



TREATMENT OF A HIGH STRENGTH ACIDIC INDUSTRIAL CHEMICAL WASTEWATER USING EXPANDED BED ADSORBER

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ABSTRACT

Treatment of a high strength acidic industrial wastewater was attempted by activated carbon adsorption to evaluate the feasibility of yielding effluents of reusable qualities. The experimental methods which were employed in this investigation included batch and column studies. The former was used to evaluate the rate and equilibrium of carbon adsorption, while the latter was used to determine treatment efficiencies and performance characteristics. Fixed bed and expanded bed adsorbers were constructed in the column studies.

In this study, the adsorption behavior of acetic acid onto activated carbon was examined as a function of the concentration of the adsorbate, contact time and adsorbent dosage. The adsorption data was modeled with Freundlich and Langmuir adsorption isotherms.

The amount of acetic acid adsorbed increased with the decrease in initial concentration of acetic acid and increased with the increase in contact time and adsorbent dose. The effects of various important and influencing parameters such as flow rate, bed height, inlet adsorbate concentration on breakthrough curve are studied in details in the column studies.

KEYWORDS: Acetic acid removal, expanded bed adsorber, wastewater treatment, adsorption on activated carbon.

الخلاصة:

تم في هذه الدراسة معالجة مياه التصريف العالية الحموضة بواسطة الامتزاز على الكربون المنشط واستخدمت طريقة الامتزاز ذو الدفعات وباستخدام الاعمدة الثابتة والمتمددة. حيث استخدمت الاولى لايجاد معدل وعلاقة الامتزاز لحمض الخليك على الكربون المنشط بينما استخدمت الثانية لايجاد كفاءة عملية المعاملة وايجاد الاداء. المتغيرات التي تم دراستها هي تركيز المادة الممتازة والزمن وكمية المادة المازة. استخدمت علاقة فرويندلش ولنكمير لتمثيل النتائج. بينت النتائج بان كمية حامض الخليك الممتازة تزداد مع نقصان التركيز الابتدائي للحامض وتزداد مع زيادة زمن التماس وكمية المادة المازة. اما بالنسبة للدراسة باستخدام الاعمدة فان تأثير معدل الجريان وارتفاع الحشوة وتركيز المادة الممتازة على منحنى المقاومة تم دراستها بالتفصيل.

INTRODUCTION

Wastewater, containing organic compounds, causes great problems. Most of the organic compounds like phenols, amines and acids are classified as priority pollutants, which are to be removed from water and wastewater. A wide range of industrial effluents, especially from rubber, pharmaceutical, food processing, agro-chemical industries, municipal sewage, agricultural run-offs, decaying vegetables and animals are the major sources of organic carboxylic acid (Kannan and Xavier, 2001; Kannan, and Murugavel, 2008).

Carboxylic acids also applied in conservation and disinfections in the textile and tanning industries. During their use, a significant amount of these acids get into wastewater currents, finishing up in residual wastewaters (Alessandra et al., 2004).

Whereas the separation of acetic acid from water by conventional distillation is economic at concentrations exceeding 70 wt%, for low concentrations in water (below 5 wt %), adsorptive separations can provide a viable option (Ganguly and Goswami, 1996).

Activated carbon is the most well known and widely used commercial adsorbent in water purification. The adsorption on activated carbon posses some advantages over other technologies due to the possibility of recovering a pure, high removal efficiency at low concentration and low energy (Benkhedda et al., 2000).

The most common reason for using expanded bed adsorber in this study is to obtain vigorous agitation of the solids in contact with the fluid, leading to excellent contact of the solid and the fluid and the solid and the wall. This means that nearly uniform concentrations can be obtained (McCabe et al., 2001).

Both batch and column-type carbon adsorption operations were employed in this investigation. The batch test was conducted to evaluate the adsorption rate and capacity.

The column operations were conducted in two different manners, fixed-bed and expanded. A comparison of the treatment efficiency and performance characteristics between the two different modes of carbon adsorption was made.

EXPERIMENTAL PROCEDURE

The adsorbent used in this study was a granular activated carbon. The characteristics of this carbon are reported in Table 1.

