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Treatment on industrial effluent by using activated carbon prepared from animal horns as adsorbent

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Abstract
The present study was undertaken to compare the adsorption efficiency of activated carbon prepared from animal horns (AHC), which is both a waste and a pollutant and a commercial activated carbon (CAC) with respect to uptake of the organic components responsible for the chemical oxygen demand (COD) of industrial wastewater. The adsorption process was examined in terms of its equilibria and its kinetics. The effect of pH, contact time and adsorbent dose were investigated. The most effective pH was found to be 5 for AHC and 6 for CAC. The equilibrium data for COD removal fitted the Linear, Langmuir and the Freundlich models. The mechanisms of the rate of adsorption of COD were analysed using the pseudo second-order model. The model provided a very high degree of correlation of the experimental adsorption rate data suggesting that this model could be used in design applications.

Keywords: Adsorption, batch, kinetics, Langmuir, Freundlich, adsorbent.

1. Introduction

Pollution of water by organic and inorganic chemicals is of serious environmental concern. Industrial wastewater differs in characteristics from the domestic wastewater. Industrial wastewaters result from spills, leaks, and product washing and water resulting from cooling processes. The organic content of wastewater is traditionally measured using lumped parameters such as biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS) and total organic carbon (TOC). These parameters as such do not show any chemical identity of organic matter. In recent years, increasing awareness of the environmental impact of COD has prompted a demand for the purification of industrial wastewaters prior to discharge into natural waters. This has led to the introduction of more strict legislation to control water pollution, such as the Environmental Quality (Scheduled Wastes) Regulation 1989 in Malaysia (Quek *et al*. 1998) [11]. This effect is likely to be even pronounced for small and medium scale industries where profit is small and expertise on wastewater treatment is unlikely to be available. 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. However, due to its high cost and about 10 - 15% loss during regeneration, unconventional adsorbents like fly ash, peat, lignite, bagasse pith, wood, saw dust, periwinkle shells, etc. Have attracted the attention of several investigations and adsorption characteristics have been widely investigated for the removal of refractory materials (Pandey *et al*. 1985; Badmus *et al*. 2007; Mall *et al*. 1994) [10, 3, 6]. for varying degree of success. This study is aimed at analyzing the adsorption capacity of activated carbon prepared from animal horns on industrial wastewater effluent using a brewing industry as a case study; and also to demonstrate the use of activated carbon prepared from animal horns as an alternative media over conventional activated carbon. This paper deals with the results of the batch adsorption tests to establish adsorption isotherms and adsorption capacity of the activated carbon prepared from animal horns (AHC) for the removal of COD in wastewater.

2. Materials and methods

The wastewater sample used was collected at the point of discharge from the industry. Materials used for sample collection were pretreated by washing the container with dilute hydrochloric acid and later rinsed with distilled water. The containers were later dried in an oven for 1 h at 110±5 ºC and allowed to cool to ambient temperature. At the collection point, containers were rinsed with samples thrice and then filled with sample, corked tightly and taken to the laboratory for treatment and analysis. The method of analysis was consistent with the standard methods (APHA, 1985; Goltermann, 1978) [1, 4]. The pH of the sample was measured on the site and other parameters were measured in the laboratory. Samples were stored at a temperature below 3 ºC to avoid any change in physic-chemical characteristics. The COD of the samples were estimated before and after adsorption giving different treatment

2.1 Adsorption Studies

All the experiments were carried out at ambient temperature in batch mode. Batch mode was selected because of its relative simplicity. The batch experiments were run in different glass flask of 250 ml capacity using average speed shaker. Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The stirring was kept constant for each run throughout the experiment ensuring equal mixing. The desired pH was maintained using dilute NaOH/HCl solutions. Each flask was filled with a known volume of sample having desired pH commenced the stirring. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered through whatmann No. 44 filter paper. The experiments were carried out under different experimental conditions.

