



Biological oxygen demand (BOD) removal of sugar industry waste water- A comparative study of adsorption capacity of PAC and GAC

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ABSTRACT

Rapid globalization leads us on the way to industrialization. Pollution of water by organic and inorganic chemicals is of serious environmental concern. Various treatment technologies have been utilized for organic load removal in waste water expressed as COD and BOD. Nevertheless, yet there is an extreme need to ascertain alternative and effective low cost treatment methods. Therefore, in this study potentials of waste water was analyzed and study of Powdered Activated Carbon (PAC) and Granular Activated Carbon (GAC) to remove variety of contaminants like COD and BOD was investigated. Both these material were prepared from wood and nutshell charcoal. PAC with specific surface area of 5602.352 cm²/gm and particle size 44 μ m and GAC with specific surface area of 10.50 cm²/gm and particle size 1.08 mm are used as adsorbents to the combined waste water of Sugar mill at room temperature. The different dosage of PAC and GAC is kept in contact for 24 hours and analyzed before and after treatment. The results of BOD removal follow the Freundlich and Langmuir adsorption isotherm. Among PAC and GAC -PAC removes 93.24% of BOD at the dose of 20 gm/L, whereas GAC removes 80% of BOD at the dose of 30 gm/L dosages. It proves that rates of adsorption increases with the reduction in particle size.

Key words: Adsorption isotherm, Adsorption intensity (1/n), Adsorption energy (b x 10³), Adsorption capacity (K, Θ₀)

INTRODUCTION

Environment is a complex and dynamic system in which all life forms are interdependent. The effect of industrial waste on plant and animal life in closed bodies of water in nature is catastrophic. Industries are the largest user of water so causes water pollution. Some of the waste problems in nature are taken care of by the large amount of living spaces, unfortunately where living space becomes limited, dilution is no longer a satisfactory solution, and other means must be taken to reduce the ratio of waste to space [1,2]. Textile, food and sugar industries play a vital role in the economic increases in India. Water is one of the major products of nature used enormously by human beings and it is not unnatural that any growing community generates enormous wastewater or sewage [3]. In recent years, increasing awareness of the environmental impact of chemical and bio-chemical oxygen demands (COD and BOD) has prompted a demand for the purification of industrial wastewaters prior to discharge into natural waters. Pollution of water by organic chemicals has become serious environmental concern. The past two decades have witnessed a tremendous upsurge in the search for cost effective, environmentally friendly and sound alternatives to the conventional methods for wastes treatment. Among them, adsorption process is found to be the most effective method [4-8].

In the present study, it was aimed to carry out experiments using Powdered Activated Carbon and Granular Activated Carbon for the removal of organic contaminants especially BOD contributing components from the combined waste water of Sugar Industry, which is situated in South Gujarat region of India. BOD [9] can be determined by 5 day incubation method, in which Whinkler method is used for Dissolved Oxygen measurement. It is an acid azide modified iodometric titration method [10].

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.[11,12] Adsorption of various substances onto carbon surface is an exceedingly complex process to solve the water quality problem has been discussed thoroughly [13] 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.[14] Various activated carbons were tested for its better quality and quantity of different particle size for a comparison of its adsorption characteristics.[15] Rates of adsorption increases with the reduction in particle size and it is inversely proportional to the square of the carbon particle diameter. Adsorption is a water treatment process that removes a soluble substance from the water. As carbon adsorption method is effective in removing pollutants. [16] 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 [17].

EXPERIMENTAL SECTION

Powdered Activated Carbon (PAC) with specific surface area 5602.352 cm²/gm and particle size 44 μ m and Granular Activated Carbon (GAC) with specific surface area 10.50 cm²/gm and particle size 1.08 mm were used as adsorbents for the treatment of sugar industry waste water. For present research work the adsorbent samples were prepared from wood and nutshell charcoal. The process of manufacturing of activated carbons included carbonization followed by activation. Where-in on pyrolysis of raw materials polynuclear aromatic system get resulted. The carbon formed would be further activated by burning it in atmosphere of CO₂, CO, O₂, H₂O vapour, air or other selected gases at temperature between 300 to 1000⁰ C. Wastewater samples were collected from the Khedut Sahakari Khand Udhyog Mandali Ltd, Bardoli. 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 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 amount of Powdered Activated Carbon and 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 especially for BOD removal. The method for determination of BOD practicable is Winkler method followed from 'Standard methods for the water and waste water' [18].