ADSORPTION ISOTHERM MEASUREMENTS

A stock solution of acetic acid (0.2 N) was prepared and diluted to the required initial concentrations (C_0 range: 600-6000 ppm). Equilibrium studies were made at room temperatures by employing the batch adsorption technique. Weighed amounts of activated carbon (12-28 gm/l) were taken in conical flasks containing 50 ml of aqueous solutions of acetic acid of known concentration. The flasks were stoppered and attached to a mechanical shaker for a specified period of contact time (range: 5-45 min). After equilibrium, the aqueous phase was filtered and titrated with sodium hydroxide (0.25 N) to determine the equilibrium concentration of the acetic acid. The indicator used was phenolphthalein (0.5%).

COLUMN STUDIES

The schematic representation of experimental set-up is shown in Fig. (1); it consists of a glass column of 2.45 cm internal diameter and a height of 75 cm. The column was packed with activated carbon (0.5) mm in diameter, to a height of 8 cm. The activated carbon particles are supported by a wire mesh fitted at the column bottom. The liquid from the storage tank was pumped through a rotameter connected on the line.



The flow rate of wastewater was (50) l/hr. the effluents from the bed were analyzed for acetic acid content by titration with NaOH at chosen intervals of time until breakthrough occurs. The minimum fluidized velocity for particles (V_{mf}) had been estimated to be (5.17×10^{-4} m/s) using the following equation (Ramaswamy et al, 2008):

$$V_{mf} = \frac{\mu_l}{d_p \rho_l} \left[\sqrt{(33.7)^2 + 0.0408 \frac{d_p^3 \rho_l (\rho_p - \rho_l) g}{\mu_l^2}} - 33.7 \right] \quad (1)$$

Another set of experiments were made using closed circuit expanded bed in which liquid was continuously recycled through the system as shown in Fig. (2).

RESULTS AND DISCUSSION

Adsorption Isotherms

Among the many models of isotherms of adsorption found in the literature involving aqueous solutions, the experimental data of equilibrium of this study were correlated with Freundlich and Langmuir models described below in Eqs. (2) and (3) respectively, (Adamson, 1960; Alessendra, 2005)

Freundlich isotherm:

$$\log(q_e) = \log k + n \log C_e \quad (2)$$

Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{C_e}{a} \quad (3)$$

Where, k and n are the constants of Freundlich related to the capacity and intensity of the adsorption; q_e is the amount of acid adsorbed per unit weight of the adsorbent, C_e is the equilibrium concentration of acid (ppm), a and b are the constants of the Langmuir model that represents the capacity and the energy of adsorption.

The values of k and n were obtained from the linear correlation of $\log q_e$ against $\log C_e$ and the Langmuir constants were also determined from the linear correlation of C_e/q_e

against C_e . The isotherm parameters along with the correlation coefficients are represented in Table 2. The observed linear relationships of Figs. (3) and (4) confirm that these two adsorption isotherms are applicable. The applicability of Langmuir isotherm model indicates the formation of monolayer coverage of adsorbate on outer surface of the adsorbent (Ghosh and Philip, 2005). Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor R_L , which is defined by (Weber and Chakravorti, 1974):

$$R_L = \frac{1}{(1 + b C_0)} \quad (4)$$

The separation factor R_L indicates the isotherm's shape and the nature of the adsorption process as unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$). In the present study the value of R_L being 0.381 indicating that the sorption process is favorable.

EFFECT OF CONTACT TIME

In the adsorption systems contact time plays an important role. In order to study the kinetics and dynamics of adsorption of acetic acid by activated carbon, the adsorption experiments were conducted and the extent of removal of acetic acid was obtained by varying the contact time (range 5-45 min) at fixed concentration of acetic acid (600 ppm) with a fixed dose of adsorbent (20 g/l).

Fig. (5) indicates that the removal of acetic acid by activated carbon is rapid at the initial period and becomes slow, stagnant and then decreases with the increase in contact time. The relative increase in the extent of removal of acetic acid is very low after 30 min of contact time, which is fixed as the optimum contact time. This indicates that the rate of removal of acid is higher in initial stages, due to the availability of adequate surface area of the adsorbent, and with increase in contact time, due to decrease of surface area availability, the adsorption decreases. The decrease in the extent of removal of acid after 30 min of contact time maybe due to the desorption process. Similar

results have been reported for the removal of acids by Ramu et al, 1992.