2.2 Adsorbent Dose
The studies were conducted by varying the amount of adsorbent. 100 ml of wastewater sample was treated with different doses of prepared periwinkle carbon, 30 – 240 g/l. The samples were agitated for 60 min, filtered and then analyzed.

2.3 Contact Time
These studies were conducted by agitating 100 ml sample with best adsorbent dose in and agitating it for different time period, 30 – 300 min. After the predetermined time intervals, the samples were withdrawn, filtered and analyzed.

2.4 pH
PH effect was performed taking a specific concentration, adsorbent dose, and contact time and varying the pH values from 1 - 8 using dilute NaOH/HCl solutions. The samples were agitated for specific time, filtered and then analysed.

3. Results and discussion
The wastewater sample was characterized in terms of the parameters pH, COD and BOD
(Table 1).

3.1 Effect of Adsorbent Dose

Table 1: Sample wastewater characterization.

Parameter	Value
pH	8.7
BOD_5 (mg/l)	112.49
COD (mg/l)	692.57
TSS (mg/l)	44

BOD, Biological oxygen demand; COD, chemical oxygen demand; TSS, total suspended solids.

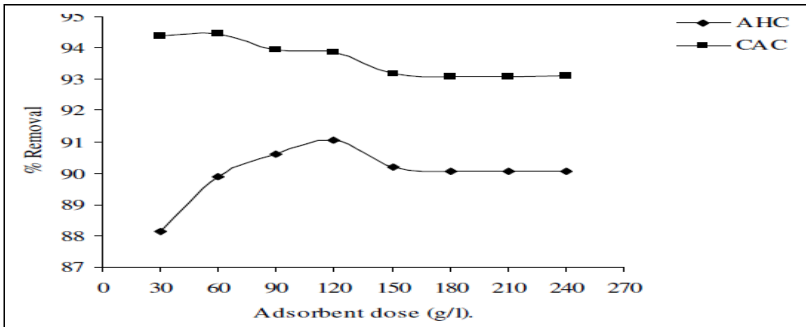

Figure 1. Effect of adsorbent dose on COD removal using activated carbon prepared from animal horns (AHC) and commercial activated carbon (CAC).

Fig 1: shows the effect of adsorbent dose on COD removal.

The result shows that optimum dosage of adsorbents for COD was 90 and 60 g/l of wastewater for activated carbon prepared from animal horns (AHC) and commercial activated carbon (CAC), respectively. About 90.62 and 94.45% removal was achieved for AHC and CAC, respectively.

3.2 Effect of pH
Fig 2: depicts the effect of pH on percent removal of COD. For AHC, at pH 5, the COD removal was 90%, which then decreased as the pH was increased. The same trend was observed for CAC. About 94% COD removal was achieved for CAC at pH 6. The reason for the better adsorption capacity observed at pH 5 and pH 6 may be attributed to the larger number of H
$^+$ Ions present, which in turn neutralize the negatively charged adsorbent surface, thereby reducing, Hindrance to the diffusion of organics at higher pH. At higher pH, the capacity of the adsorbent recessed. The reduction in adsorption may be possible due to the abundance of OH ions, causing increased hindrance to diffusion of organics contributing to COD) ions. Similar observations have also been reported by the workers (Mohan and Karthikeyan, 1997; Liskowitz *et al*. 1980; Mott and Weber, 1992; Pandey *et al*. 1985) [7, 5, 9].

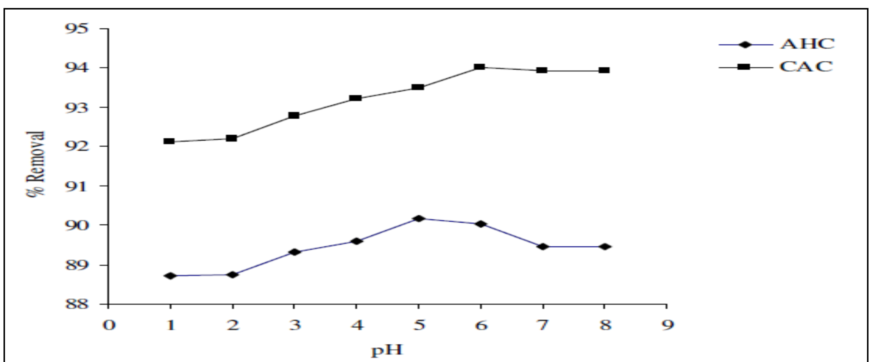

Figure 2. Effect of pH on COD removal activated carbon prepared from animal horns (AHC) and commercial activated carbon (CAC).

