International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10, No.1, pp 496-500, 2017

Adsorption Isothermal Studies on the Removal of Bod and Cod of a Leather Tannery Effluent using Clinoptilolite

Maria Frank Omer[1]*., V. Renuga[2]., N. Sripriya[3] and N.K. Udaya Prakash[3]

[1]Ekdant Enviro Services, 28/41, Park Road, Anna Nagar West Extension, Chennai 600101, India
[2]Department of Chemistry, National College, Tiruchirapalli 620001, India
[3]R and D, Marina Labs, 14, Kavya Gardens, N.T. Patel Road, Nerkundram, Chennai 600107, India

Abstract : Biochemical oxygen demand and chemical oxygen demands are two major factors responsible for the existence of life in an aquatic system. Thus, the effluents discharged by industries must have their BOD and COD at prescribed levels. Controlling BOD and COD is a herculean task for industries,for which adsorbents are widely employed. Industries are on the lookout of low cost adsorbents and one such available adsorbent is Clinoptilolite, a form of Zeolite. In this study, leather tannery effluent was treated with Clinoptilolite at different parameters of varying concentrations, pH and time interval. BOD and COD were adsorbed upto 75 % and 65% respectively. Studies on Langmuir and Freundlich isotherms reveal that the experimental data fits best in the Langmuir isotherm.
Keywords : Clinoptilolite, Adsorbent, Leather Tannery Effluent, Freundlich Isotherm, Langmuir Isotherm.

Introduction

Biochemical oxygen demand and chemical oxygen demands are two major factors responsible for the existence of life in an aquatic system. Industrial wastewater possesses several compounds, depending on the type of the industry. Tannery industries, in particular, process all kinds of leather, from dehairing, fleshing, deliming, bating, pickling, tanning, dyeing and finishing. These lead to discharge of sulfides, chlorides, sulphates, proteins, etc., which contribute to increase in the Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in the effluent.The effluents discharged by industries must have them at the prescribed levels. For this, industries are employing several methods (1-4). Controlling BOD and COD is a herculean task for industries, for which adsorbents are widely employed. Industries are on the lookout of low cost adsorbents and one such available adsorbent is Clinoptilolite, a natural form of Zeolite. Naturally found in volcanic ashes, Clinoptilolite is a mineral comprising silica and alumina tetrahedral microporous complex with the formula $(Na,K,Ca)_{23}Al_3(Al,Si)_2Si_{13}O_{36}.12H_2O$. The microporous nature, high resistance and neutral basic structure of Clinoptilolite makes it a potential adsorbent for wide range of pollutants.Natural and modified Clinoptilolite have been used for the adsorption of reactive dyes (5-6), Azomethines (7), heavy metals (8-9), ammonium (10), etc. The present study is focused on the adsorption of BOD and COD from leather tannery effluent and the adsorption isotherms.

Materials and Methods

Collection of effluent

The effluent was collected at the point of discharge from the leather tannery present in Nagalkeni, Chennai. Containers pre cleaned with dilute hydrochloric acid and distilled water were used for collection of the effluent. On collection, the container was sealed tightly and analyzed immediately.

Adsorption studies

Clinoptilolite, procured from the company, Tree of life, Chennai, Tamil Nadu, India was used as the adsorbent. The adsorption studies were carried out at different parameters, i.e. adsorbent dose, pH and time interval. The pH of the effluent was verified at the point of discharge in the industry and further varied to 5, 7 and 9 in the laboratory. To 100 ml of the pH altered effluent, different amounts of the adsorbent (1, 2 & 3 g) was added. The adsorbent and the adsorbate were allowed to react at varying time intervals, viz 10, 20 & 30 min, after which the solutions were filtered and analyzed.

Determination of BOD

The BOD in the raw and treated effluent were calculated according to Clesceri et al., (1989) (11). The raw and treated effluents were aerated and maintained at 20º C for 5 days in a BOD incubator. To this, 2 ml of $MnSO_4$, 2 ml of alkali azide iodide and 2 ml of concentrated H_2SO_4. To 200 ml of the sample, starch solution was added and titrated with 0.025 N sodium thiosulphate until end point was attained (Purple to colorless).

