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Equilibrium and Kinetic Studies of Adsorption Organic Compounds of Vinasse onto Granular Activated Carbon

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ABSTRACT: Distilleries wastewater (vinasse) because of its pollution problems is serious environmental concern. In this study the equilibrium and kinetic studies of adsorption organic compounds of vinasse onto granular activated carbon was investigated. In order to determine the effect of initial COD (Chemical Oxygen Demand) concentration on the adsorption efficiency, different COD concentrations with granular activated carbon (GAC) dosage of 50 g/l were tested. The COD removal trends for different concentration vinasse solution was investigated at different initial concentration, pH=2 and temperature of 25 °C. The ultimate or equilibrium concentrations were determined for all initial COD concentration. The q_e values for different COD concentrations of 1957, 3391, 5222, 6558 and 8975 mg/l were found to be 29.3, 46.2, 50.6, 58 and 68.1 mg/g, respectively. An increase in q_e was obtained by increasing initial COD concentration, indicating selective nature of GAC in particular organic matters. Equilibrium qe values of five initial COD concentrations that were fitted by isotherm models. Both Freundlich (R^2 = 0.983) and Langmuir (R^2 = 0.976) isotherms give a good correlation for GAC adsorption of total organic maters in terms of R^2 values, however it is slightly higher in Freundlich model and Temkin model demonstrated a low fitness (R^2=0.92). The maximum adsorption capacity of GAC (q_m) predicted by Langmuir model was 71.14 mg/g. The empirical value of q_e in our study was 68.1 mg/g with a good vicinity to predicted value by Langmuir isotherm model (71.149 mg/g).

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1- Introduction

Distilleries wastewater (Vinasse) because of its pollution problems has serious environmental concern, due to high COD, BOD (Biological Oxygen Demand), COD/BOD ratio, potassium, phosphate and solphate [1]. A typical distillery factory releases 1300 m3 vinasse in production of 100 m^3 ethanol with BOD of about 30000-60000 mg/l [2], COD of about 80000-100000 mg/l and dark brown color [3]. Activated carbon has been normally used as adsorbent for removal of organic and color causing compounds in wastewater treatment processes. Adsorption ability of activated carbon for organic compounds essentially is related to textural and surface chemical and physical characterizations of activated carbon [3]. Complete decolorization (> 99%) can be obtained with 70% of the eluted sample, which also displayed over 90% BOD and COD removal [4]. whereas other researchers have reported that powdered activated carbon (PAC) concluded only 18% color removal. In the present study, adsorption of organic compounds (as a function of COD removal) onto granular activated carbon (GAC) has been investigated. Data have been examined with isotherm models and for the first time adsorption kinetics of process has been surveyed.

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2- Methodology

The raw vinasse was prepared from laboratory ethanol production by cane molasses fermentation by Saccharomyces cerevisiae in continuous mode. The wastewater characterization was conducted according to standard method [5] as listed in Table 1.

Table 1. Physicochemical characteristic parameters of vinasse

Characteristics	Value
Color	Dark-brown
pH	5
COD (mg/l)	40700
BOD_5 (mg/l)	23300
Total solids (TS) (g/l)	42
Ash or solid matter (g/l)	14.62
Phosphate (mg/l)	300
Sulfate (mg/l)	17500
Nitrate (mg/l)	3.99
Nitrite (mg/l)	0.7
Ammonia (mg/l)	3360
Chloride (mg/l)	36

In order to investigation the effect of initial COD concentration on adsorption efficiency of GAC and also fitting data with isotherm models, different initial COD concentrations (1957, 3391, 5222, 6558 and 8975 mg/l) with GAC dosage of 50 g/l, pH=2, room temperature and 200 rpm were tested in batch system. The COD removal and uptake capacity of GAC for different concentration of vinasse solution also were investigated. Equilibrium time considered as 180 min and the maximum adsorption capacity (q_m) calculated as Equation 1 [6].