3.3 Effect of Contact Time

The result obtained shows that the mixing time had greater impact on COD removal (Figure 3). At an optimum time of 150 min, about 95.67% COD Removal was achieved for AHC, while about 96. 4% COD removal was achieved for CAC at 180 min. The smooth and independent nature of curve indicates formation of monolayer cover of the adsorbate on the outer surface of the adsorbents.

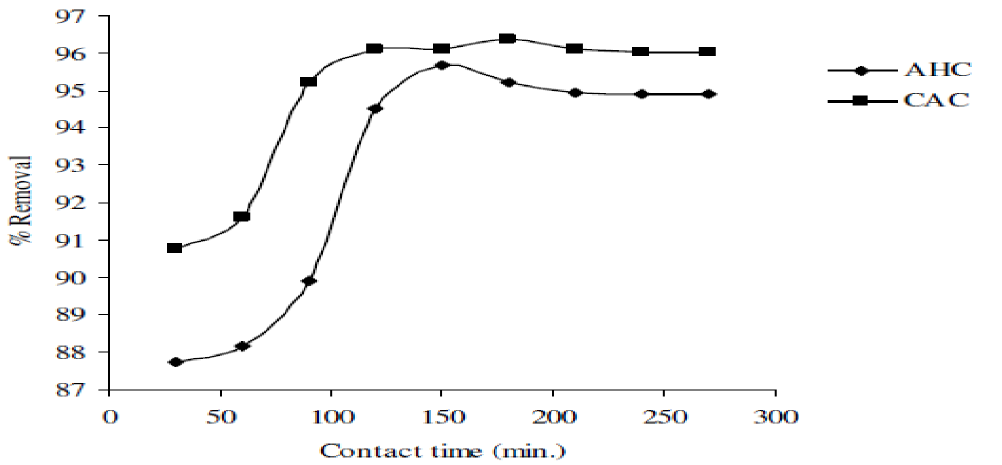

Figure 3. Effect of contact on COD removal activated carbon prepared from animal horns (AHC) and commercial activated carbon (CAC).

3.4 Adsorption Isotherms

Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are equilibria of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. The equations for the three types of adsorption isotherms are expressed by:

Linear isotherm $$q_e = \frac{x}{m} = k_p C_e$$

Langmuir isotherm $$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o k}$$

Where Ce is the equilibrium concentration of COD in water sample (mg/l), x/m is the amount of COD adsorbed per unit of adsorbent (mg/g), qo is a constant related to the area occupied by a monolayer of adsorbate, thus reflecting the adsorption capacity (mg/g), k is a direct measure of the intensity of the adsorption process, energy of adsorption (l/mg).

Freundlich isotherm $$\log\left[\frac{x}{m}\right] = \log k + \frac{1}{n}\log C_e$$

Where *k* is the quantity of COD adsorbed in mg/g adsorbent for a unit equilibrium concentration of the sample, that is, Ce = 1 and 1/n is a measure of the adsorption intensity. For n = 1, the partition between the two phases is independent of the concentration. In this case, k = kp (linear isotherm). A value of 1/n < 1 shows a normal Langmuir isotherm, while 1/n > 1 is indicative of a Cooperative adsorption (Atkins, 1970; Mohan and Karthikeyan, 1997; Badmus, *et al*. 2007) [2, 7, 3]. In order to decide which type of isotherm fits better the adsorption experimental data, a plot of x/m vs Ce was made for the linear isotherm (Figure 4); Ce/qe vs Ce was made for the Langmuir isotherm (Figure 5) and log (x/m) vs log Ce for the Freundlich isotherm (Figure 6). The r^2 values (goodness fit criterion) were computed using linear regression for the three types of isotherms. The results obtained show that the three types of adsorption isotherms are best suited for adsorption of COD. The coefficients of determination (r^2) and the isotherm constants are given in Table 2. The high values of r – squared (> 95%) for the three isotherms indicate that the adsorption of COD could be well described by the Linear, Langmuir and Freundlich isotherms.