Biochemical Oxygen Demand (BOD):

Biochemical Oxygen Demand (BOD) by definition is the quantity of oxygen utilized by a mixed population of microorganisms to destabilize the organic matter under aerobic condition (of the organic matter in a sample of wastewater). The test is carried out for 5 days at 20⁰C as 70-80% of the organic waste is oxidized during this period. In this method, measured amount of wastewater, diluted with prepared water, were placed in 300 ml BOD bottles. The dilution water, containing phosphate buffer (pH 7.2), magnesium sulphate, calcium chloride, ferric chloride was saturated with dissolved oxygen. Acclimatized seed organisms were added to oxidize the waste organics if sufficient microorganisms were not already present in the wastewater samples [18].

The BOD test is widely used to determine:

- Pollution load of wastewater
- Degree of pollution in lakes and streams at any time and their self- purification capacity,
- Efficiency of wastewater treatment systems

The results for each dose are presented in Table 1, 2 and figure 1, 2 & 3.

RESULTS AND DISCUSSION

Table 1 represents the data for Freundlich and Langmuir adsorption isotherms along with percent removal of BOD exerting components of sugar industry waste water on to PAC. It can be observed that the percent removal of BOD increases with increase in PAC concentration upto 93.24%. The removal per unit weight is found to be decreased from 917.6 mg/gm to 62 mg/gm with increase in PAC dose. The logarithmic values of equilibrium concentration (C_{eq}) and removal per unit weight (x/m) were given in table were used for the explanation of Freundlich adsorption isotherm model and plot whereas the inverse values needed for Langmuir isotherm model.

Table 2 represents the data for Freundlich and Langmuir adsorption isotherms along with percent removal of BOD exerting components of sugar industry waste water on to GAC. Percent removal of BOD increases with increase in GAC concentration upto 80% with 30 gm/L of GAC and remain constant for higher dose. The removal per unit weight is found to be decreased from 37.2 mg/gm to 8.27 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 $\log x/m$ (BOD) for PAC & 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 2.4767 for BOD while intercept K on Y-axis related to adsorption capacity is found to be 1.00 for PAC. For GAC $1/n$ is related to adsorption intensity whose value is 0.1714 for BOD while intercept K on Y-axis related to adsorption capacity is found to be 0.90.

Figure 2 represents the plot of Langmuir parameters viz, $1/C_{eq} \times 10^3$ and $1/q_e \times 10^3$. The nature of the curve for BOD onto PAC and GAC is linear however the intercept on X-axis related to adsorption energy (L/mg) i.e. $b \times 10^3$ is 3.9 L/mg (PAC) and 2.9 L/mg (GAC) for BOD exerting components. These values can be used to calculate the adsorption capacity Θ_0 i.e 318.81 (mg/gm) for PAC and 291.51 (mg/gm) for GAC. Figure 3 represents the % removal of BOD contributing components of the waste water from sugar industry in presence of PAC and GAC, clearly indicates that the maximum BOD removal is found at 20gm/L of PAC concentration i.e. 93.24% whereas 80% for GAC at 30gm/L.

The data presented in Table 1 and 2 represent the Influence of different dose of PAC and GAC on BOD contributing components. The removal of BOD is explained on the basis of adsorption phenomenon and the extent can be co-related with increasing adsorption sites with increase in the dose. The other information are used to prove the adsorption isotherm- Freundlich and Langmuir adsorption isotherms for COD onto PAC and GAC which is used for the calculation of the Adsorption intensity, Adsorption energy and Adsorption capacity. The percent removal of COD seems to be increased with increase in dose of adsorbent for PAC. The plateau nature of the plot after 20gm/L for PAC is due to the exhaustion of the adsorbent site. It can be explained on the basis of particle size. Rates of adsorption increases with the reduction in particle size and it is inversely proportional to the square of the carbon particle diameter. 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 BOD by PAC and 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 BOD by PAC and GAC. Langmuir isotherm is a plot of the amount of impurity adsorbed by PAC against the amount of impurity that remains in solution. It is a preliminary test to check the efficiency of particular material.

These mode 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 BOD contributing components onto PAC and 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 $b \times 10^3$ L/mg related to adsorption energy in terms of x/m is a characteristic of the system.

