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Article

Temperature effect on adsorption capacity of powdered and granular activated carbon for biological oxygen demand and chemical oxygen demand

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- **Novelty and Highlights:**

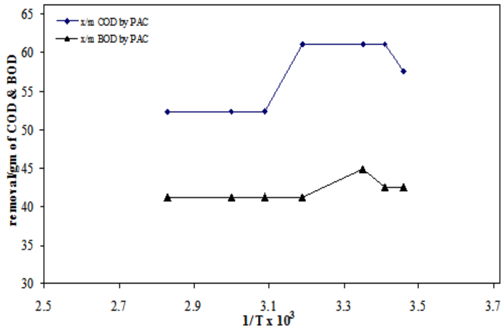
1 – BOD and COD removal from combined waste water of sugar industry

2 – Powdered activated carbon removes 61% of COD and 98% of BOD at 298K

3 – Granular activated carbon removes 66% of COD and 60% of BOD at 298K

- **Graphical Abstract:**

Temperature effect of powdered activated carbon (PAC) on removal of COD and BOD shows that while increasing the temperature increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution.



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Abstract:

Effluent originating from sugar industry containing organic contaminants leads to extensive soil and water pollution. From environmental and aesthetic point of view, removal of pollutants containing organic contaminants from effluent is very important. Due to the organics loads, the treatment of removal efficiency is rather challenging by conventional methods. Therefore, adsorption process is found to be the most effective method. Numerous approaches have been studied for the development of low–cost adsorbents. To overcome this burning issue some adsorption methods were utilized. During present study, powdered activated carbon (PAC) with specific surface area 0.560 $m^2\ gm^{-1}$ and particle size 44 μm and granular activated carbon (GAC) with specific surface area 0.001 $m^2\ gm^{-1}$ and particle size 1.08 mm were used for removal of biochemical oxygen demand and chemical oxygen demand (BOD and COD) from combined waste water of sugar industry. Present study is emphasizing on temperature parameter. The change in temperature changes the equilibrium capacity of the adsorbent for a particular adsorbate; this study leads us to the conclusion that PAC removes 61.009% of COD and 97.97% of BOD at 298 °K whereas GAC removes 66.04% of COD and 60% of BOD at 298K. With increase in temperature, considerable decrease in COD and BOD for both the adsorbents was observed.

Keywords: Powdered Activated Carbon; Granular Activated Carbon; Adsorption.

Introduction

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 [1–5]. Numerous approaches have been studied for the development of low-cost adsorbents. The use of low–cost adsorbents may contribute to the sustainability of the surrounding environment and offer promising benefits for commercial purpose in the future. Commercial activated carbon is regarded as the most effective material for controlling the organic load [6–10] for removal of the organic contaminants from industrial waste water. Adsorption has become one of the best effective and economical methods. Thus, this process has aroused considerable interest during recent years. Current research is focused on modified or innovative approach for the removal of organic pollutants. 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.

In the present study, it was aimed to carry out the experiments to remove COD and BOD from the waste water of sugar industry using Powdered Activated Carbon (PAC) and Granular Activated Carbon (GAC) with specific surface area and particle size. We have emphasizing only on temperature parameter and its effect on adsorption capacity. The change in temperature changes the equilibrium capacity of the adsorbent for a particular adsorbate [11]. GAC shows advantages in its application because it exhibits high porosity, large surface area, easy to reactivate after its exhaustion and easy to handle.

Experimental

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 were 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. The effect of particle size and shape of adsorbent on adsorption is measured by computerized image analyzer [12]. A rate of adsorption increases with the reduction in particle size and it is inversely proportional to the square of the carbon particle diameter [13].

Powdered Activated Carbon (PAC) with specific surface area 0.560 $cm^2\ gm^{-1}$ and particle size 44 μm and Granular Activated Carbon (GAC) with specific surface area 0.001 $cm^2\ gm^{-1}$ and particle size 1.08mm were used as an adsorbent for the treatment of sugar industry waste water. The adsorbent sample was prepared from wood and nutshell charcoal. Activated carbon was prepared by carbonization of charcoal and followed by activation. 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 300 to 1000 ˚C. Wastewater samples were collected from the Shree Khedut Sahakari Khand Udhyog Mandali Ltd, Bardoli and the other local sugar industries located in the southern part of Gujarat–INDIA. The bottle (polythene or glass) for sample collection should be thoroughly cleaned by rinsing with 8.0 M HNO_3 followed by repeated washing with deionized distilled water. They should be rinsed thrice with the sample water before collection [14]. Samples were stored at temperature below 3˚C to avoid any change in the physicochemical characteristics. The pH and electrical conductivity of the samples were measured on the site and the other parameters were analyzed in the laboratory according to the Standard methods for the examination of water and waste water by American Public Health Association, Washington DC: 1989.

