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The effect of low cost material Bagasse Fly ash to the removal of COD Contributing component of combined waste water of Sugar Industry

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ABSTRACT

To minimize the industrial pollution, advanced wastewater treatment techniques, such as adsorption, are economically and environmentally essential in the removal of organic and inorganic compounds from industrial wastewater. The present study focuses on the use of low cost adsorbent sugarcane bagasse fly ash to adsorb COD content of the combined wastewater of sugar industry. Bagasse Fly ash with specific surface area of 2637.784 cm^2/gm is used as a clarifier to the combined waste water of Sugar mill at room temperature. The different dosage of bagasse fly ash is kept in contact for 24 hours and analyzed before and after treatment. The results of COD removal is up to 27.04% and is follow the Freundlich and Langmuir adsorption isotherm.

Key words: Bagasse Fly ash, Adsorption, COD, Adsorption isotherm, Adsorption intensity (1/n), Adsorption energy (b x 10^3), Adsorption capacity (K, Θ_0).

INTRODUCTION

The Sugar Industry in India is one of the oldest and largest industry in the country. These mills require large volume of water of high and purity and generate equally large volume of waste water which is highly complex and pollute **[1]**. 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 **[2]**. In the present study, it was aimed to carry out experiments using low cost material like bagasse fly ash from Sugar manufacturing unit for the removal of organic contaminants especially COD contributing components from the combined waste water of Sugar Industry itself. The activated carbon adsorbent prepared from pod of wood apple **[3]**, Alternanthera Bettzichiana (Regel) Nicols plant material **[4]** and neem leaf powder **[5]** can be used as an efficient low cost adsorbent for Cr (VI) and organics removal from aqueous solution.

Sugar cane bagasse is an industrial waste which is used worldwide as fuel in the same sugar-cane industry. The combustion yields ashes containing high amounts of unburned matter, silicon and aluminum oxides as main components. These sugar-cane bagasse ashes (SCBA) have been chemically, physically and mineralogically characterized, in order to evaluate the possibility of their use as a cement-replacing material in the concrete industry and as an adsorbent in surface chemistry**[6]**. One of the research group have used bagasse fly ash as an adsorbent which is a byproduct of cane sugar industry, itself causes a great disposal problem and it is currently being used as filler in building materials. The effect of various operating variables, viz., solution pH, contact time, concentrations

of metal ions, adsorbent dose and particle sizes have been studied for the removal of cadmium and nickel ions. The material exhibits good adsorption capacity and follows both the Langmuir and the Freundlich models **[7]**. The effect of particle size and shape of adsorbent on adsorption is measured by computerized image analyzer **[8] .** Rate of adsorption increases with the reduction in particle size and it is inversely proportional to the square of the carbon particle diameter **[9]**. The BOD content of the sugar industry waste water can be removed up to 27.04% with bagasse fly ash and this phenomena can be well explained by Freundlich and Langmuir adsorption isotherms **[10].**
The adsorption of phenol on carbon rich bagasse fly ash (BFA) and activated carbon-commercial grade (ACC) and laboratory grade (ACL) were well studied. Batch studies were performed to evaluate the influences of various experimental parameters like initial pH (pH_0), contact time, adsorbent dose and initial concentration (C_0) on the removal of phenol. C_0 varied from 75 to 300 mg/l for the adsorption isotherm studies and the effect of temperature on adsorption **[11]**. The adsorption of brilliant green (BG) on carbon rich bagasse fly ash (BFA) by/with Batch studies were performed to evaluate the influences of various experimental parameters like initial pH (pH_0), contact time, adsorbent dose and initial concentration (C_0). Equilibrium isotherms for the adsorption of BG on BFA were analyzed by Freundlich, Langmuir, Redlich–Peterson, Dubnin–Radushkevich, and Temkin isotherm models using non-linear regression technique. Redlich–Peterson and Langmuir isotherms were found to best represent the data for BG adsorption onto BFA **[12].** The removal of lead from synthetic wastewater using sugar factory wastes, bagasse and bagasse fly ash like low cost material were well studied. Adsorption by these wastes can be used as an alternative to conventional treatment methods. Bagasse was treated under acidic condition while bagasse fly ash was untreated. Batch study indicated that the removal efficiency increased with increasing solution pH and adsorbent dose. Adsorption isotherms revealed that the Freundlich equation fitted the isotherm data better than the Langmuir. Bagasse fly ash was more favorable than bagasse in removing lead and thus was a better adsorbent **[13]**.