Table 2. Adsorption isotherm constants and coefficient of determination for deffetent adsorbents.

Adsorbent	Langmuir isotherm constants			Freundlich isotherm constants		
	q_o (mg/g)	k (l/mg)	r^2	k (mg/g)	1/n	r^2
AHC	6.46	0.248	0.9998	9.863	- 11.820	0.9933
CAC	10.11	0.412	0.9999	13.712	- 15.576	0.9946

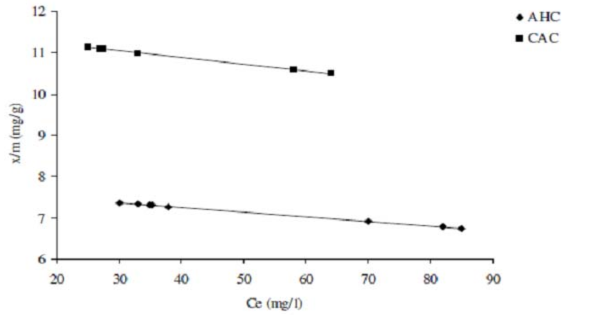

Figure 4. Adsorption isotherm of COD on activated carbon prepared from animal horns (AHC) and commercial activated carbon (CAC).

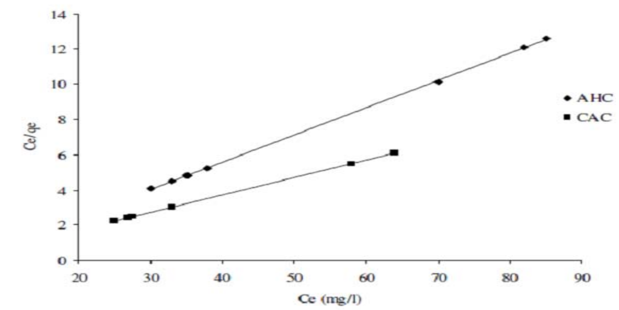

Figure 5. Comparison of Langmuir isotherms of activated carbon prepared from animal horns (AHC) and commercial activated carbon (CAC).

3.5 Adsorption Kinetics

The study of the adsorption kinetics is the main factor for designing an appropriate adsorption system and quantifying the changes in adsorption with time requires that an appropriate kinetic model is used. In order to consider the kinetics effects, the following Lagergren pseudo-first order equation can be used to determine the rate constants (Mohan *et al*. 2002; Badmus *et al*. 2007) [8, 3].