COD and BOD measurement

COD measurement [15–16] can be done by dichromate reflux method and BOD [17] 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 [18]. Activated carbons were added to sugar industry waste water sample and the mixture was stirred well and was kept in contact for 3 hours. The influence of temperature was studied by treating 1.0 liter of combined waste water of sugar mill using 20 gm of activated carbons (PAC and GAC). The temperature study was carried out at 283, 293, 298, 303, 313, 323, 333 and 353 °K. Then the samples were filtered and analyzed for various physico–chemical characteristics. This study was especially concentrated on COD and

BOD removal. The dichromate reflux method is used for determination of COD. After 5 days incubation, BOD was measured by using iodometric titration method according to the Standard Method for Examination of Water and Waste Water, American Public Health Association, Washington DC: 1992.

Results and discussion

Table 1 represents the temperature effect on physico-chemical parameters in presence of PAC. It can be concluded that, with increasing the temperature, pH of the sample was increased up to 298 °K i.e. room temperature. After 298 °K, pH of the sample was decreased which may be due to the concentrating or evaporation of the sample. Alkalinity of the sample was remained constant up to room temperature. After this temperature, alkalinity was continuously increased with the increase in temperature. Conductance of the sample was increased with increasing the temperature. It could be explained by the increasing amount of ionic species in the system. The hardness of the sample was found constant up to 313K. After this temperature the hardness was increased noticeably up to 1380 $mg.L^{-1}$. It suggested that PAC itself may contribute some hardness causing components at higher temperature to the sample. Similar conclusion can be drawn for chloride content, COD and BOD. The COD removal is 66.04% at 313 K and the removal of BOD is 97.97% obtained at room temperature.

The effect of temperature on the various physicochemical parameters of the combined waste water in presence of GAC is represented in table 2. It can be explained as follows: with increasing temperature, the pH and conductance of the sample also increases. It also suggested the increase of basic as well as ionic species in the system. Alkalinity decreased up to 25% at room temperature and remained the same for higher temperature which indicated the removal of alkaline matter. The hardness decreased up to room temperature and then increased with the increasing temperature may be explained by the adsorption of hardness causing component up to room temperature which contribute to solution, means, desorption took place above 298K. Similar conclusion could be drawn for COD and BOD exerting component as they follow the same trend for removal i.e. adsorption and desorption.

Results were presented in tables clearly indicated that increase in adsorption with increase in temperature up to 298 °K i.e. room temperature. This could be related to decrease in ordering of the adsorbed molecular layers with rise in temperature. This could also be explained considering flat orientation of theses adsorbate molecules on the adsorbent surface. This was due to decrease in adsorption (at higher temperature) with parallel orientation reported earlier. This increase in percent removal of COD and BOD with increase in temperature may be explained on the basis of various thermodynamic parameters such as entropy, enthalpies, free energies as well as increasing surface coverage. It also reflected light on the specific interaction between molecules contributing to COD or BOD present in the solution and the basal plane surface of carbon. Increase in lateral interaction between the adsorbed molecules and the process of heteroflocculation or surface nucleation of larger aggregates might be contributed to the increase in adsorption process from the waste water sample with increase in temperature. It had been observed that, from liquid phase to solid phase did not favour adsorption process particularly at higher temperature as the extent of adsorption would not be of much usefulness as the process of adsorption was exothermic in nature. Net enthalpy of adsorption ΔH which could be correlated to Langmuir constant 'b' when correlated by the expression

$$\ln b \ = lnb'^{-\Delta H/RT}$$

The behaviour could be explained considering possibility of weak bonding between active centres of adsorbate and adsorbent species and this bond weakening increased with increase in temperature. Figure 1 and 2 showed the plot of x/m versus 1/T x 10^3 for the removal of COD and BOD respectively from combined waste water of sugar industry by PAC and GAC. It could be seen from the plot that the COD removal occurred up to 298 °K slowly and then COD exerting components were added into the solution similar trend was followed for BOD removal.