One of the work involves the study of Se(IV) adsorption onto bagasse fly ash. The adsorbents were coated with a ferric chloride solution for the effective removal of selenium. Equilibrium isotherms were analyzed using Langmuir, Freundlich, and Temkin isotherms. Error analyses were also carried out using hybrid fractional error function and Marquardt's percent standard deviation **[14]**. Nevertheless, sugarcane bagasse proved to be a better adsorbent than coal fly ash in the uptake of direct red dyes from textile wastewater. Direct red 80 (DR 80) was the highest adsorbed dye by both sugarcane bagasse (6.536 mg/g) and coal fly ash (1.560 mg/g). Equilibrium data for metal removal conformed well to the Freundlich isotherm whereas phenol and direct dye removal complied with the Langmuir adsorption isotherm model **[15]**.

MATERIALS AND METHODS

During the production of Sugar bagasse Fly ash is obtained as a waste product in large quantities from Sugar mill. The total amount and physico-chemical characteristics of Fly ash which is occurred on burning Bagasse generated in boiler varies from boiler to boiler depending upon the boiler’s efficiency. Bagasse Fly ash used in present research work is collected from Sahakari Khand Udhyog Mandali Ltd, Bardoli (Gujarat). It was washed to remove excess fines and oven dried at 100^0C for 24 hours before its use in experiments. It is light black colored material having specific surface area 2637.784 cm^2/gm. Bagasse Fly ash mainly consists of unburned carbon, SiO_2 - 51 to 55%, Al_2O_3 – 10 to 11%, CaO -5 to 6 %, Fe_2O_3 - 4 to 5%, and trace of MgO. The known quantity (1 liter) of sample is treated with different amount of fly ash viz 2, 5, 10, 15, 20, 40 and100gm/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’ **[16]**. The results for each dose are presented in Table I, II and figure 1, 2.

RESULTS

Table I shows the effect of different dosages of Bagasse Fly ash onto various physico-chemical characteristic of the combined Waste Water Sugar Industry at room temperature. It is clear from the data that the pH and conductivity is increased alkalinity and hardness is decreased with increase in adsorbent concentration. pH increases from 6.5 initial to 8.82, conductivity increases from 3.05 m mho to 5.04 m mho, whereas alkalinity and hardness first drops and then increases from 1660 mg/L (initial) to 800 with 2gm/L adsorbent and further to 1250 mg/L at 100 gm/L and hardness decreases to 600 mg/L (2 gm/L) from 2075 mg/L (initial)and then increases upto 860 mg/L at 100gm/L of bagasse fly ash. The chloride content of the sample remains constant upto 15gm/L of adsorbent dose and then increases rapidly i.e. 204.936 mg/L (initial) to 167.448 mg/L upto 15 gm/L to 424.868 mg/L (100 gm/L). The initial

COD content 5089.56 mg/L decreases to 3695.16 mg/L with 40 gm/L of bagasse fly ash and remains constant at higher dose. The initial BOD content is 1581 mg/L is decreased to 328.6 mg/L with same dosage 40gm/L and remains constant for higher dose.

Table II represents the data for Freundlich and Langmuir adsorption isotherms along with percent removal of COD exerting components. There is a considerable decrease in adsorption per unit weight of adsorbent with increase in adsorbent concentration. The removal of COD contributing components is found to decrease from 69.72 mg/gm to 13.94 mg/gm respectively with varying amounts of fly ash from 2 gm/L to 100gm/L. The logarithmic and inverse values of equilibrium concentration and removal per unit weight are used for plots of isotherm.

Fig. I represents the plot of log C_{eq} Vs log x/m for COD on bagasse fly ash. 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 4.2432 for COD while intercept K on Y-axis related to adsorption capacity is found to be 1.25

Fig. II 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 COD onto bagasse fly ash from sugar industry is linear however the intercept on X-axis related to adsorption energy (L/mg) i.e. $b \times 10^3$ is 0.2170 L/mg for COD exerting components. These values can be used to calculate the adsorption capacity Θ_0 i.e 118.1631 (mg/gm).