EFFECT OF DOSE OF ADSORBENT

The percentage removal of acetic acid by adsorption was obtained with various doses of adsorbent (range: 12-28 g/l) with initial concentration of acetic acid (600 ppm) and contact time (30 min).

Fig. (6) shows that the amount removal of acid increases exponentially with increase in dose of adsorbent. This maybe due to the increase in availability of active sites due to the increase in the effective surface area resulting from increase in dose of adsorbent especially at higher adsorbent doses. Similar observation has been reported by McKay et al, 1983; Annadural and Krishnan, 1997 and Kannan and Xavier, 2001.

OPEN CIRCUIT EXPANDED BED BREAK-THROUGH CURVE

Successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve for the effluent. The maximum adsorption capacity of an adsorbent is also needed in design.

There are many factors that affect the adsorption capacity in the column such as flow rate, bed depth and influent concentration.

Effect of Inlet Concentration

The effect of inlet adsorbate concentration on effluent concentration is shown in Fig. (7).

The inlet adsorbate concentrations considered are 6000, 3000 and 1500 ppm. During these studies other parameters such as bed height and flow rate are kept constant. For higher feed concentration, steeper breakthrough curves are found, because of the lower mass-transfer flux from the bulk solution to the particle surface due to the weaker driving force. In addition, at high concentration, the isotherm gradient is

lower, yielding a higher driving force along the pores. Thus the equilibrium is attained faster for values of higher adsorbate concentration (Babu and Gupta, 2004).

Volesky and Prasetyo (1994) reported that the driving force for adsorption is the concentration difference between solute on the sorbent and the solute in the solution. So at high concentrations the activated carbon becomes more quickly saturated, thereby decreasing the breakthrough time.

EFFECT OF FLOW RATE

The results for different solution flow rates are plotted for a bed height of 8 cm and an inlet adsorbate concentration of 3000 ppm in Fig. (8). The flow rates considered are 50, 75 and 100 l/hr. Fig. (8) reveals that as the flow rate increases, the breakthrough curve becomes steeper. This is because of the residence time of the solute in the column, which is not long enough for adsorption equilibrium to be reached at high flow rates. So at high flow rate the adsorbate solution leaves the column before equilibrium occurs (Babu and Gupta, 2004).

EFFECT OF BED HEIGHT

The effect of bed height on the effluent adsorbate concentration is presented for flow rate 50 l/hr and inlet adsorbate concentration of 3000 ppm in Fig. (9). The bed heights considered are 8 and 12 cm. It is observed that at smaller bed height the effluent adsorbate concentration ratio increases more rapidly than for a higher bed height. Furthermore, the bed is saturated in less time for smaller bed heights. Smaller bed height corresponds to less amount of adsorbent, so the adsorbent gets saturated early (Huang and Hardie, 1971).

COMPARISON BETWEEN EXPANDED BED AND FIXED BED ADSORBERS

In order to compare the relative treatment between the expanded bed and fixed bed



adsorbers, the solution was forced downward through the fixed bed with a controllable flow rate (50 l/hr) and initial concentration of 3000 ppm.

In a packed bed, the adsorbent particles are stationary and liquid flow through the bed approximates to plug flow. In contrast, due to the mixing of the adsorbent, a fluidized bed would be expected to show an inferior adsorption performance compared with the packed bed. The conclusion is already drawn from Fig. (10), which is in agreement with the work of Shahavi et al, (2008).

In addition, in up flow adsorption column, the contact between adsorbent and adsorbate are better compared to down flow mode-Up flow mode was selected to minimize the channeling effects inside the column.

CLOSED CIRCUIT EXPANDED BED

Effect of Inlet Concentration

Three initial concentrations of acetic acid in water were tested: 6000, 3000 and 1500 ppm, for a constant flow rate of 50 l/hr.