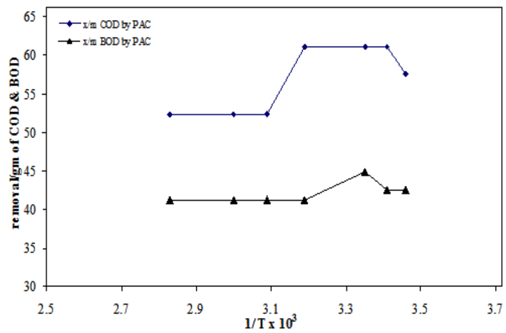

Figure 1 Temperature effect of PAC on removal of COD and BOD

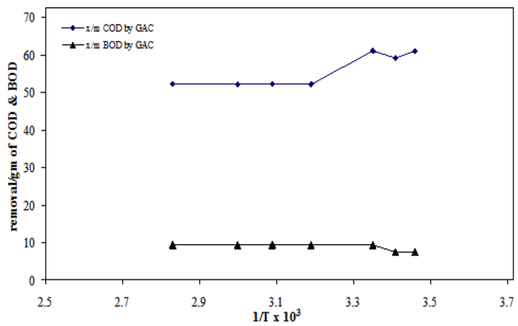

Figure 2 Temperature effect of GAC on removal of COD and BOD

It suggested the process was endothermic for both the adsorbent PAC and GAC. Increasing the temperature was known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution.

Conclusions

From the present studies we can conclude that, PAC and GAC can be used as a low-cost adsorbent compared to commercial adsorbent for the removal of organic matter. It also decreases the amount of BOD and COD from the Waste water of Sugar Industry. The COD removal is 66.04% at 313K and the removal of BOD is 97.97% obtained at room temperature and remains constant for higher temperature. Other water quality parameters such as alkalinity, chloride, hardness and total dissolved solids showing significant reduction up to room temperature but shows inverse effect at higher temperature. Our another study for dosage variation proves that both this adsorbents are very efficient for the removal of COD and BOD content and that data is well discussed by Fruendlich and Langmuir Adsorption Isotherm.

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Table 1 Temperature effect on physicochemical parameters in presence of PAC

parameter	**Untreated**	**289 K**	**293 K**	**298 K**	**313 K**	**323 K**	**333 K**	**353 K**
pH	5.68	7.44	7.55	7.77	7.69	7.69	7.68	7.28
Conductance m mho	1.737	2.24	2.24	2.43	2.51	3.09	3.36	3.36
COD mg/L	1847.58	697.2	627.48	627.48	627.48	801.78	801.78	801.78
BOD mg/L	917.6	68.2	68.2	18.6	93	93	93	93
Alkalinity mg/L	1020	950	950	950	1060	1240	1520	2770
Hardness mg/L	850	650	650	650	650	750	1000	1380
Chloride mg/L	137.457	137.457	137.457	137.457	172.446	192.44	224.93	724.77
m COD	-	57.52	61.005	61.005	61.005	52.29	52.29	52.29
% removal COD	-	62.26	66.04	66.04	66.04	56.6	56.6	56.6
x/m BOD	-	42.57	42.57	44.95	41.23	41.23	41.23	41.23
% removal BOD	-	93.22	93.22	97.97	89.86	89.86	89.86	89.86

Table 2 Temperature effect on physicochemical parameters in presence of GAC

parameter	Untreated	289 K	293 K	298 K	313 K	323 K	333 K	353 K
pH	5.68	7.21	7.21	7.23	7.38	7.6	7.6	7.6
Conductance m mho	1.737	2.04	2.15	2.18	2.37	2.37	2.37	2.37
COD mg/L	1847.58	627.48	662.34	627.48	801.78	801.78	801.78	801.78
BOD mg/L	310	161.2	161.2	124	124	124	124	124
Alkalinity mg/L	1000	920	920	750	750	750	750	750
Hardness mg/L	850	520	520	500	650	650	650	650
Chloride mg/L	137.457	137.457	137.457	137.457	162.449	162.449	162.449	162.449
x/m COD	-	61.005	59.262	61.005	52.24	52.24	52.24	52.24
% removal COD	-	66.04	64.15	66.04	56.6	56.6	56.6	56.6
x/m BOD	-	7.44	7.44	9.3	9.3	9.3	9.3	9.3
% removal BOD	-	48	48	60	60	60	60	60