RESEARCH PAPER:

Isotherm studies for cod removal and devolorization of distillery waste by activated carbons

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SUMMARY

Treatment technology was developed for decolorization of effluent using three different types of activated carbons *i.e.* peanut, walnut, almond shells. Maximum decolorization occurred at dosage of 5g/100ml with PAC and AAC; 6g/100ml with WAC at pH 2, contact time of 105 minutes (PAC, WAC) and 120 minutes (AAC) and agitation speed of 100 rpm (PAC, AAC) and 150 rpm (AAC). Trend of decolorization and COD removal by three activated carbons was found to be: PAC > WAC > AAC. Peanut activated carbon was found to be best as it showed 92.47% colour removal and 44.93% COD reduction. From Freundlich isotherm, values of adsorption capacity, K_F is 11.5 L/g and sorption intensity was 7.751. Coefficient of determination, r^2, for Freundlich was 0.8661. Maximum sorption capacity for Langmuir-1 was 52.9 mg/g, for Langmuir-2 was 47.6 mg/g, for Langmuir-3 was 49 mg/g and for Langmuir-4 was 45.30 mg/g. RL value for all the four forms was less than zero from which it could be concluded that adsorption process was favourable and reversible in nature.

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Key words :
Activated carbon, Sorbent, Isotherms, Decolorization, Kinetics.

Dark brown colour of distillery spentwash is due to pigment, melanoidin which is recalcitrant in nature. Conventional treatments can degrade melanoidins only upto 6 to 7% (Kalavathi *et al.,* 2001). High COD, total nitrogen and total phosphate content of effluent may lead to eutrophication of natural water bodies Disposal of sugarcane molasses wastewater on land is equally hazardous to vegetation by reducing soil alkalinity and manganese availability, thus inhibiting seed germination (Kumar, 1997). Coloured components of molasses wastewater reduce sunlight penetration in rivers, lakes which in turn decrease both photosynthetic activity and dissolved oxygen content affecting aquatic life (Mane *et al.,* 2006).

The aim of this work was to see the efficacy of three activated carbons- peanut (*Arachis hypoguea*), almond (*Prunus dulcis*) and walnut (*Juglans regia)* shell powder to decolourize the effluent and reduce COD and to study adsorption isotherms.

MATERIALS AND METHODS

Procurement, characterization of effluent and activation of raw carbon:

Effluent used was biomethanated molasses spent wash and characterized for various parameters like pH 8.2, TS 42,400, TDS 38300, TSS 4100, hardness 1660, alkalinity 1360, DO 490, BOD 2200, COD 3800, heavy metals like chromium 1.73, nickel 0.35 and zinc 1.41 ppm, respectively were determined by standard methods (Peavy *et al*., 1985). Peanut, almond and walnut shells were treated with concentrated sulphuric acid and formaldehyde in ratio of 4:1.5. After acidification, carbon mixtures were kept in oven at 150 ^{0}C for 12 hours. The char obtained was washed with distilled water and then soaked in 1 per cent sodium carbonate to remove residual acid.

RESULTS AND DISCUSSION

The findings obtained from the present study have been discussed in the following sub heads:

Effect of adsorbent dose and contact time:

The rate of per cent decolorization was maximum for 5g of all the sorbents which slows down as the adsorbent dose was increased. The rate of adsorption increases with increase in adsorbent dosages because

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Table 1: Effect of concentration on % decolorization of effluent				
Type of adsorbent	% decolorization of effluent by varying effluent concentration as:			
	100%	75%	50%	25%
Peanut	92.4	95.22	97.42	99.02
Walnut	88.89	91.53	93.24	98.83
Almond	79.92	82.54	85.05	89.92

of increase in surface area of adsorbent (Kannan and Srinivasan, 1998). The optimum contact time for adsorption was 105 minutes for PAC and WAC (91-92%) whereas for AAC (85%) it was 120 minutes. Generally the rate of adsorption increases with time and after sometime it remains constant due to equilibrium condition. Similar results have been reported in literature for removal of organic acids (Kannan and Xavier, 2001).