The closed circuit fluidized bed was adequately modeled as stirred batch adsorption equipment. The intense pump recycling rate produces similar mixing effects as those of a mechanical device, which supports this strategy. It is well established that adsorption rates are generally fast higher than other rates (e.g., diffusion of mass and heat) in such systems. Physical adsorption, the topic of this work, is particularly very fast. On this basis it will be assumed that at any time during adsorption, a condition close to equilibrium is established in the vicinity of the adsorbent surface (Corrêa et al., 2007)

Fig. 11 shows the time profile of acetic acid concentration in the circulating liquid of the closed circuit fluidized bed adsorption system developed in this work. Acetic acid concentration didn't change after around 900 s (15 min), suggesting that a condition near adsorption equilibrium was achieved in the system.

CONCLUSIONS

The following conclusions are drawn from the above-discussed results:

For batch studies:

- The adsorption data fit well with both Freundlich and Langmuir isotherms.
- The removal of acetic acid by activated carbon is rapid at the initial period and becomes slow, stagnant and then decreases with the increase in contact time.
- The amount removal of acid increases exponentially with increase in dose of adsorbent.

For open circuit expanded bed:

- For higher feed concentration, steeper breakthrough curves are obtained and break point time is achieved sooner.
- As the flow rate increased, the breakthrough curve becomes steeper. The break point time is obtained earlier and effluent adsorbate concentration ratio increases more rapidly.
- For smaller bed height, the effluent adsorbate concentration ratio increases more rapidly than for a higher bed height.
- A fluidized bed would be expected to show better adsorption performance compared with the packed bed.

In closed circuit expanded bed, a condition near adsorption equilibrium was achieved in the system.

NOMENCLATURE

a Monolayer (maximum) adsorption capacity (mg/ g)

b Langmuir constant related to energy of adsorption (l/mg)

C The concentration of acid at time t (ppm)

C_0 The concentration of acid at time zero (ppm)

C_e Equilibrium concentration of acid (ppm)

d_p Particle diameter (m)

g Acceleration due to gravity (m/s^2)
 k Adsorption capacity ($(g/l)^{1/n}$)
 L Column length (cm)
 n Order/intensity of adsorption (-)
 Q Flow rate (l/hr)
 q_e Amount of acid adsorbed per unit
weight of adsorbent (mg/g)
 R_t Separation factor (-)
 t Time (s)
 V_{mf} Particle minimum fluidization velocity
(m/s)

Greek letters

ρ_l Density of fluid (kg/m^3)
 ρ_p Density of particle (kg/m^3)
 μ_l Dynamic viscosity of fluid ($kg/m.s$)

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Table 1: Major characteristics of activated carbon.

Density, kg/m ³	1350
BET surface area, m ² /g	1100
Particle porosity	0.5
Bed porosity	0.41
particle diameter (d_p), mm	0.5

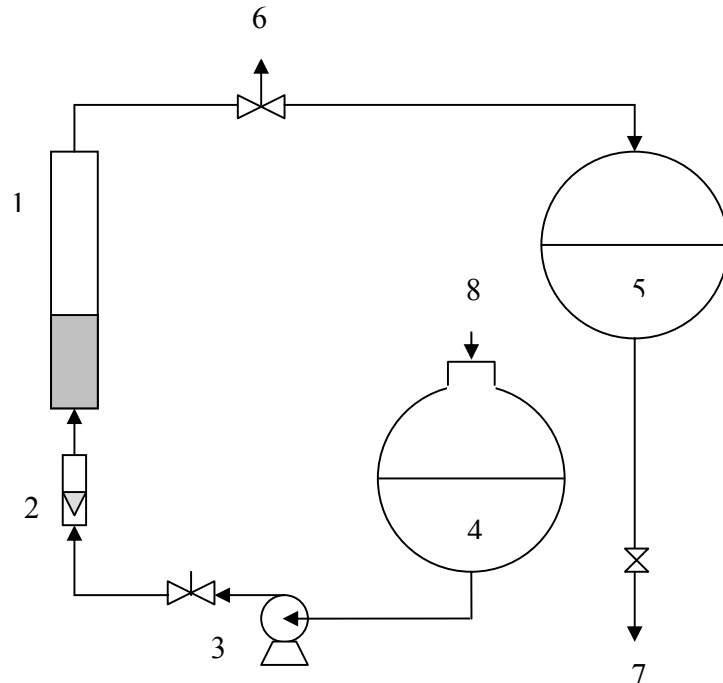


Fig.1: Schematic diagram of opened circuit expanded bed (1.adsorber, 2 flow meter, 3.pump, 4.feed tank, 5.effluent tank, 6.samplng point, 7.to drain, 8.feed).

