ISSN : 0974-7419 Volume 10 Issue 8

Trade Science Inc.

Analytical CHEMISTRY
An Indian Journal

Full Paper

ACAIJ, 10(8) 2011 [527-532]

The influence of dosage variation of granular activated carbon (GAC) to the removal of COD content of sugar industry waste water

Milan Lakdawala*[1], Kiran Nimavat[1], B.N.Oza[2]

[1]Chemistry Department, Government Science College, Gandhinagar, Gujarat, (INDIA)

[2]Chemistry Department, Veer Nurmad South Gujarat University, Surat, Gujarat, (INDIA)

E-mail: drmilan_ml@yahoo.com; kirankartik@yahoo.com

Received: 29th December, 2010 ; Accepted: 8th January, 2011

ABSTRACT

Pollution of water by organic and inorganic chemicals is of serious environmental concern. Sugar industry is one of the biggest consumer of water, and can also introduce serious pollutant to the environment. Water utilities use granular activated carbon (GAC) to remove variety of contaminants like COD and BOD. Which are well studied during this study, whose results follow the Freundlich and Langmuir adsorption isotherm. Granular Activated Carbon (GAC) prepared from wood and nutshell charcoal with specific surface area of 10.50 cm^2/gm and particle size 1.08 mm is used as an adsorbent to the combined waste water of Sugar mill at room temperature. The different dosage of GAC is kept in contact for 24 hours, then they will analyzed before and after treatment.

KEYWORDS

Granular activated carbon (GAC);
Adsorption;
COD;
Adsorption isotherm;
Adsorption intensity (1/n);
Adsorption energy (b x 10^3);
Adsorption capacity (K, Θ_0).

INTRODUCTION

Water is one of the most essential substances needed to sustain any animal/organism as well as industries. Sugar industry is one of the biggest consumer of water, and can also introduce serious pollutant to the environment. Chemical as well as biological treatment to these waste waters are in practice since long[1]. In the present study, it was aimed to carry out experiments using Granular Activated Carbon for the removal of organic contaminants especially COD contributing components from the combined waste water of Sugar Industry, which is situated in South Gujarat region of India. A number of conventional treatment technologies have been considered for treatment of wastewater contaminated with organic substances. Among them, adsorption process is found to be the most effective method. Adsorption as a wastewater treatment process has aroused considerable interest during recent years. Commercial activated carbon is regarded as the most effective material for controlling the organic load[2]. For removal of the organic contaminants from industrial waste water adsorption has become one of the best effective and economical method, thus this process has aroused considerable interest during recent years. Current research has focused on modified or innovative approach that more adequately address the removal of organic pollutants[3]. Adsorption of various substances onto carbon surface is an exceedingly complex process to solve the water quality problem has been discussed thoroughly[4]. The presentation of the solute adsorbed per unit weight/ volume of the adsorbent as the function of the equilibrium concentration in the bulk solution at constant temperature is termed as the 'Adsorption Isotherm'[5]. A novel Freundlich type multi-components adsorption isotherm was employed successfully to describe the adsorption of organic pollutants on activated carbon from the multi-component aqueous solution[6]. Some investigators found that particular organic suspended solids could interfere with the adsorption process, both in term of adsorption capacity and adsorption rate, however the effect of the solids diminished as the size of the adsorbent increased[7].

GAC shows advantages in its application because it exhibits high porosity, large surface and is easy to reactivate after its exhaustion and is easy to handle. Adsorption is a surface phenomenon. Physical adsorption takes place at lower temperatures, while chemical adsorption is effective with localized high energy producing ionic bonds. So, isotherm tests are carried out for the effective dose of carbon by batch experiments. Column tests are conducted to find out operating capacity of the carbon with optimum flow rate and bed depth. Reactivation of spent carbon from waste water effluent is performed by thermal regeneration process or electro chemical process. Activated carbon is widely used and adsorption models have been effectively applied for partial or complete removal of various substances[8].