DISCUSSION

The effect of different dose of bagasse fly ash on various physico-chemical characteristics is presented in table I indicate continuous increase in pH, conductivity, alkalinity, hardness and also of chloride content after 15 gm/L of dose suggest addition of some soluble inorganic material and ionic species causes the increase of results. Early at the first stage of the reaction the values seen to be decreased suggest adsorption of contaminants causing alkalinity, hardness and chloride content which is then shifts towards desorption with increase in dose. The COD and BOD content are adsorbed on the bagasse fly ash surface and removed by simple filtration, after optimum dose equilibrium condition attained and then no further removal is found even with higher dose.

Table II represents the data for Freundlich and Langmuir adsorption isotherms along with percent removal for COD onto bagasse fly ash. 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 bagasse fly ash 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 bagasse fly ash. Langmuir isotherm is a plot of the amount of impurity adsorbed by bagasse fly ash 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

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

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-I 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-II represents the plot of Langmuir adsorption isotherm for COD contributing components onto bagasse fly ash. 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.

Table I The effect of different dosages of Bagasse Fly ash onto various physico-chemical characteristic of the combined Waste Water Sugar Industry

Adsorbent: Bagasse Fly ash *Room temperature: 25± 1 ^{0}C*
Specific Surface Area: 2637.784 Cm^2/ gm *Contact duration: 24 Hours*

Parameter	Untreated	2 gm/L	5 gm/L	10 gm/L	15 gm/L	20 gm/L	40 gm/L	100 gm/L
pH	6.5	8.17	8.47	8.64	8.67	8.70	8.78	8.82
Conductance (m mho)	3.05	2.10	2.14	2.41	2.59	2.98	3.48	5.04
COD (mg/L)	5089.56	4950.12	4601.52	4392.36	4183.2	4043.76	3695.16	3695.16
BOD (mg/L)	1581	589	496	434	403	372	328.6	325.6
Alkalinity (mg/L)	1660	800	820	860	920	1060	1175	1250
Hardness (mg/L)	2075	600	625	675	700	725	860	860
Chloride (mg/L)	204.936	167.448	167.448	167.448	167.448	192.44	237.426	424.868

Table II Freundlich and Langmuir adsorption isotherm parameters for COD along with percent removal of COD onto Bagasse Fly ash

Adsorbent: Bagasse Fly ash *Room temperature: 25± 1 ^{0}C*
Specific Surface Area: 2637.784 Cm^2/ gm *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	$1/C_{eq}x10^3$	$1/q_e x10^2$
1	0	5089.56	------	-----	-----	3.7066	-----	0.1964	-----
2	2	4950.12	139.44	64.72	2.74	3.6946	1.8433	0.2020	1.4343
3	5	4601.52	488.04	97.61	9.59	3.6629	1.9895	0.2173	1.0244
4	10	4392.2	679.2	69.72	13.7	3.6407	1.8433	0.2278	1.4343
5	15	4183.2	906.36	60.424	17.18	3.6215	1.7812	0.2330	1.6549
6	20	4043.76	1045.8	52.29	20.54	3.6067	1.7184	0.2472	1.9124
7	40	3695.16	1394.4	34.86	27.40	3.5676	1.5423	0.2706	2.8686
8	100	3695.16	1394.4	13.94	27.40	3.5676	1.1442	0.2706	7.1736