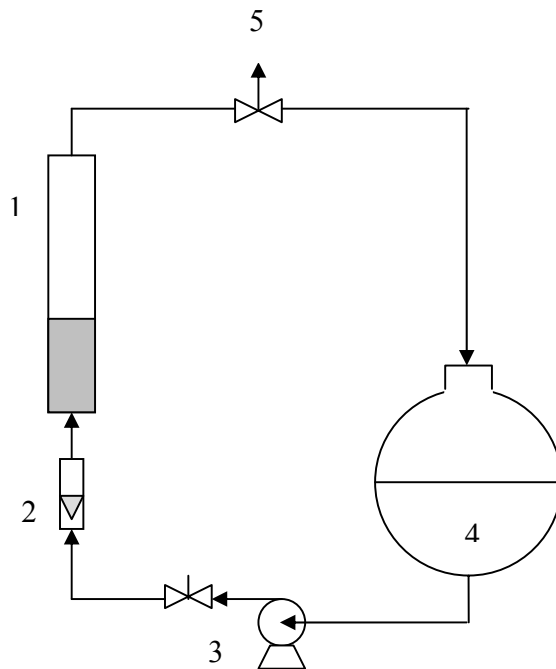


Fig.2: Schematic diagram of closed circuit expanded bed (1.adsorber, 2 flow meter, 3.pump, 4.feed tank, 5.samplng point).

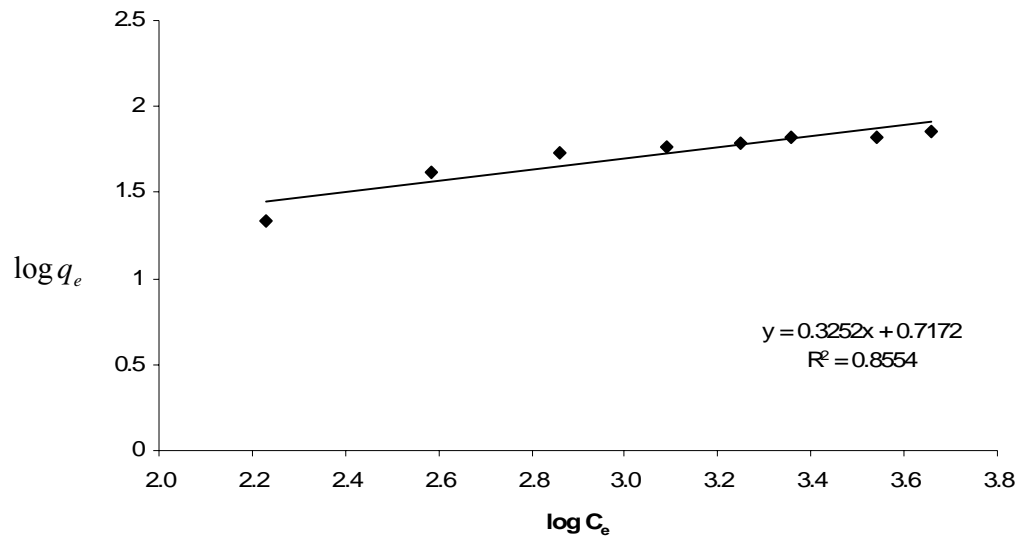


Fig. 3: Linearized Freundlich isotherm for acetic acid adsorption by activated carbon.