The effect of particle size and shape of adsorbent on adsorption is measured by computerized image analyzer[9]. Rates of adsorption increases with the reduction in particle size and it is inversely proportional to the square of the carbon particle diameter[10]. The adsorption characteristics of three types of activated carbon for 17β-estradiol were studied by long term experiments to assess the time which is necessary to reach equilibrium between the solid and the liquid phase. The equilibrium concentrations were calculated to be at 49–81% of the initial concentration in the concentration range between 1 and 100 μg/l, with 0.51 μg/l for a 1 μg/l and between 5.9 and 14.6 μg/l for 100 μg/l initial concentration[11].

One of the drinking waterworks supply was studied by bench-scale experiments examining effects of different particle size of granular activated carbon (GAC), pH, dosage, and temperature, and by forming the Freundlich adsorption model. The adsorption performance could be significantly improved by using small-size GAC, low pH, low temperature, and an increase in the dosage of GAC[12]. The study of two algal odorants dimethyl trisulfide and β-cyclocitral adsorption on granular activated carbon (GAC) was investigated. It was concluded that among the four isotherm models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich), Freundlich isotherm showed the best fitting with the equilibrium data in terms of the coefficient of determination (R^2) and Chi-square (χ^2)[13].

Volatile Organic Compounds (VOCs) such as methanol, ethanol, methyl ethyl keton, benzene, n-propanol, toluene, and o-xylene were adsorbed in a laboratory-scale packed-bed adsorber using granular activated carbon (GAC) at 101.3 kPa.. The adsorption isotherm, and adsorbed amount and adsorption heat of VOCs were obtained using the breakthrough curve: the former for comparison with the conventional isotherm models, the latter for correlation with the physical properties of VOCs[14]. Chromium is mainly used in the leather and wood industries can be removed from waste by various processes like adsorption. The Cr(VI) adsorption by commercial granular activated carbon (GAC) as adsorbent from diluted solutions, and batch systems with controlled pH, In addition- effect of pH on the Cr(VI) adsorption, adsorption equilibrium, and kinetic were studied under experimental conditions (pH = 6, MA = 6g, for 90min.). On the GAC surface, carboxylic groups were found to be in higher concentrations (MAS=0,43 mmol/gCAG), which increase the Cr(VI) adsorption, principally in acidic pH values[15].

The performance of the granular activated carbon (GAC) fixed bed adsorption, the continuous photocatalysis systems and a combination of the two were studied to evaluate their capabilities in removing the herbicide of metsulfuron-methyl (MM) from waste water. Removal of MM via adsorption using GAC fixed beds of 5, 10 and 15 cm depths (operated at meter per hour) achieved a removal of 35, 55 and 65% of MM respectively[16]. The performances of GAC adsorption and GAC bioadsorption in terms of dissolved organic carbon (DOC) removal were investigated with synthetic biologically treated sewage effluent (BTSE), synthetic primary treated sewage effluent (PTSE), real BTSE and real PTSE. The main aims of the study are to verify and compare the efficiency of DOC removal by GAC (adsorption) and acclimatized GAC (bioadsorption). The results indicated that the performance of bioadsorption was significantly better than that of adsorption in all cases, showing the practical use of biological granular activated carbon (BGAC) in filtration process. The most significance was observed at a real PTSE with a GAC dose of 5 g/L, having 54% and 96% of DOC removal by adsorption and bioadsorption, respectively[17].

EXPERIMENTAL

Wastewater samples were collected from the urbanized village. The pH and EC of the samples were measured on the site and the other parameters were analyzed in the lab according to the APHA (1989). Samples were stored at temperature below 3°C to avoid any change in the physic-chemical characteristics. The COD of the samples were estimated before and after adsorption giving different treatment.