Figure 3 represents the % removal of BOD content of sugar industry waste water. The percent removal of BOD seems to be increased with increase in dose of adsorbent for PAC. The plautue nature of the plot after 20gm/L for PAC and 30gm/L for GAC is due to the exhaustion of the adsorbent site. It can be explained on the basis of particle size. Rates of adsorption increases with the reduction in particle size and it is inversely proportional to the square of the carbon particle diameter.

Table 1: Freundlich and Langmuir adsorption isotherms for BOD contributing component and percent removal of BOD in Presence of PAC

Adsorbent: Powdered Activated Carbon (PAC) Room temperature: $26 \pm 1^\circ\text{C}$
 Specific Surface Area: $5802.352 \text{ cm}^2/\text{gm}$ Contact duration: 24 Hours
 Particle size: $44 \mu\text{m}$

No	PAC Dosage 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	$1/C_{eq} \times 10^3$	$1/q_e \times 10^2$
1	0	917.6	-	-	-	2.9627	-	1.0898	-
2	1	229.4	688.2	688.20	75.00	2.3606	2.8377	4.3592	0.1453
3	2	186	731.6	365.80	79.73	2.2695	2.5632	5.3763	0.2734
4	5	124	793.6	158.72	86.49	2.0934	2.2006	8.0645	0.6300
5	10	93	824.6	82.46	89.86	1.9685	1.9162	10.7527	1.2127
6	15	86.8	830.8	55.39	90.54	1.9385	1.7434	11.5207	1.8055
7	20	62	855.6	42.78	93.24	1.7924	1.6312	16.1290	2.3375
8	30	62	855.6	28.52	93.24	1.7924	1.4551	16.1290	3.5063

Table-2: Freundlich and Langmuir adsorption isotherms for BOD contributing component and percent removal of BOD in Presence of GAC

Adsorbent: Granular Activated Carbon (GAC) Room temperature: 26± 1°C
 Specific Surface Area: 10.50 cm²/ gm Contact duration: 24 Hours

Particle size: 1.08 mm

No	GAC Dosage 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} ×10 ³	1/q _e ×10 ²
1	0	310	-	-	-	2.4914	-	3.2258	-
2	1	272.8	37.2	37.20	12	2.4358	1.5705	3.6657	2.6882
3	2	248	62	31.00	20	2.3945	1.4914	4.0323	3.2258
4	5	223.2	86.8	17.36	28	2.3487	1.2395	4.4803	5.7604
5	10	186	124	12.40	40	2.2695	1.0934	5.3763	8.0645
6	15	161.2	148.8	9.92	48	2.2074	0.9965	6.2035	10.0806
7	20	124	186	9.30	60	2.0974	0.9685	8.0645	10.7527
8	30	62	248	8.27	80	1.7924	0.9173	16.1290	12.0968