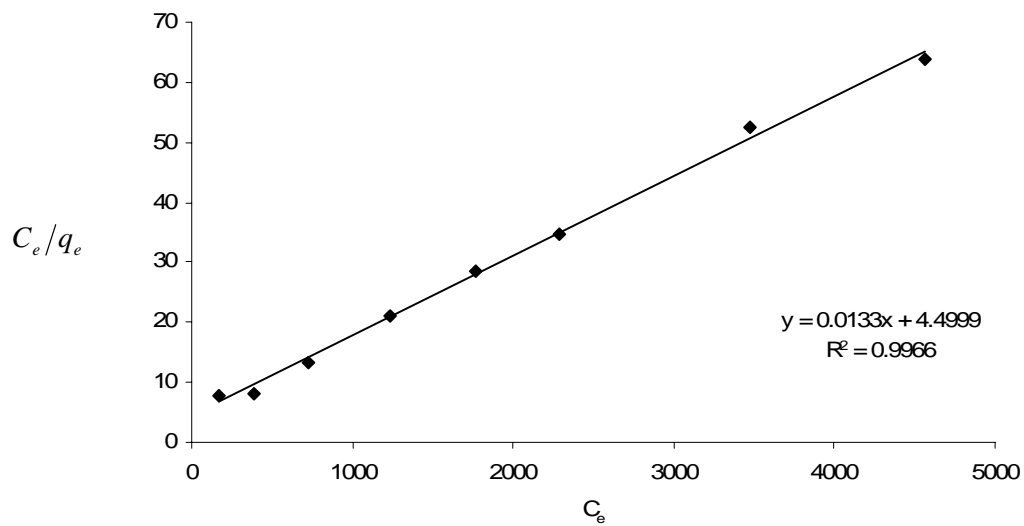


Fig.4: Linearized Langmuir isotherm for acetic acid adsorption by activated carbon.

Table 2: Freundlich and Langmuir parameters of adsorption isotherms for the removal of acetic acid by activated carbon.

Freundlich isotherm			Langmuir isotherm		
n (-)	k (g/l) ^{1/n}	Correlation coeff. (R ²)	a (mg/g)	b (g/l)	Correlation coeff. (R ²)
0.325	5.212	0.8554	75.19	2.96×10 ⁻³	0.9966

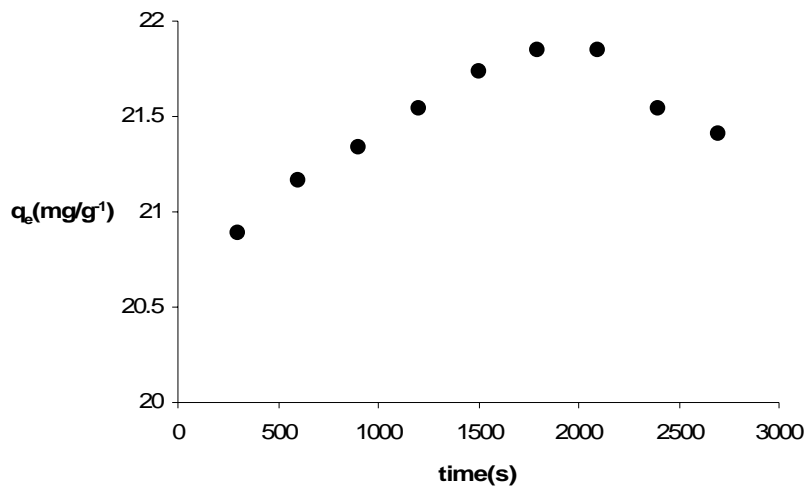


Fig.5: Effect of contact time on the amount of acetic acid adsorbed on activated carbon.

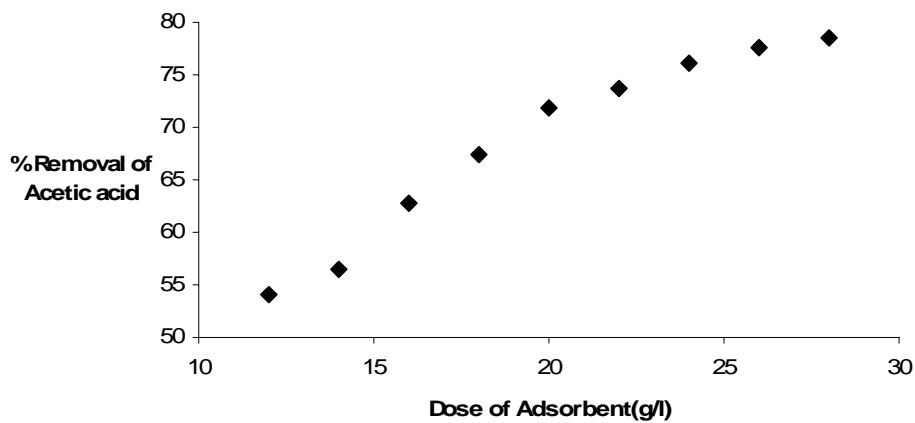


Fig. 6: Effect of dose of adsorbent on the percentage removal of acetic acid.

