent. The removal floowed better fit to a straightline(Fig.1B).

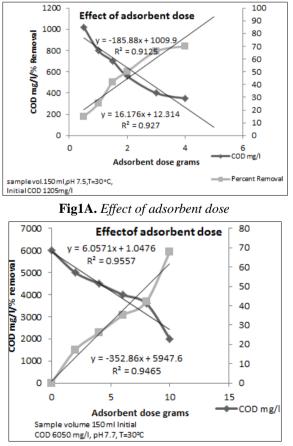
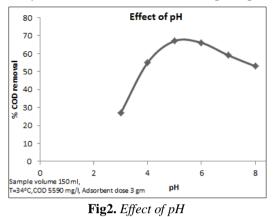


Fig1B. Effect of adsorbent dose

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.



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.

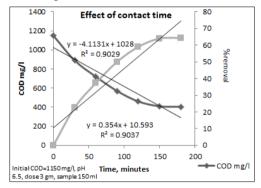


Fig3. Effect of contact time

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 = 0.0223x+6.3with R² = 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 equationy = 0.0025x+46.667 with R² = 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.

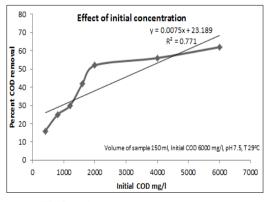


Fig4. Effect of initial concentration

4.5. Freundlich Isotherm

Freundlich equation is given by

 $X/M = K C^{1/n}$, C is equilibrium concentration, X, adsorbate adsorbed and m, amount of adsorbent. The

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.

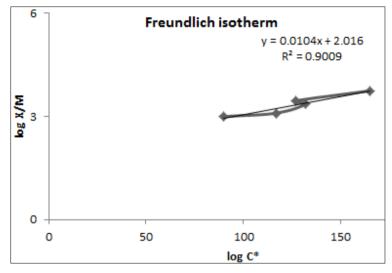


Fig5. Freundlich isotherm

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.

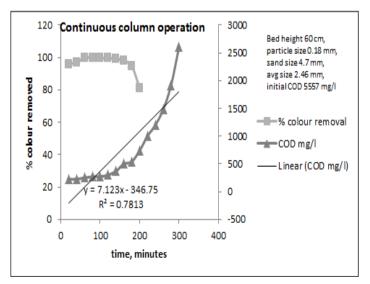


Fig6. Continuous column operation

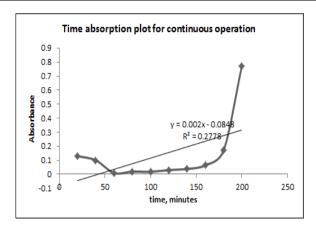


Fig7. Time-absorption plot for continuous operation

4.7. Kinetics of COD Removal

Removal curve can be expresses as

$$As = K t^m$$

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.

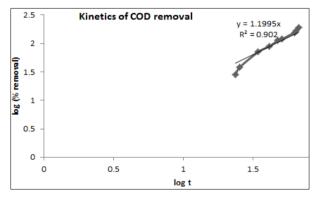


Fig8. Kinetics of COD removal

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 resluts 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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AUTHOR'S BIOGRAPHY



Sunil J. Kulkarni, has completed his PhD from Sant Gadge baba Amravati University and Masters in Chemical Engineering from Tatyasaheb Kore Institute of Engineering and Technology, Warananagar. He is working as Assistant Professor in Chemical Engineering Department of Datta Meghe College of Engineering, Airoli, Navi Mumbai, India. He has 15 years of teaching and research experience. Dr. Sunil is involved with different academic activities across the universities in Maharashtra. His area of investigation in doctoral studies is phenol and heavy metal

removal from waste water. He has also worked on kinetics and isotherms of various sorption operations. He has published more than 200 international review and research papers and presented 15 research papers in international conferences. He has also published four books on heat recovery, wastewater treatment and biotechnology related subjects. His area of research includes adsorption, clean technology and environmental biotechnology. He is on the reviewer board of many international journals and reviewed many international papers. He is also governing body member, promotional editor and executive member of many reputed international journals.

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