Figure 1: Freundlich Adsorption Isotherm for BOD on to PAC and GAC

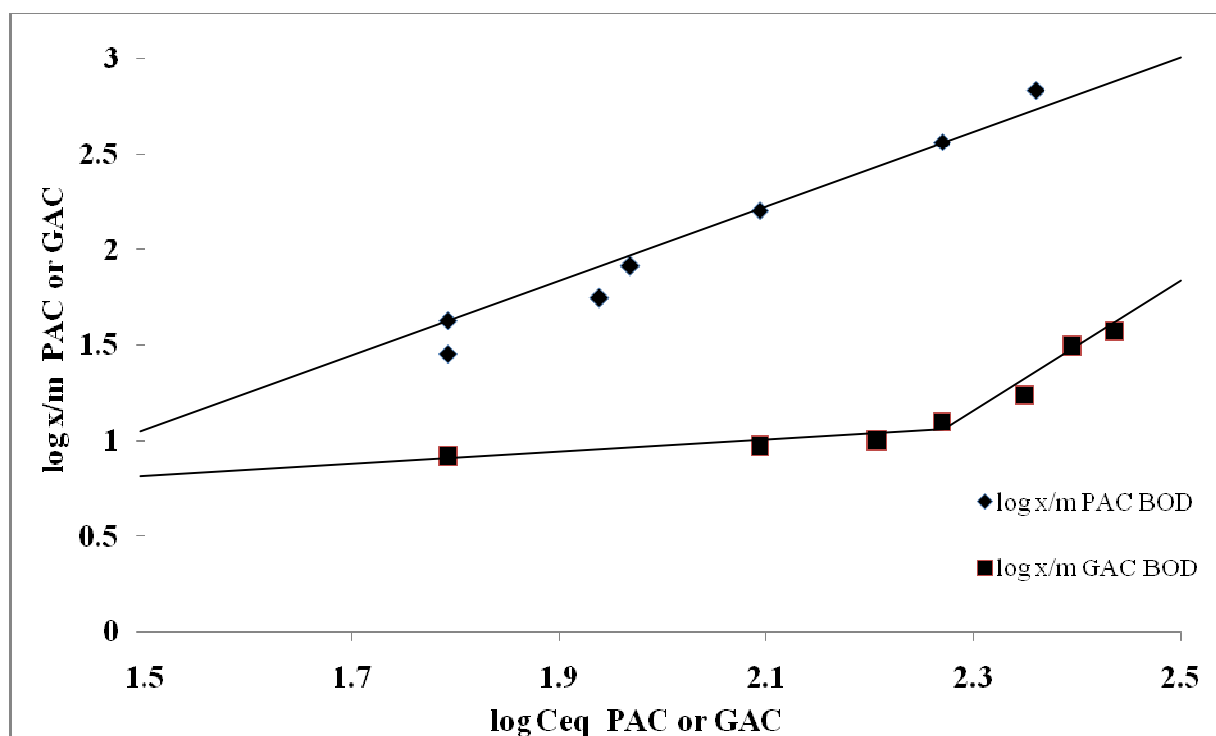


Figure 2: Langmuir Adsorption Isotherm for BOD on to PAC and GAC

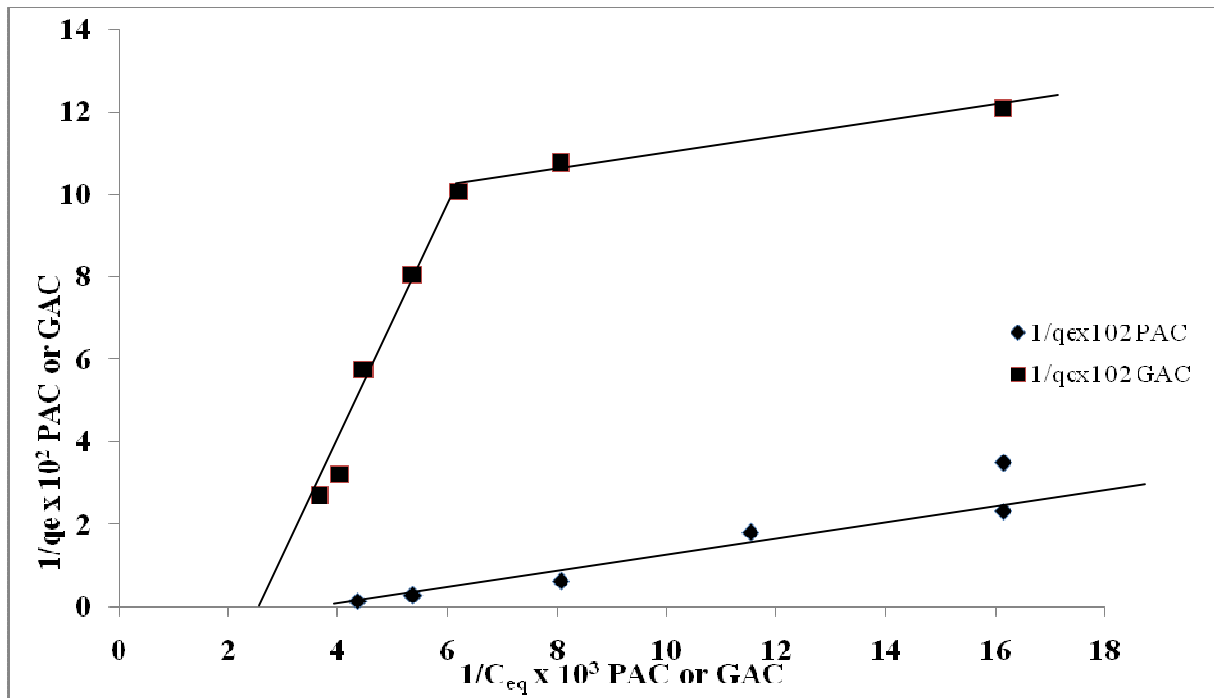
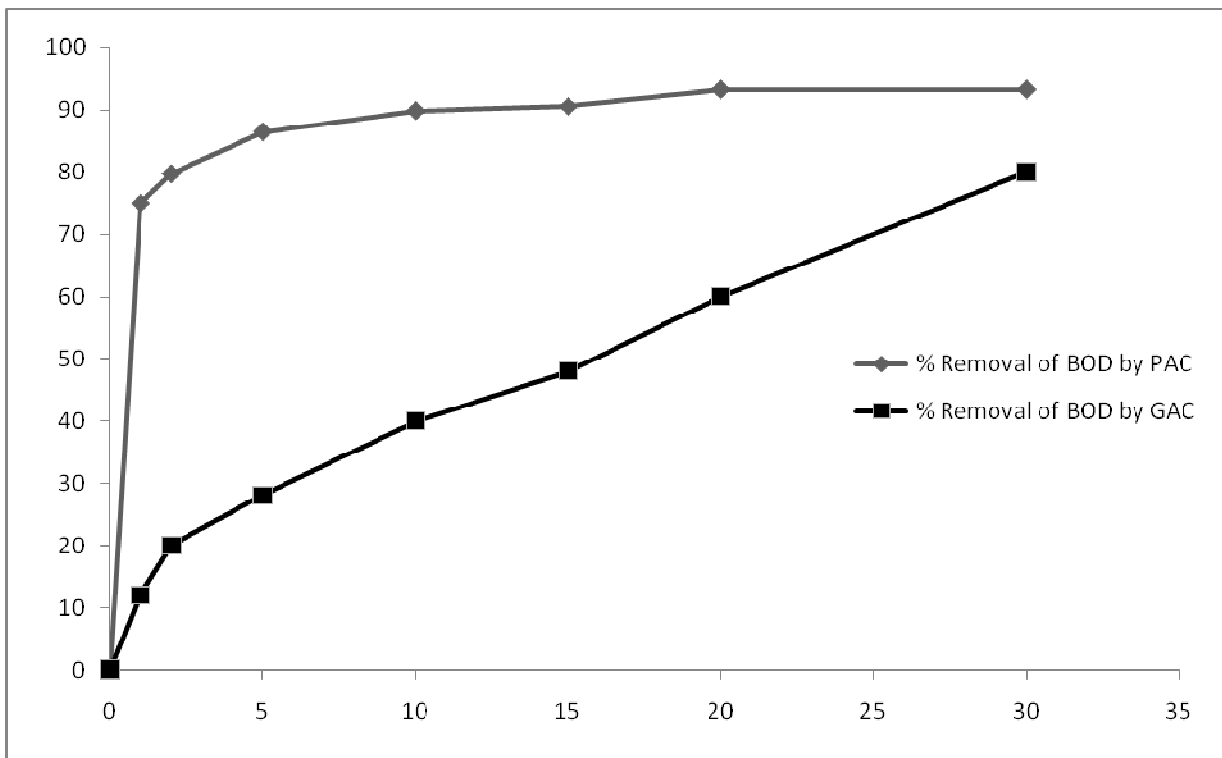


Figure 3: % removal of BOD by PAC and GAC



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CONCLUSION

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

- i. The maximum BOD removal is found at 20gm/L of PAC concentration i.e. 93.24% and remains constant for higher dose, whereas 20 gm/L of GAC removes 60% of BOD and increases up to 80% with 30gm/L.
- ii. Comparison of PAC and GAC for removal of BOD proves that Adsorption is a surface phenomenon. Rates of adsorption increases with the reduction in particle size and it is inversely proportional to the square of the carbon particle diameter.
- iii. At room temperature PAC and GAC work as adsorbents for the removal of BOD contributing components 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 1.0 while the slope $1/n$ is related to adsorption intensity is found to be 2.4767 for PAC
 - b. The straight line of the Langmuir plot gives intercept on Y axis called $b \times 10^3$ L/mg i.e. adsorption energy is 3.9 and the calculated adsorption capacity Θ_0 mg/gm is 318.81 for PAC
 - c. The Freundlich constant K an intercept on X axis is related to adsorption capacity is found to be 0.90 while the slope $1/n$ is related to adsorption intensity is found to be 0.1714 for GAC
 - d. The straight line of the Langmuir plot gives intercept on Y axis called $b \times 10^3$ L/mg i.e. adsorption energy is 2.9 and the calculated adsorption capacity Θ_0 mg/gm is 291.51 for GAC.

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