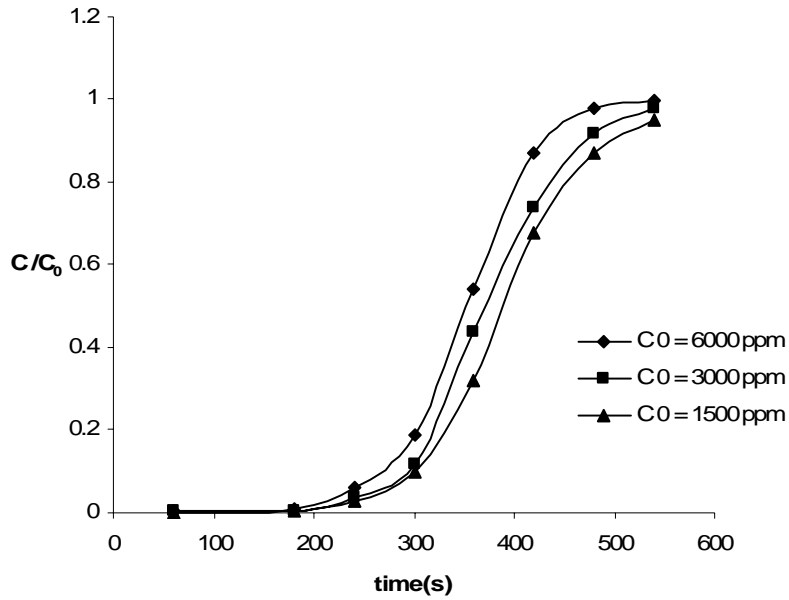


Figure 7: Effect of inlet adsorbate concentration on breakthrough curve.

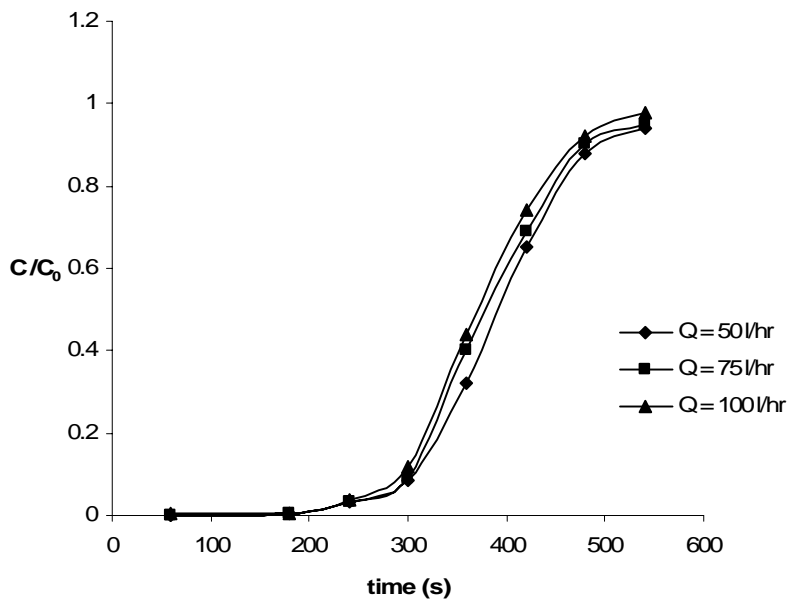


Figure 8: Effect of flow rate on breakthrough curve.