BOD = (blank value-titrated value) ×300/volume of sample

Determination of COD

To 2.5 ml of the sample, 1.5 ml of 0.25 N $K_2Cr_2O_7$, a pinch of mercuric sulphate and 3.5 ml of HCl were added and maintained at 150º C for 2 h in a reactor. Upon cooling, the samples were titrated against 0.1 N ferrous ammonium sulfate until the end point of reddish brown color was attained (11).

COD (mg/l) = (blank value-titrated value) ×N of FAS×8000/ volume of sample

Adsorption isotherms

The relationship between the adsorbent and adsorbate was studied by Langmuir and Freundlich isotherms. The Langmuir isotherm, describing the homogenous adsorption is given by the linear form :

$$\frac{Ce}{Qe} = \frac{1}{QmKL} + \frac{Ce}{Qm}$$

where Q_e is the equilibrium amount of the BOD / COD exchanged byclinoptilolite (g/g), C_e is the equilibrium concentration of BOD / COD in the solution (g/L), Q_m (g/g) is the maximum uptake of BOD / COD exchanged and K_L is the Langmuir constant (L/g).

The Langmuir constants Q_m and K_L were evaluated from the linear regression analysis of the plot C_e vs C_e/Q_e. R_L is the dimensionless separator which provides the essential features of Langmuir isotherm (12).

$$RL = \frac{1}{1 + KLCo}$$

where Co is the initial concentration of the BOC / COD in the effluent.

The Freundlich isotherm describes the heterogenic nature of adsorption process.The linear form of it is given by

$$\ln Qe = \ln KF + \frac{1}{n} \ln Ce$$

where K_F is Freundlich constant (L/g) and 1/n is the heterogeneity factor. The constants n and K_f were evaluated from the linear regression analysis of the plot ln C_e vs ln Q_e.

The regression coefficients (R^2) derived from the linear regression plots of the adsorption studies enable in assessing the best model that fits the experiment.

Results and Discussion

In the present study, the parameters – pH of the effluent, adsorbent dosage and time were varied to study the adsorption of BOD and COD by Clinoptilolite. BOD was adsorbed from the effluent by Clinoptilolite in the range of 39.3-75%. The maximum adsorption was observed at the adsorbent dosage of 3 g against the adsorbate pH of 9, in 30 min time interval. The percent of BOD adsorbed by Clinoptilolite is depicted in Fig.1.

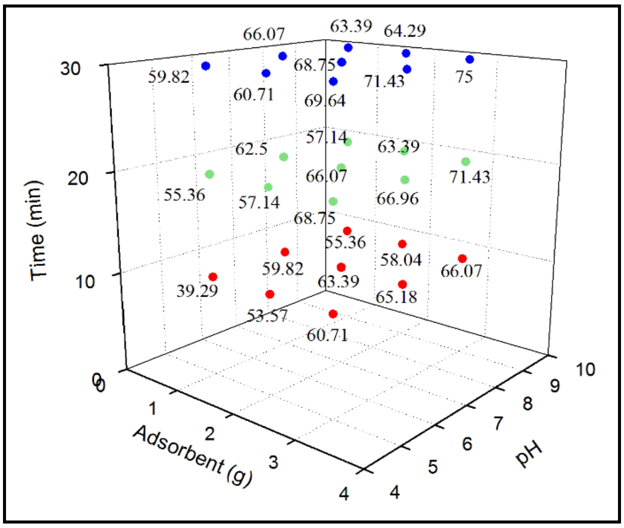

Fig.1.Adsorption percentof BOD using Clinoptilolite

The Chemical Oxygen Demand was adsorbed by Clinoptilolite to an extent of 65.32%. Among the parameters varied, greater percent removal was observed at the pH of 7, irrespective of the adsorbent dosage. The percent of COD adsorbed by Clinoptilolite is presented in Fig.2.