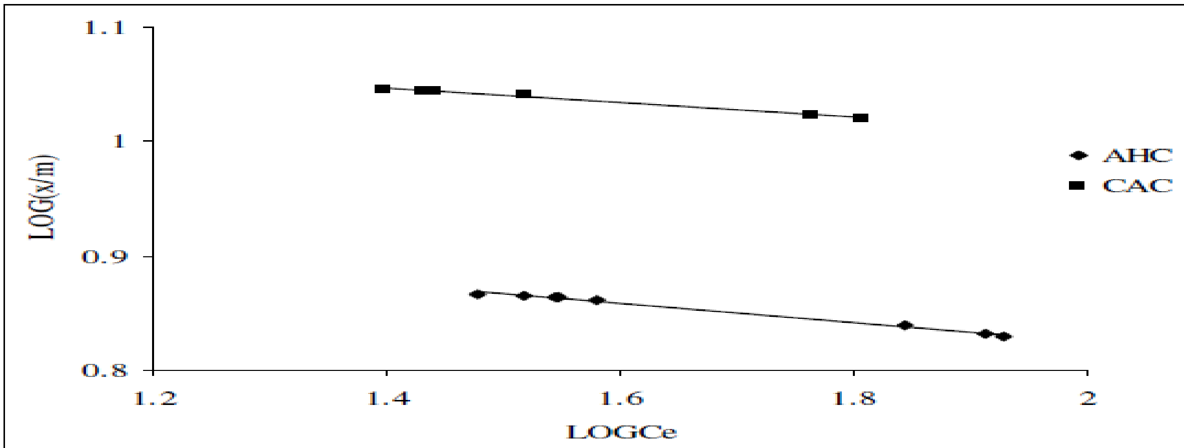

Figure 6. Comparison of Freundlich isotherms of activated carbon prepared from animal horns (AHC) and commercial activated carbon (CAC).

$$\log(q_e - q_t) = \log q_e - \frac{K_{1,ad}}{2.303}(t)$$

Where qe is the amount of COD adsorbed at equilibrium (mg/g); qt is the amount of COD adsorbed at time t (mg/g); K_1, ad is the pseudo-first order rate constant (min^{-1}); and t is the time (min). In many cases, the Equation 4 cannot be used to describe the kinetics of the adsorption process. In such cases, a pseudo-second order expression may be used and this is more appropriate for describing this type of adsorption. Hence, this model reduces to:

$$\frac{t}{q_t} = \frac{1}{K_{2,ad}\, q_e^2} + \frac{1}{q_e}(t)$$

Where K_2, ad is the pseudo–second order rate constant ($gmg^{-1}min^{-1}$). In this study, second order kinetics model was considered for the adsorption process of COD. Figure 7 shows the linearised form of the pseudo-second order model for the adsorption of COD onto AHC and CAC. The correlation coefficients, R^2, and the pseudo-second order rate parameters are shown in Table 3. The agreement between the sets of data reflects the extreme high correlation coefficient obtained and shown in Table 3. In order words, the data also show good compliance with the proposed pseudo-second order equation. Indeed, the regression coefficients for the linear plots were higher than 0.999 for both systems in these studies. Due to the correlation of the experimental results with the pseudo-second order model, the main adsorption mechanism is probably a chemisorption reaction.

Table 3. Pseudo-second order parameter and coefficient of determination for different adsorbents

Adsorbent	Pseudo-second order equation		
	q_e	k	r^2
AHC	0.7224	3.5266	0.9997
CAC	11.1732	0.0499	0.9999

