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Research Article

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Treatment of fenvalerate manufacturing process wastewaters using activated coconut shell carbon

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ABSTRACT

Wastewaters obtained from fenvalerate manufacturing process were treated for its safe disposal using activated coconut shell carbon (acc) as adsorbent. In this work, the removal efficiency of organic matter in terms of chemical oxygen demand (COD) utilizing acc has been investigated. Various parameters which can influence the adsorption like adsorbent dosage, contact time of solution with adsorbent and pH were optimized. Isotherms for adsorption were developed and the equilibrium data was fitted in to linearized equation of Langmiur and Freundlich isotherms models.

Key words: Activated coconut shell carbon (acc), wastewater from Fenvalerate pesticide manufacture, Langmuir, Freundlich isotherms

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INTRODUCTION

Fenvalerate is a pyrethroid pesticide and is used in the control of a wide range of insects and crops like vegetables, cereals, maize etc. Indiscriminate use of pesticides in agriculture is one of the important factors contributing to environmental pollution. Large quantities of wastewaters are being discharged by pesticide manufacturing industries. These wastewaters usually contain undesirable organic matter, which pollute the aquatic system for which appropriate treatment is desirable before discharge into inland surface waters. A number of methods were reported in literature for the treatment of wastewaters from pesticide industries. Some of the important methods are UV irradiation [1], ozonation [2], alkaline hydrolysis [3], coagulation [4], membrane filtration [5], and oxidation processes [6]. These methods are expensive and treatment procedures are generally long. Adsorption has developed into a well-established technique to remove pollutants as it is having the potential for regeneration, recovery and recycling of the adsorbent materials. Various materials [7-13] were used as adsorbents for the treatment of wastewaters. Coconut shells which occur abundantly in nature are utilized as activated carbon adsorbents [14-20] after processing.

Adsorption behavior of any adsorbent is generally inferred from both adsorption kinetics and equilibrium isotherms. A thorough literature survey revealed that no literature reports are available on the kinetic and equilibrium adsorption studies of the constituents of wastewaters from fenvalerate manufacturing industry using coconut shell activated carbon.

The aim of the present study is to investigate the adsorption efficiency of coconut shell based activated carbon (acc) in the treatment of wastewaters obtained from fenvalerate manufacturing process under different experimental conditions. Further, detailed kinetic and equilibrium studies are also carried out and the data is fitted into linear forms of Freundlich and Langmuir adsorption isotherm models. The applicability of different kinetic models are studied and discussed in the present communication.

EXPERIMENTAL SECTION

Materials

All the reagents and chemicals used were of analytical reagent grade. pH and COD measurements were carried out using a pH meter (LI-120, ELICO Ltd, Hyderabad, India) and COD meter (HACH DR/2010 model from Colorado, USA) respectively.

Sample collection

Composite wastewaters from fenvalerate manufacturing process were collected from the pilot plants of Indian Institute of Chemical Technology (IICT) Hyderabad. The wastewaters were characterized according to standard analytical procedures [21]. Activated coconut shell carbon (acc) was prepared in the laboratory by the following procedure [22]. The surface area of the activated carbon was determined by employing the BET technique.

Preparation and activation of adsorbent

Coconut shell carbon

Coconut shell pieces were reduced to smaller size and mixed with zinc chloride in the ratio of 1:4. This was heated at 250^o C and then increased to 400^o C. The shell charring was carried out at 600^oC. After removing all the volatile substances, it was heated to 750 to 850^o C in the presence of steam. Size reduction took place and partial carbon removal occurred. The activated charcoal granules thus obtained were ground to powder of 200 mesh. The activated coconut shell powder was used for the treatment of the waste waters under study. The characteristics of the acc powder is given in table 2.

Adsorption experiments

Removal of organic matter (COD) from the wastewaters with varying amounts of adsorbent (1-5g/100ml) was studied keeping pH (11.83) and agitation time (1h) constant. The solutions were agitated for 1 h using a magnetic stirrer and filtered through Whatman No. 40 filter paper. The filtrates were analysed for residual COD in the wastewater. Studies on the effect of pH on the removal of COD were also carried out by keeping the quantity of the adsorbent (5g) and agitation time (1h) constant. The pH of the wastewater was varied from 11.83 to 3. In a similar manner, the effect of agitation time was also carried out by keeping the other two parameters viz; adsorbent dosage (5g) and pH (11.0) constant. The solutions were filtered at each stage of the experiment and analysed for equilibrium COD load. The extent of decolourization was calculated on the filtered solutions by APHA platinum cobalt method.