Granular Activated Carbon (GAC) with specific surface area 10.50 cm^2/gm and particle size 1.08 mm was used as an adsorbent for the treatment of sugar industry waste water. For present research work the adsorbent sample was prepared from wood and nutshell charcoal. The process of manufacturing of activated carbon included carbonization followed by activation. Wherein on pyrolysis of raw materials polynuclear aromatic system get resulted. The carbon formed would be further activated by burning it in atmosphere of CO_2, CO, O_2, H_2O vapour, air or other selected gases at temperature between 300 to 1000^0 C.

These activated carbons were added to sugar industry waste water sample and the mixture was stirred well and was kept in contact until equilibrium state attain and that was 24 hours for this system. The known quantity (1 liter) of sample was treated with different

TABLE 1 : The influence of dosage variation of granular activated carbon (GAC) on various physico-chemical characteristic of sugar industry waste water

Adsorbent: Granular Activated Carbon (GAC)
Specific Surface Area: 10.50 cm^2/ gm
Particle size: 1.08 mm

Room temperature: 26± 1^{0}C
Contact duration: 24 Hours

Parameter	Untreated Sample	1 gm/L	2 gm/L	5 gm/L	10 gm/L	15 gm/L	20 gm/L	30 gm/L
pH	5.68	7.18	7.23	7.32	7.45	7.84	7.84	7.84
Conductance (m mho)	1.737	1.71	1.713	1.713	1.791	1.792	1.799	1.799
COD (mg/L)	1847.58	1254.96	1150.38	1080.66	836.64	766.92	697.2	697.2
BOD (mg/L)	310	272.8	248	223.2	186	161.2	124	62
Alkalinity (mg/L)	1000	750	750	750	750	750	750	750
Hardness (mg/L)	850	520	520	520	520	520	520	520
Chloride (mg/L)	137.457	137.457	137.457	137.457	137.457	137.457	137.457	137.457

TABLE 2 : Freundlich and Langmuir adsorption isotherm parameters for COD contributing components and percent removal of COD in presence of GAC

Adsorbent: Granular activated carbon (GAC)
Specific surface area: 10.50 cm^2/ gm
Particle size: 1.08 mm

Room temperature: 26± 1^{0}C
Contact duration: 24 Hours

No	Adsorbent concentration m (gm/L)	Eq. Conc. C_{eq} (mg/L)	Removal $x=C_0-C_{eq}$ (mg/L)	q_e= x/m (mg/gm)	Removal %	log C_{eq}	log x/m	$1/C_{eq}x10^3$	$1/q_ex10^2$
1	0	1847.58	-------	------	-------	3.2666	--------	0.5412	-------
2	1	1254.96	592.62	592.64	32.08	3.0986	2.7728	0.7968	0.1687
3	2	1150.38	697.2	348.6	37.73	3.0608	2.5423	0.8693	0.2869
4	5	1080.66	766.92	153.384	41.51	3.0337	2.1858	0.9254	0.6520
5	10	836.64	1020.94	101.094	54.72	2.9225	2.0047	1.1953	0.9892
6	15	766.92	1080.66	72.044	58.49	2.8848	1.8576	1.3039	1.3880
7	20	697.2	1150.38	57.519	62.26	2.8434	1.7598	1.4343	1.7386
8	30	697.2	1150.38	38.346	62.26	2.8434	1.5837	1.4343	2.6078

amount of Granular Activated Carbon viz 1, 2, 5, 10, 15, 20, 30 gm/L stirred well and kept in contact for 24 hours at room temperature. Then the samples were filtered and analyzed for various physico-chemical characteristics. This study was especially concentrated on COD removal. The method for determination of COD practicable is dichromate reflux method followed from 'Standard methods for the water and waste water'[18]. The results for each dose are presented in TABLE 1, 2 and figure 1, 2.