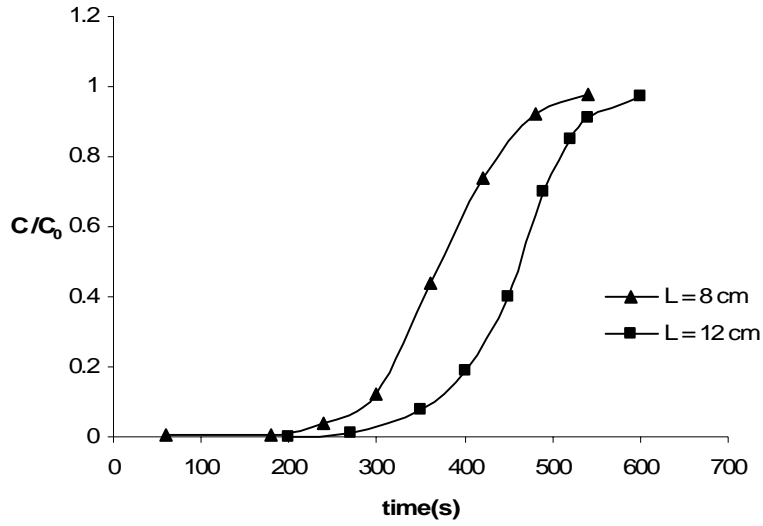


Fig.9: Effect of bed height on the breakthrough curve.

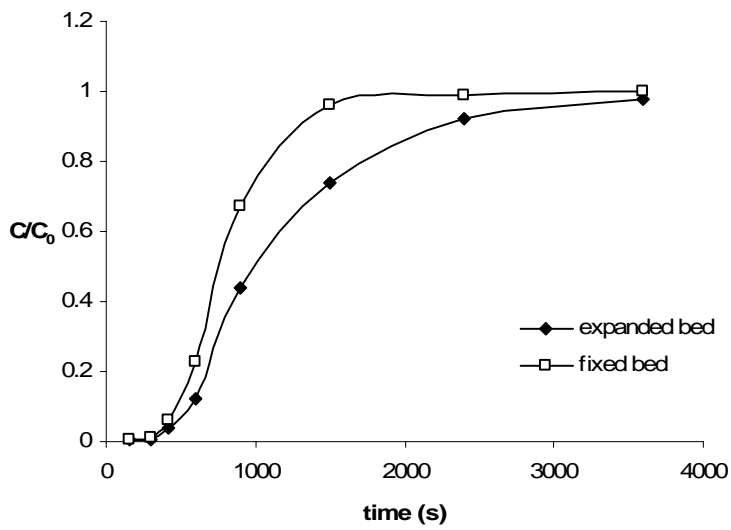


Fig.10: Comparison between fixed-bed and expanded-bed adsorbers.

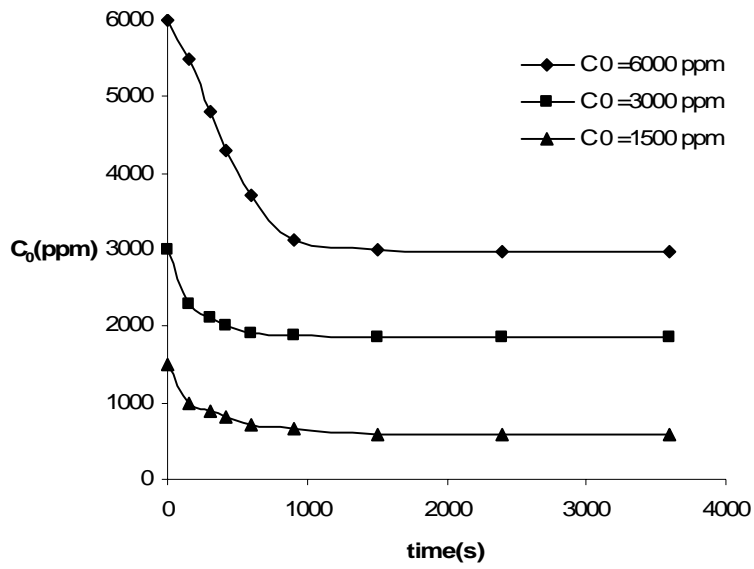


Fig.11: Acetic acid concentration in the closed circuit fluidized bed experiments.