Wastewater samples (20, 40, 60 and 80 ml) were diluted to 100 ml with distilled water in polyethylene bottles of 125 ml capacity and another sample of 100 ml as such was taken, 5g of acc was added to each of the bottles. The bottles were kept on a mechanical shaker at 150 rpm for 24 h. After the equilibrium period the samples were filtered and analysed for equilibrium COD load. Adsorption isotherms were drawn by using the data obtained. Kinetic studies were carried out by measuring the COD of the wastewaters at regular intervals of 15 min upto 150 min of contact period under optimal conditions of the experiment.

RESULTS AND DISCUSSION

The evaluated physico-chemical properties of the wastewaters (**Table 1**) were found to be above standard disposable limits [23]. Hence, it is desirable to treat the wastewaters before they are discharged into public sewage systems. The acc prepared in the laboratory was characterized for various parameters and the results are given in **Table 2**. The surface area of the activated carbon was found to be 800 m^2/g.

Adsorption dynamics

Effect of adsorbent concentration

The effect of adsorbent concentration on the removal of organic matter was studied at different adsorbent doses (1-5g/100ml). **Fig. 1** shows the removal efficiency of activated carbon on COD. It could be seen from the figure that an increase in carbon dose increased the sorption. This may be due to the fact that adsorption of organic matter is a function of carbon surface area and availability of more adsorption sites [24]. The effect of adsorbent concentration on COD removal was expressed as the removal efficiency of the adsorbent, which can be represented,

$$E(\%) = \frac{[C_i - C_f]}{C_i} \times 100 \qquad (1)$$

Where C_i and C_f are the initial and equilibrium load of COD (mg/L) respectively. The removal efficiency of acc in the present study at 5g/100 ml was found to be 94.75%.

Effect of pH

The pH of the aqueous system is an important operational parameter in the adsorption process. The influence of hydrogen ion concentration was examined on COD removal efficiency. The pH was varied from 3-11 keeping other operational parameters (adsorbent dosage, agitation time) constant. COD measurements were taken at each pH value. The observations are graphically represented in **Fig. 2**. The increase in pH of the solution from 3-11 caused linear increase in COD removal. There was a marginal increase in the removal of COD upto pH 7.0 and afterwards the variation was observed to be significant. A maximum removal of COD by the activated carbon was observed at p^H 11.0.

Effect of agitation time

Another operational parameter which plays an important role in adsorption process is agitation time. The effect of agitation time on the removal of COD was also studied by varying the time of agitation from 60-150 min. The equilibrium COD was measured at every 15min of time interval. **Fig. 3** shows the COD removal efficiency as a function of agitation time. It could be seen from the figure that increase in agitation time increased the removal efficiency until equilibrium was attained. Equilibrium adsorption was established within 150 min with a maximum of 98.90% COD removal efficiency.

Under optimized conditions (carbon dosage 5g/100ml, pH 11.0 and equilibrium time 150 min) the prepared coconut shell activated carbon (acc) showed 98.90% removal efficiency for organic matter (as COD) and complete decolourization of wastewater under study.

Adsorption Isotherms

Langmuir model

The data was fitted to Langmuir adsorption isotherm model. The model describes the maximum adsorption corresponding to a saturated monolayer of solute molecules on the adsorbent surface, which is represented [25] by the following equation,

$$C_e/(x/m) = (1/ab) + (1/b)\, C_e \qquad (2)$$

Where $C_e/(x/m)$ is the COD concentration in wastewater at equilibrium (mg/L) to the COD adsorbed per unit mass of the adsorbent (mg/g) and a & b are the constants from which intensity and sorption capacity are evaluated.

The linear plot of specific sorption $[C_e/(x/m)]$ against the equilibrium concentration (C_e) showed that the adsorption followed the Langmuir model (**Fig. 4**). The linear correlation coefficient and the Langmuir constants a & b are given in **Table 3**.

Freundlich model

The Freundlich adsorption isotherm is based on the relationship between the amount of organic matter adsorbed per unit mass of adsorbent and concentration of the organic matter in solution at equilibrium. This can be represented [25] as,

$$\log x/m = \log K + (1/n) \log Ce \qquad (3)$$

Where, x/m is the amount of COD adsorbed per unit mass of the adsorbent, Ce is the equilibrium COD concentration in wastewaters and 1/n & K are constants. The data was obtained in the present study was fitted into the Freundlich adsorption model.