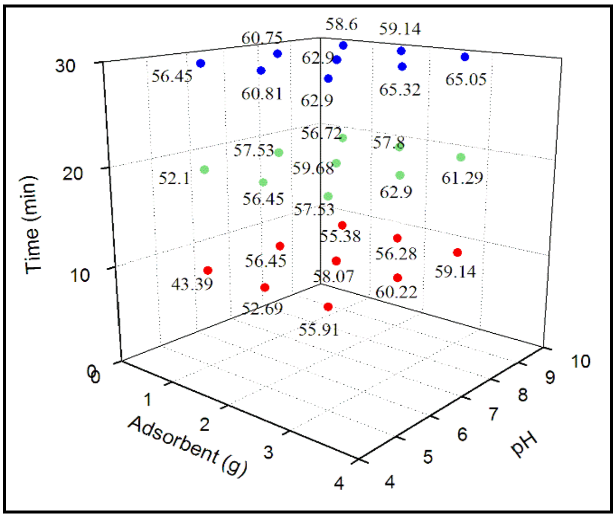

Fig.2. Adsorption percent of COD using Clinoptilolite

The equilibrium data for BOD analyzed by Langmuir and Freundlich isotherms reveals that the Langmuir isotherm fitted accurately than the Freundlich isotherm, implying the homogeneity of the adsorption process. TheLangmuir constant Q_m, represents the monolayer saturation at equilibrium condition, when the surface is fully covered with molecules of adsorbate. The Q_m values were found to increase with increase in adsorbent dosage, irrespective of the pH. The maximum Q_m was observed at the pH of 9 in the presence of 3 g of adsorbent and reaction time of 30 min, which is in correlation with the maximal percent of BOD removed from the effluent at the same conditions. The values of the dimensionless parameter, R_L were in the range 0-1, which indicates favorable adsorption in the Langmuir model. Increase in the values of the constant K_L indicates the greater affinity of binding between the adsorbent and the adsorbate. The Freundlich adsorption isotherm represents heterogenic process. From the linear plot of ln Q_e vs ln C_e, the constants K_f and n are calculated. The higher the value of K_f, greater is the adsorption intensity. Though the isotherm is considered favorable based on the 1/n values obtained, the regression coefficient is comparatively lower than that of Langmuir isotherm. The constants derived in the Langmuir and Freundlich isotherms are tabulated in Table 1.

Table1. Adsorption isotherms for BOD

pH	Zeolite (g)	Langmuir				Freundlich		
		Q_m	K_L	R_L	R^2	n	K_f	R^2
5	1	12.8866	0.5474	0.7654	0.9959	0.9613	6.6656	0.9945
	2	18.2149	0.5382	0.7684	0.9987	1.3360	24.5096	0.9982
	3	23.5849	0.6199	0.7423	0.9999	1.8643	157.654	0.9997
7	1	22.173	0.5982	0.7491	0.9992	1.7082	90.8358	0.9986
	2	24.3902	0.6465	0.7342	0.9995	1.952	218.0099	0.9988
	3	26.1780	0.6949	0.7199	0.9996	2.1787	495.3323	0.999
9	1	19.802	0.5544	0.7631	0.9993	1.4789	40.2421	0.9991
	2	20.7900	0.5643	0.7599	0.9999	1.5664	54.8811	0.9997
	3	27.6243	0.7280	0.7104	0.9988	2.3987	1102.435	0.9964

The adsorption isotherms studied for COD reveals that the Langmuir isotherm fitted accurately, thus implying the homogeneity of the adsorption process. Similar to the observation in adsorption of BOD, the Q_m values were found to increase with increase in adsorbent dosage, irrespective of the pH. At pH 7, adsorbent dose of 3 g and time interval of 30 min, the Q_m was the maximum, representing the maximum monolayer saturation. Favorable adsorption is indicated by the $R_L$value. The Freundlich isotherm constants are derived from the plot of ln Q_e vs ln C_e. The values of 1/n are found to show favorable process. However, from the regression coefficients for the Langmuir and Freundlich isotherms, the experimental data is found to fit the Langmuir isotherm. The Langmuir and Freundlich isotherm constants are tabulated in Table 2.

Table 2. Adsorption isotherms for COD

pH	Zeolite (g)	Langmuir				Freundlich		
		Q_m	K_L	R_L	R^2	n	K_f	R^2
5	1	45.0450	0.0474	0.9190	0.9963	0.9865	80.3670	0.9958
	2	59.5238	0.0487	0.9170	0.9983	1.3179	371.4823	0.9978
	3	65.7895	0.0502	0.9146	0.9995	1.4784	788.4096	0.9993
7	1	64.1026	0.0497	0.9154	0.9998	1.4237	611.4663	0.9997
	2	68.0272	0.0515	0.9127	0.9996	1.5396	1055.2245	0.9994
	3	72.9927	0.0536	0.9093	0.9995	1.6872	2123.9709	0.9990
9	1	60.6061	0.0478	0.9184	0.9997	1.3278	390.8787	0.9997
	2	61.7284	0.0486	0.9171	0.9998	1.3646	464.1853	0.9997
	3	71.9424	0.0522	0.9115	0.9994	1.6499	1777.1365	0.9989