Effect of pH, agitation speed and dilution on adsorption:

The per cent decolorization decreases as the pH increases from 2-4 in PAC (91.49-76.2), WAC (91.33-80.32) and AAC (88.8-72). Negligible decolorization occurred at pH 6. This might be due to large availability of H^+ ions at low pH which neutralizes the negative adsorption sites on the surface of adsorbent reducing the hindrance to diffusion of organics (Aluyor and Badmus, 2008). There is an increase in % decolorization with increase in agitation speed till equilibrium is attained. After equilibrium is achieved, there might occur some desorption due to saturation of adsorbent sites. Increase of initial concentration of effluent from 25% to 100% reduces decolorization. This is due to saturation of adsorption sites at higher concentrations (Ojyo *et al.,*2010) It was concluded that PAC is more efficient in removing colour (92.47%) and COD (44.93%) as compared to WAC and AAC. So, PAC was chosen for further study.

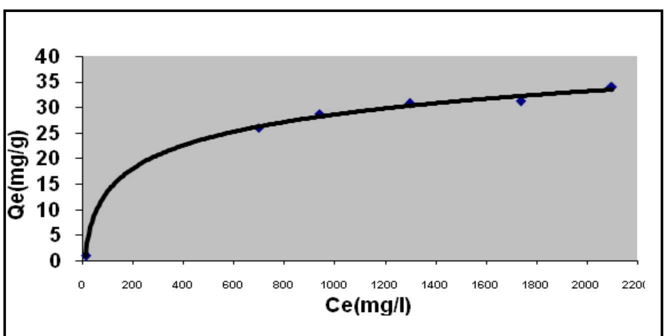

Fig. 1: Freundlich isotherm using non-linear method for COD sorption onto PAC

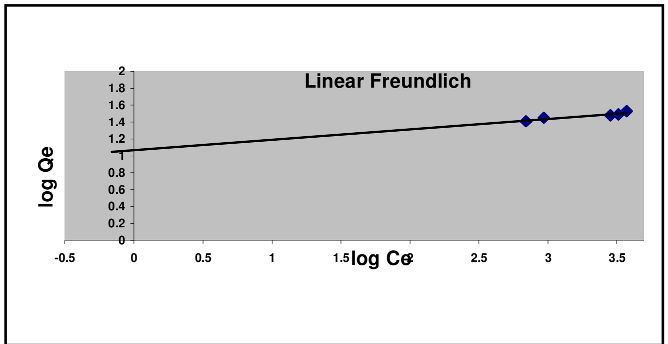

Fig. 2: Freundlich isotherm using linear method for COD sorption onto PAC

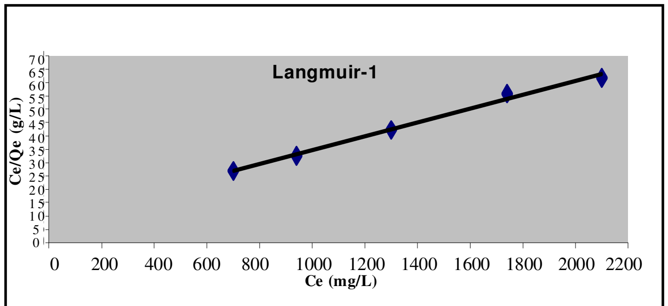

Fig. 3: Langmuir-1 isotherm using linear method for COD sorption onto PAC

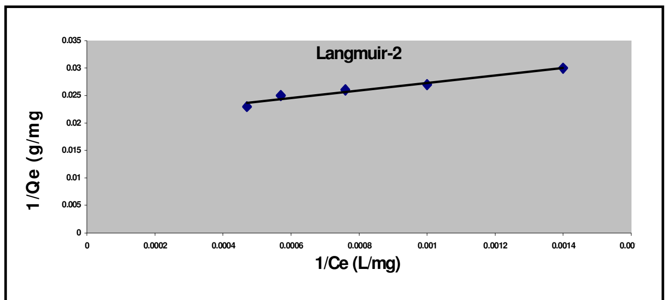

Fig. 4: Langmuir-2 isotherm using linear method for COD sorption onto PAC

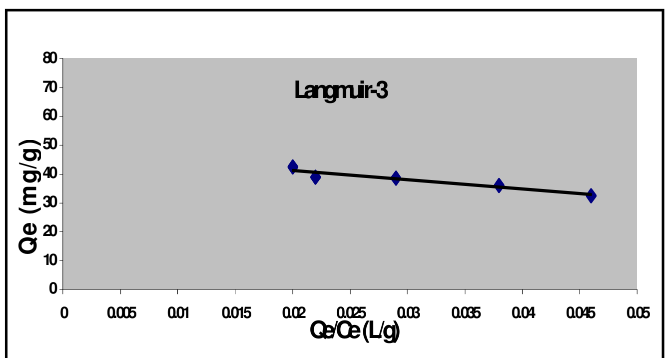

Fig. 5: Langmuir-3 isotherm using linear method for COD sorption onto PAC

Table 2: Calculated values for Ce, Qe, log Qe, log Ce

Effluent conc.	Initial COD (Co) mg/l	Equilibrium COD (Ce)mg/l	Qe	logQe	logCe
100%	3800	2100	34.0	1.53	3.57
80%	3300	1740	31.2	1.49	3.51
60%	2840	1300	30.8	1.48	3.45
40%	2380	940	28.8	1.45	2.97
20%	2000	700	26.0	1.41	2.84

Table 3: Values of parameters determined from linear forms of isotherms

	Qm (mg/g)	b (L/mg)	r^2	R_L
Langmuir-1	52.9	0.0021	0.9932	0.111
Langmuir-2	47.6	0.0028	0.9599	0.085
Langmuir-3	49	0.0025	0.9168	0.095