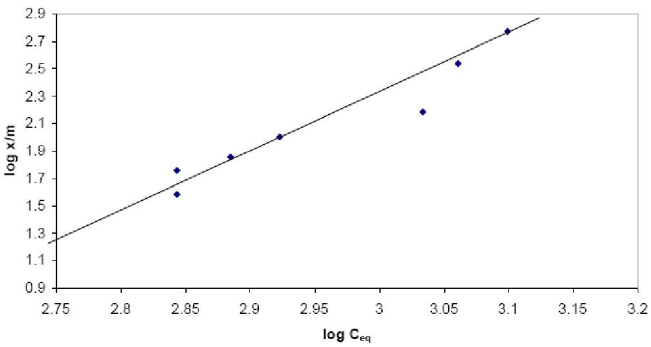

Figure 1 : Freundlich adsorption isotherm for COD into GAC

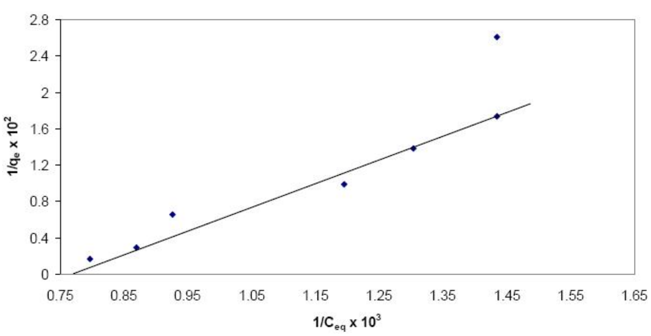

Figure 2 : Langmuir adsorption isotherm for COD onto GAC

RESULTS AND DISCUSSION

TABLE 1 shows the influence of dose variation of Granular Activated Carbon onto various physico-chemical characteristics of the combined waste water of Sugar Industry at room temperature. The pH of the untreated sample is 5.68 which increase upto 7.84 at the dose of 15 gm/L dose of GAC and remain constant for higher dose. The conductance increased from 1.737 m mho (initial) to 1.799 m mho at the dose of 20 gm/L of GAC. The initial COD content of the waste water was 1847.58 mg/L which is reduced to 697.2 mg/L with 20gm/L of GAC and remains constant for higher dose. The BOD content of the waste water is 310 mg/L is reduced to 62 mg/L with increasing dose of GAC. The alkalinity and hardness removal are found to be 750mg/L and 520 mg/L respectively from 1000mg/L and 850 mg/L of initial stage which remains constant at each dose. The chloride content is not affected at any concentration of GAC.

TABLE 2 represents the data for Freundlich and Langmuir adsorption isotherms along with percent removal of COD exerting components of sugar industry waste water on to GAC. It can be seen that the percent removal of COD increases with increase in GAC concentration from 32.07% to 62.26% with 20 gm/L of GAC and remain constant for higher dose.. The removal per unit weight is found to be decreased from 592.62 mg/gm to 38.346 mg/gm with increase in GAC dose. The logarithmic values of equilibrium concentration (C_{eq}) and removal per unit weight (x/m) were given in table which were used for the explanation of Freundlich adsorption isotherm model whereas the inverse values needed for Langmuir isotherm model.

Figure 1 represents the plot of log C_{eq} Vs log x/m (COD) for fly GAC. The straight line nature of the plot corresponds to slope 1/n and intercept K. 1/n is related to adsorption intensity whose value is 5.3158 for COD while intercept K on Y-axis related to adsorption capacity is found to be 1.15

Figure 2 represents the plot of Langmuir parameters viz, $1/C_{eq}$ x 10^3 and $1/q_e$ x 10^3. The nature of the curve for COD onto GAC is linear however the intercept on X-axis related to adsorption energy (L/mg) i.e. b x 10^3 is 0.76 L/mg for COD exerting components. These values can be used to calculate the adsorption capacity Θ_0 i.e 279.18 (mg/gm).