$$q_e=(V(C_0-C_e))/W \quad (1)$$

Where q_e is the adsorbed COD quantity per unit mass of dried GAC at equilibrium (mg/g); V is the treated vinasse volume (l); W is the mass of GAC (g) and Co and Ct are initial and equilibrium COD concentration of solution, respectively. The Langmuir model offering adsorption process occurs on a homogeneous surface by monolayer sorption without interaction between sorbed molecules as following equation;

$$q_e=(q_m\, bC_e)/(1+bC_e) \quad (2)$$

Where C_e is the COD concentration of vinasse at equilibrium time, q_m is the removed COD per unit mass of dried GAC at equilibrium (mg/g) and b is the Langmuir constant explaining the ability of solution for adsorption (l/mg). The Freundlich model suggests a multilayer sorption with a heterogeneous energetic distribution of active sites on adsorbent, and with interaction between sorbed molecules in non-linear form as following equation:

$$q_e=K_F\, C_e^{(1/n)} \quad (3)$$

Where K_f (mg/g.(l/mg)$^{1/n}$) is a Freundlich constant taken as an indicator of adsorption capacity and 1/n (dimensionless) is an empirical constant which relating to the adsorption intensity i.e. the affinity of the molecule with the GAC [7]. Data also fitted by Temkin and Dubinin–Radushkevich isotherms. The kinetic studies also were carried out by using pseudo-first-order rate equation to describe the kinetic process. This model is presented as follows [8]:

$$Log(q_e-q_t)=Logq_e-k_1/2.303\ t \quad (4)$$

The pseudo-second-order rate equation was also used to describe the kinetics of adsorption of organic matters and it is expressed as follows [9]:

$$t/q_t=1/(k_2\, q_e^2)+t/q_e \quad (5)$$

where q_e and qt are presenting the amount of adsorbed organic matters in mg.g^{-1} on the adsorbent (GAC), at equilibrium and time t, respectively, while k_1 in min^{-1} and k_2 in g.mg^{-1}min^{-1} are the rate constants of the first and second-order rate equation, respectively.

3- Results and Discussion

Figure 1 shows the q_e and COD removal in terms of different GAC values. Increasing GAC dose concluded increasing COD removal. The more q_e values obtained in lowest GAC amount (10 g/l). This indicates selective nature of GAC in particular organic matters.

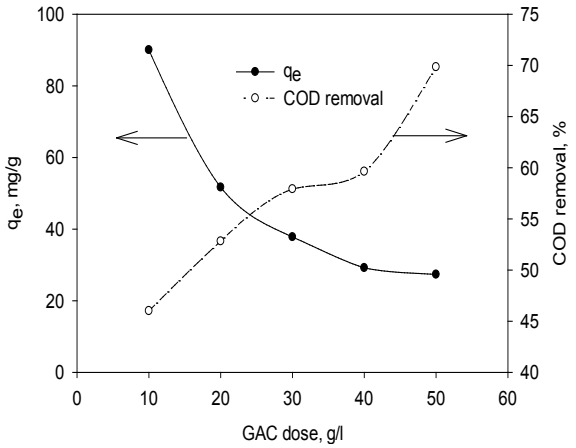

Figure 1. Plotting of q_e and COD removal with different GAC doses

Figure 2 demonstrates the non-linear Langmuir, Freundlich and Dubinin–Radushkevich adsorption isotherms of organic compounds of vinasse onto the GAC.

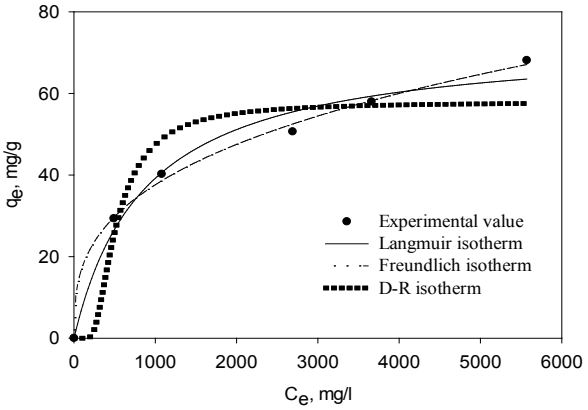

Figure 2. Fitness of data with isotherm models

Table 2 shows isotherm parameters at 25 °C in the adsorption studies. From Figure 2 and Table 2 can be concluded that both Freundlich (R^2=0.983) and Langmuir (R^2=0.976) isotherms give a good correlation for GAC adsorption of total organic maters in terms of R^2 values, however the Freundlich model presents a slightly better goodness of fit. However Temkin and Dubinin-Radushkevich isotherms also demonstrate fairly logical fitness (R^2=0.92).