Langmuir-4	45.30	0.0030	0.9168	0.080
Freundlich	n	K_F (L/g)	r^2	---------
	7.751	11.5	0.8661	---------

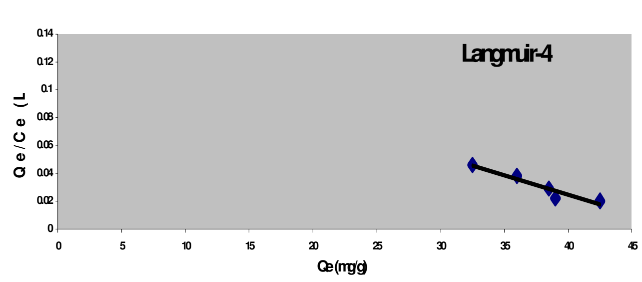

Fig. 6: Langmuir-4 isotherm using linear method for COD sorption onto PAC

Adsorption isotherms for COD removal from effluent treated with peanut activated carbon:

The analysis of equilibrium data by fitting them onto Freundlich and Langmuir isotherm models was done. Equilibrium COD concentration for each dilution was estimated (Table 2). Linear forms of Langmuir-1, 2, 3, 4 and Freundlich adsorption isotherms were used for comparison. Freundlich isotherm values of KF, 11.5 L/g and sorption intensity 7.751, coefficient of determination, r^2, 0.8661 were observed. The separation factor, RL, indicates nature of adsorption process. RL value of 0.111 for Langmuir-1, 0.085 for Langmuir-2, 0.095 for Langmuir-3 and 0.080 for Langmuir-4 (Table 3) indicate that adsorption process is favourable and reversible in nature (Bello *et al.,* 2010). All Langmuir forms, Langmuir-1, 2, 3 and 4 show higher value of r^2 as compared to Freundlich isotherm. The value of the coefficient of determination, r^2, obtained from Langmuir-1 is very close to unity (0.9932), indicated that there was a strong positive evidence that the sorption of COD causing compounds onto peanut shell activated carbon follows the Langmuir isotherm. Thus, it is concluded that Langmuir-1 isotherm was more suitable for experimental data than Freundlich isotherm because of higher value of the coefficient of determination r^2 (Allen *et al.,* 2003).

The maximum sorption capacity, Qm as determined from linear plot of Langmuir-1 was 52.9 mg/g.

Conclusion:

Peanut activated carbon can be successfully used to reduce colour and COD content of biomethanated molasses spentwash with maximum sorption capacity of 52.9 mg/g.

Abbreviations:

PAC- Peanut activated carbon, AAC (Almond activated carbon), WAC (Walnut activated carbon), COD (chemical oxygen demand).

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