Several materials have been studied for the adsorption of BOD and COD, such as animal horns (13), avocado peel carbon (14), etc. Lakdawala et al., (2015) (15) reported adsorption of BOD upto 30.77%, suggesting the best model to be Langmuir isotherm. Similarly, in the present study, Langmuir isotherm fits the experimental study.

Conclusion

In the present study, Clinoptilolite, a natural form of Zeolite, was used as the adsorbent against BOD and COD. The percent adsorption of BOD was 75% while that of CODwas 65% by the adsorbent. Studies on Langmuir and Freundlich isotherms reveal that the experimental data fits best in the Langmuir isotherm. The efficient ability of Clinoptilolite in adsorbing BOD and COD is evident from the present study.

References

1. Parmar N. and Upadhyay K., Treatability Study of Pharmaceutical Wastewater byCoagulation Process, International Journal of ChemTech Research, 2013, 5(5), 2278-2283.
2. Sivakumar D., Murugan N., Rajeshwaran R., Shobana T., Soundarya C., and Vanitha V.S., Role of Rice Husk Silica Powder for removing Cr (VI) in a Tannery Industry Wastewater, International Journal of ChemTech Research, 2014, 6(9), 4373-4378.
3. Solanki M., Suresh D., Das D.N., and Shukla K., Treatment Of Real Textile Wastewater Using Coagulation Technology, International Journal of ChemTech Research, 2013, 5(2), 610-615.
4. Sivakumar P., and Palanisamy P.N., Adsorption studies of basic red 29 by a nonconventional activated carbon prepared from *Euphorbia antiquorum* L., International Journal of ChemTech Research, 2009, 1(3), 502-510.
5. Alver E. and Metin A.U., Anionic dye removal from aqueous solutions using modified zeolite: Adsorption kinetics and isotherm studies, Chemical Engineering Journal, 2012, 200–202, 59–67.
6. Armagan B., Turan M., Ozdemir O. and Celik M.S., Color Removal of Reactive Dyes from Water by Clinoptilolite, Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering, 2004, A39(5), 1251–1261.
7. Cobzaru C., Cernatescu C. and Marinoiu A., Modified clinoptilolite used for removing azomethines from wastewaters. II. Adsorption of azomethines from wastewaters on clinoptilolite, Revue Roumaine de Chimie, 2014, 59(11-12), 1089-1096.
8. Mier M.V., Callejas R.L., Gehr R., Cisneros B.E.J. and Alvarez P.J.J., Heavy metal removal with Mexican clinoptilolite: Multi-component ionic exchange, Wat. Res., 2001, 35(2), 373-378.
9. Rao G.B., Prasad M.K. and Murthy C.V.R., Development of modelling equations for the removal of Nickel (II) from aqueous solutions, International Journal of ChemTech Research, 2015, 8(11), 200-210.
10. Huang H., Xiao X., Yan B. and Yang L., Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent, Journal of Hazardous Materials, 2010, 175, 247–252.
11. Clesceri L.S., Greenberg A.E. and Trussel R.R. Eds. In standard methods for the examination of water and wastewater, 17th ed, American public health association Washington DC, 1989.
12. Ho Y.S. and McKay G., The sorption of lead(II) ions on peat, Water Res., 1999, 33, 578–584.
13. Aluyor E.O. and Badmus O.A.M. COD removal from industrial wastewater using activated carbon prepared from animal horns, African Journal of Biotechnology, 2008, 7 (21), 3887-3891.
14. Devi R., Singh V. and Kumar A., COD and BOD reduction from coffee processing wastewater using Avacado peel carbon, Bioresource Technology, 2008, 99, 1853–1860.
15. Lakdawala M.M. and Patel Y.S., Studies on Adsorption Capacity of Zeolite for Removal of Chemical and Bio-Chemical Oxygen Demands, Chemistry Journal, 2015,1(4), 139-143.

*****