Influence of different dose of GAC on various physico-chemical characteristics can be explained as the pH increases with increasing amount of GAC dose can be linked with removal of components contributing to acidic character of the waste water sample, similar conclusion can be drawn for increasing removal of alkalinity and hardness. At higher dose of GAC the conductance of the waste water is seems to be increased also suggest the increasing amount of ionic species. The results for COD clearly establishes the removal of COD contributors can be explained on the basis of adsorption phenomenon and the extent can be co-related with increasing adsorption sites with increase in the dose, the similar adsorption phenomenon occurs for the removal of BOD causing contaminants. It is evident from the result that the presence of the GAC sites has no effect on initial chloride content of the waste water sample.

TABLE 2 represents the data for Freundlich and Langmuir adsorption isotherms along with percent removal for COD onto GAC. These information are used to prove the adsorption isotherm model and from that the Adsorption intensity, Adsorption energy and Adsorption capacity can be calculated. The percent removal of COD seems to be increased with increase in dose of adsorbent. The logarithmic and inverse values of C_{eq} and x/m are used for plot of isotherm.

The logarithmic value of equilibrium concentration and removal per unit weight gives the linear plot for COD by GAC confirm the applicability of Freundlich adsorption isotherm. It is the most widely used mathematical description of adsorption in aqueous systems. The equation is an empirical expression that covers the heterogeneity of the surface and exponential distribution of sites and their energies. With the purpose of linearization the equation is represented in logarithmic form as—

$$\log x/m = \log K + 1/n \log C_{eq}$$

The plot of log C_{eq} versus log x/m gives straight line with a slope of 1/n and log K is the intercept of log x/m at log C_{eq} = 0 which indicates that Freundlich adsorption isotherm model is applicable.

The same table shows the Langmuir adsorption isotherm for COD by GAC. Langmuir isotherm is a plot of the amount of impurity adsorbed by GAC against the amount of impurity that remains in solution. It is a preliminary test to check the efficiency of particular material.

These modes of action can be explained on the basis of Langmuir's model, i.e. 'Ideal localized monolayer model' according to which:

1. The molecules are adsorbed at definite sites on the surface of the adsorbent.
2. Each site can accommodate only one molecule (monolayer).
3. The area of each site is a fixed quantity determine solely by the geometry of the surface.
4. The adsorption energy is the same at all the sites. Such behavior on the basis of kinetic consideration, presuming that the adsorbed molecules cannot migrate across the surface of the interact with another neighboring molecules can be mathematically expressed as under

$$1/q_e = 1/\Theta_0 b \times 1/C_{eq} + 1/\Theta_0$$

Where q_e = amount of solute adsorbed per unit weight of adsorbent(mg/gm); = x/m i.e. x is amount of adsorbate adsorbed (mg/L); m is weight of adsorbent (gm/L); C_{eq} = equilibrium concentration of the solute (mg/L); Θ_0 = Langmuir constant related to adsorption capacity (mg/gm); b = Langmuir constant related to adsorption energy (L/mg)

Plot of log C_{eq} versus log x/m is a straight line in nature, presented in figure 1 suggests the applicability of this isotherm and indicate a monolayer coverage of the adsorbate on the outer surface of the adsorbent. The steep slope indicates high adsorptive intensity at high equilibrium concentration that rapidly diminished at lower equilibrium concentration covered by the isotherm. As Freundlich equation indicates the adsorptive capacity x/m is a function of the equilibrium concentration of the solute. Therefore, higher capacity is obtained at higher equilibrium concentrations.

Figure 2 represents the plot of Langmuir adsorption isotherm for COD contributing components onto GAC. The straight line nature of the plot confirms the applicability of the Langmuir model and also the monolayer coverage. The Langmuir constant Θ_0 in mg/gm related to adsorption capacity indicate availability of more surface active region onto adsorbent site and b x 10^3 L/mg related to adsorption energy in terms of x/m is a characteristic of the system.