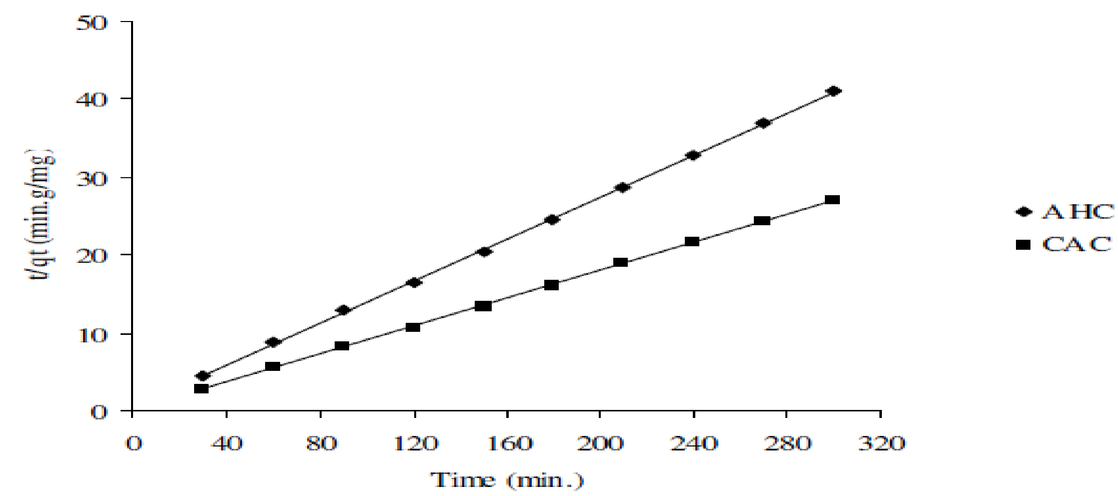

Figure 7. Pseudo-second order adsorption kinetics of COD on activated carbon prepared from animal horns (AHC) and commercial activated carbon (CAC).

4. Conclusion

The following conclusions were drawn from the present study. Activated animal horn carbon competed favorably with commercial activated carbon. The results obtained showed that AHC can be used in the removal of COD from industrial wastewaters. Trend of COD removal by AHC, 95.67%, is comparable to that of CAC with 96.34% efficiency. These results show that granular activated carbons made from agricultural waste (animal horn) can be used with greater effectiveness for organic matter removal from industrial wastewater. This would be of benefit not only to the manufacturing industry in terms of minimising cost of COD treatment, but also to minimize the impact on the environment. The adsorption data followed both Langmuir and Freundlich isotherms. In addition, a pseudo-second order kinetics appears to model the rate of adsorption.

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6. References

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Biography

Dr. Sachin Madhavrao Kanawade was born in 11 March 1978 at Nashik, Maharashtra, India. His native place is Nimgaonpaga, Tal-Sangamneer, Dist-A'Nagar, Maharashtra, India. He received his Bachelor's Degree in Chemical Engineering from Pravara Rural Education Society's Pravara Rural Engineering College, Pravaranagar (Loni) which is affiliated to Pune University in India in Nov.2001.Then he worked as a Production Officer in different Multinational Chemical Industries in India (2001 to 2008) like M/S Watson Pharma Ltd, Ambernath, MIDC, Mumbai, MS,M/S Glenmark Pharmaceuticals Ltd, Mohol, Dist. Solapur, MS, M/S Sun Pharmaceutical Industries Ltd, A. Nagar, MIDC,MS for 7 years. Then he changes his field. He joined K. K. Wagh College, Nasik, MS, India in 2008 & worked as Lecturer for 2 years. At the same time he Received his Master of Engineering in Environmental Engineering from Pravara Rural Education Society's Pravara Rural Engineering College, Loni in Dec.2010.Then he joined Pravara Rural Education Society's Sir Visvesvaraya Institute of Technology, Chincholi, Tal-Sinnar, Dist-Nasik, M.S. India in 2010 & worked as Assistant Professor in Chemical Engineering Department for 5 years. In the same period he completed his PhD Degree in Chemical Engineering in session 2011-2014 from Kumar Bhaskar Varma Sanskrit and Ancient Studies University Nalbari, Assam, India. Presently he is an Associate Professor at Dr. Vasantraodada Patil Shetkari Shikshan Mandal's Padmabhooshan Vasantraodada Patil Institute of Technology, Budhgaon, Tal-Miraj, Dist–Sangali, Maharashtra, India in Chemical Engineering Department. Presently he is Reviewer / Editorial Board Member / Advisory Board Member of 64 different International Journals of different fields. He having 21 International Professional Membership of different Organizations, He published 57 Technical Research Papers in different International Journals like International Journal of Wastewater Treatment & Green Chemistry, International Journal of Chemical Engineering, International Journal of Environmental Pollution Control & Management, International Journal of Multidisciplinary Approach & Studies, International Journal of Chemical Engineering & Applications, International Journal of Chemistry & Material Science & International Journal of Engineering Studies and Technical Approach etc. His research topic includes & interested in Chemical Engineering, Environmental Engineering, Wastewater Treatment by Adsorption, Advanced Separation Process, Chemical Engineering Design, Mass Transfer, Chemical Process Synthesis, Chemical Engineering Thermodynamics etc.