Table 2. Parameters of isotherm models

Models	Parameters			
Langmuir	q_m.exp (mg/g)	b (l/mg)	R^2	p
	71.149	0.0014	0.976	0.0002
Fereundlich	1/n	K_f	R^2	p
	0.301	4.99	0.983	0.0001
Temkin	KT (l/mol)	B_T	R^2	p
	14.007	8.85	0.926	0.0087
Dubinin_ Radushkevich	q_m (mg/g)	E (kJ/mol)	R^2	p
	57.9	0.031	0.92	0.0002

Figure 3 (a and b) shows linear regression of pseudo-first-order and pseudo-second-order rates and the regression correlation coefficients (R^2) have been delivered in Table 2. Data showed that pseudo-first-order kinetic models didn't show a good fitness (in terms of R^2 values), while the pseudo-second-order model logically describes a good fitness of data. All calculated q_{e2} values were close to those obtained experimentally (qe exp.). From other hand, when initial COD of solution differ from 1957 to 8975 mg/l constant values of pseudo-second-order kinetic model (k_2) shows a reducing trend that indicating quick saturation of active sites by organic matters of vinasses. This trend also representing the monolayer coverage of organic matter onto surface of granular activated carbon.

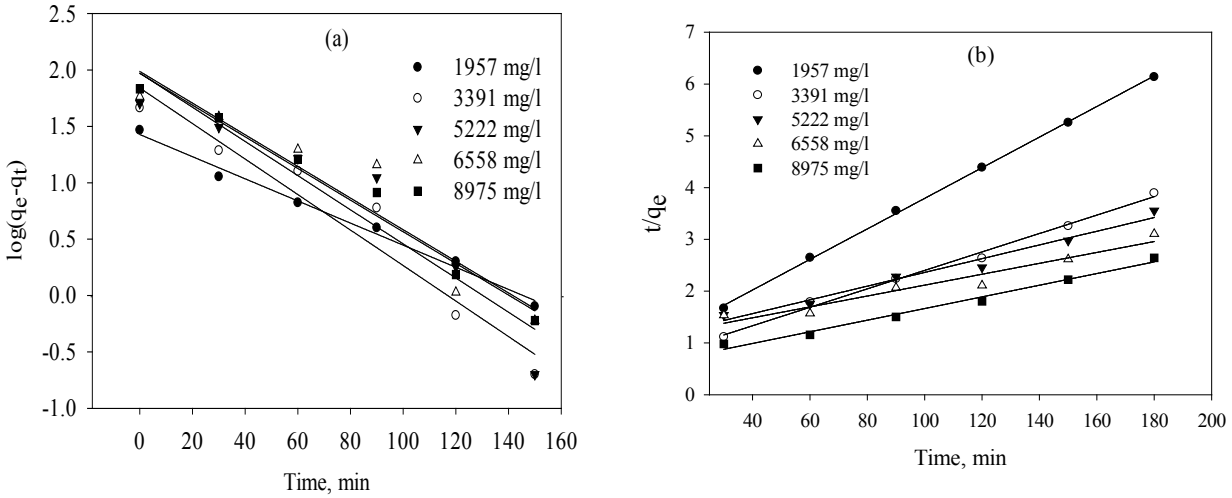

Figure 3. Linear regression of pseudo-first-order (a) and pseudo-second-order rates (b). (Temperature of 25 °C, pH=2, adsorbent dose of 50 g/l and 200 rpm)

Table 3. Adsorption kinetics parameters of pseudo-first and second-order kinetic models

Model	Initial COD concentration, mg/l				
	1957	3391	5222	6558	8975
Pseudo-first-order					
$q_{e1\ cal.}$	26.30	69.18	9375	95.05	92.89
K_1	0.0225	0.0361	0.034	0.0322	0.032
$q_{e.exp.}$	29.34	46.22	50.64	57.96	68.10
R^2	0.99	0.94	0.89	0.90	0.97
Pseudo-second-order					
$q_{e2\ cal.}$	33.89	56.18	75.19	95.23	89.28
K_2	0.0007	0.0005	0.0001	0.0001	0.0002
$q_{e.exp}$	29.34	46.22	50.64	57.96	68.10
H	0.83	1.6	0.96	0.90	1.83
R^2	0.99	0.99	0.98	0.94	0.99

4- Conclusion

In present study isothermal and kinetic manner of organic matter adsorption onto granular activated carbon were investigated. Data showed that Langmuir and Freundlich isotherm models can logically describe the adsorption process. Pseudo-second-order had a good fitness with data compared to pseudo-first-order kinetic rate.

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