CONCLUSION

This study leads us to the conclusion that the final combined waste water of Sugar manufacturing unit is highly polluted having higher COD value. Due to some practical limitation only COD parameter is emphasized in this paper when the final combined waste water of Sugar mill is treated with finely divided low cost material GAC at room temperature for 24 hours of contact duration the following results are achieved.

i. The maximum COD removal is found at 30gm/L of GAC concentration i.e. 66.04%
ii. 30 gm/L Granular Activated Carbon removes BOD contributing components of the waste water up to 62.26%
iii. The chloride content of the sample do not affected at all with increasing amount of GAC.

iv. At room temperature GAC works as an adsorbent and follow Freundlich and Langmuir isotherm models. The results give straight line which confirms the applicability of isotherm.
   a. The Freundlich constant K an intercept on X axis is related to adsorption capacity is found to be 1.15 while the slope 1/n is related to adsorption intensity is found to be 5.3146
   b. The straight line of the Langmuir plot gives intercept on Y axis called b x 10^3 L/mg i.e. adsorption energy is 0.76 and the calculated adsorption capacity Θ_0 mg/gm is 279.18

REFERENCES

[1] J.Nagraj; Industrial Safety and Pollution Control Handbook, Second Edition, National Safety Council and Associate (Data) Publishers Pvt Ltd., 423 **(1993)**.

[2] K.K.Pandey, G.Prasad, V.N.Singh; Water Res., **19**, 869-873 **(1985)**.

[3] W.J.Weber Jr., M.Benjamin, Van Vliet; J.AWWA, **73(8)**, 420-426 **(1981)**.

[4] S.D.Faust, O.M.Aly; Adsorption Processes for Water Treatment, Butterworth Publishers, Stoneham, 336 **(1987)**.

[5] I.Langmuir; J.of Amer.Chem.Soc., **39**, 1848 **(1917)**.

[6] C.Sheindrof, M.Rebhun, M.Sheintuch; J.Environ. Res., **16**, 357-362 **(1982)**.

[7] R.J.Martin, K.O.Iwugo; J.of Water Research, **16**, 73-82 **(1982)**.

[8] R.S.Dhaneshwar; Environmental Engineering Division, **67(3)**, 38-42 **(1987)**.

[9] A.P.Mathews, Inna Zayas; J.of Envron.Enginneering, **115(1)**, **(1989)**.

[10] M.S.McGuire, I.H.Suffet; J.AWWA, **10**, 621 **(1975)**.

[11] Maria Fuerhacker, Astrid Dürauer, Alois Jungbauer; J.of Chemosphere, **44(7)**, 1573-1579 **(2001)**.

[12] Paris Honglay Chen, Christina Hui Jenq, Kuei Mei Chen; J.of Environment International, **22(3)**, 343-359 **(1996)**.

[13] Ke-Jia Zhang, Nai-Yun Gao, Yang Deng, Ming-Hao Shui, Yu-Lin Tang; J.of Desalination Article in Press, Available online 16 October **(2010)**.

[14] Kwang-Joong Oh, Dae-Won Park, Seong-Soo Kim, Sang-Wook Park; Korean Journal of Chemical Engineering, **27(2)**, 632-638 **(2010)**.

[15] Renata Santos Souza, Samira Maria Leão Carvalho, Márcio Ronald Lima Garcia Jr., Rafael Santos Fernandes Sena; J.of Acta Amaz., **39(3)**, 661-668 **(2009)**.

[16] I.N.Areerachakul, S.Vigneswaran, H.H.Ngo, J.Kandasamy; J.of Separation and Purification Technology, **55(2)**, 206-211 **(2007)**.

[17] W.Xing, H.H.Ngo, S.H.Kim, W.S.Guo, P.Hagare; J.of Bioresource Technology, **99(18)**, 8674-8678 **(2008)**.

[18] Standard Method for Examination of Water and Waste Water, American Public Health Association, Washington DC, 18th Edition, 1134 **(1992)**.