Fig 1: Freundlich Adsorption Isotherm for COD onto Bagasse fly ash

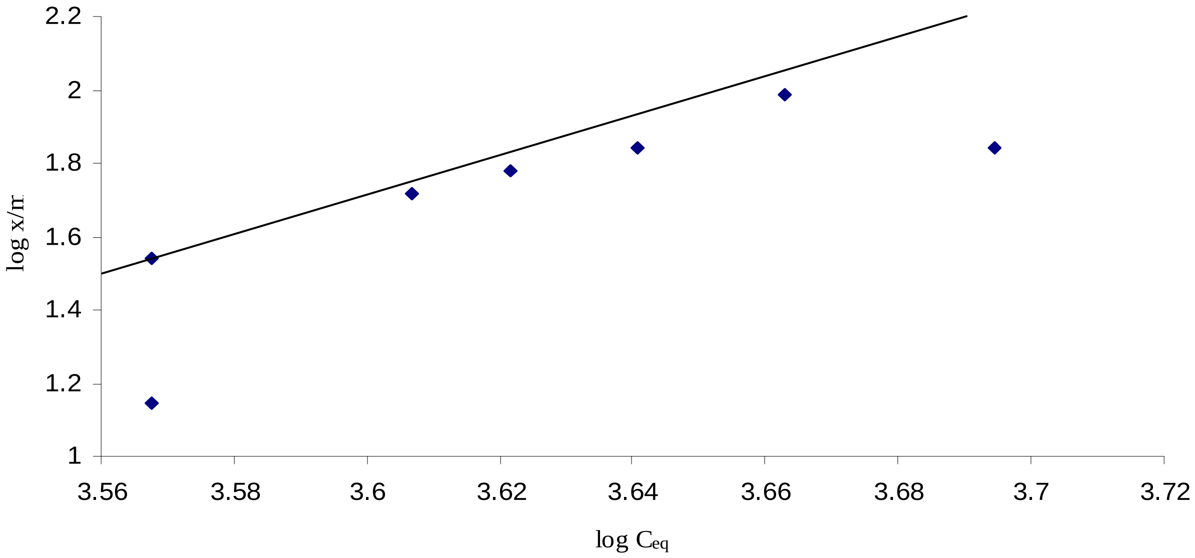
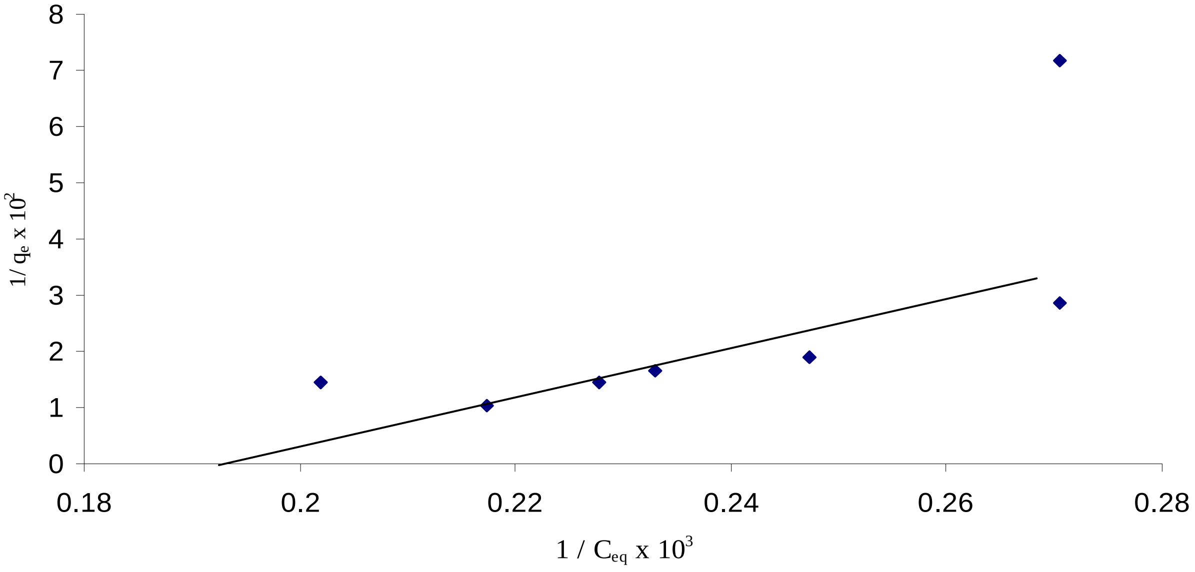


Fig. 2: Langmuir Adsorption Isotherm for COD onto Bagasse fly ash



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 bagasse fly ash at room temperature for 24 hours of contact duration the following results are achieved.

i. The maximum COD removal is found at 400gm/L of fly ash concentration i.e. 27.4%
ii. Bagasse Fly ash of sugar industry itself is a pollutant removes BOD contributing components upto 79.21% of the combined waste water.
iii. The alkalinity, hardness and chloride content of the sample first decreased and then increases with increasing amount of bagasse fly ash.
iv. At room temperature bagasse fly ash 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 1.45 while the slope 1/n is related to adsorption intensity is found to be 4.2432
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 0.1970 and the calculated adsorption capacity Θ_0 mg/gm is 118.1631

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