The logarithmic plot of the Freundlich expression (eq.3) for the amount of COD adsorbed per unit mass of adsorbent (x/m) and the COD load at equilibrium (Ce) is given in **Fig. 5**. From the slope and intercept of the plot the values of 1/n and K were calculated respectively. The Freundlich constants and linear correlation coefficients are presented in **Table 3**. The values of 1/n should be less than 1 for favorable sorption [25]. It was observed from the data (**Table 3)** that the Freundlich isotherm provided a good correlation with 1/n value less than 1 and high correlation coefficient value of 0.9942.

Sorption Kinetics

The sorption kinetics describes the rate of adsorption of adsorbate on the adsorbent and also the time of equilibrium. Many kinetic models were suggested [26-30] in recent years to study the mechanism of adsorption process. The kinetic data evaluated was fitted into three different kinetic models viz, pseudo-first-order, pseudo- second-order and intraparticle diffusion. The pseudo-first and second-order kinetic models assume that sorption is a pseudo chemical reaction and the sorption rate could be determined by the following reaction rate equations. The pseudo-first-order equation [31] is expressed as,

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

The integrated form of the above Eq. (4) may be written as,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

Where q_e and q_t are the amounts of COD adsorbed (mg/g) at equilibrium and time t (min) respectively, and k_1 is the rate constant (min^{-1}).

A graph was drawn using the data obtained in the present study by taking log (q_e-q_t) on x-axis and‘t’ on y-axis. The graph is shown in **Fig. 6**. The rate constant k_1 was calculated from the slope of this plot. The correlation coefficient (R^2) was also calculated and was found to be 0.9398. The data is presented in **Table 4**. It could be observed from the data that the sorption process did not follow first-order kinetics.

The pseudo-second-order kinetic model of Ho and McKay [32] is given by

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

The integrated form of the Eq. (6) is,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{7}$$

Where $q_{e,}$ q_t, are the amounts of COD adsorbed (mg/g) at equilibrium and time t (min) respectively, k_2 is the rate constant (mg/g / min).

Plot of (t/q_t) versus t for the pseudo-second-order is shown in **Fig. 7.** Both rate constant (k_2) and correlation coefficient (R^2) were calculated from the graph. The data is presented in **Table 4.** It could be observed from the table that the adsorption system followed pseudo-second-order kinetic model with a correlation coefficient (R^2) of 0.9998 and found to be the best-fit kinetic model for the adsorption of organic matter on acc under investigation.

The applicability of intraparticle diffusion model was also studied. The mathematical expression [33] was given by,

$$q_t \quad = \quad k_{\text{int}}\, t^{1/2} + C \tag{8}$$

Where q_t is the amount of COD adsorbed at time t, C is the intercept and K_{int} is the intraparticle diffusion rate constant (mg / g $min^{-½}$). A plot was drawn between q_t and $t^{1/2}$ to determine whether intraparticle diffusion was rate-determining (**Fig. 8**). It could be observed from the graph that the intraparticle diffusion was not the rate-controlling step, as the linear portion did not pass through the origin. The value of the correlation coefficient was also low (0.9729). The same was also confirmed from the correlation data of log% adsorption and log‘t’.

Table 1 : Physico-Chemical Characteristics of Process Wastewaters

pH	11.83
Colour (Pt. Co. Units)	10
Conductivity (mhos/cm)	0.56
Total dissolved solids (mg/L)	1,80,520
Total suspended solids (mg/L)	950
Chemical Oxygen Demand (mg/L)	41,000
Chlorides (%/V)	2.1
Nitrates (%/V)	0.5
Sulphates (%/V)	1.2

Table 2 : Characteristics of activated carbon

Surface area (m^2/g)	800
Methylene blue value (mg/L)	200
pH	8
Ash (%/wt)	12
Base	coconut shell

Table 3 : Langmuir and Freundlich Isotherm constants

Langmuir Adsorption			Freundlich Adsorption		
a	**b**	**R^2**	**1/n**	**K**	**R^2**
2.5 x 10-4	6.67 x 103	0.9979	0.482	0.55 x 10	0.9942

Table 4: Rate constants for the removal of COD on acc

S. No.	**Kinetic Model**	**Rate constant**	**R2**
1	Pseudo-first-order kinetic model	1.70 x 10-2 (min-1)	0.9398
2	Pseudo-second-order kinetic model	4.40 x 10-5 (g / mg.min)	0.9998
3	Intraparticle diffusion kinetic model	0.46 x 102 (mg / (g.min1/2)	0.9729

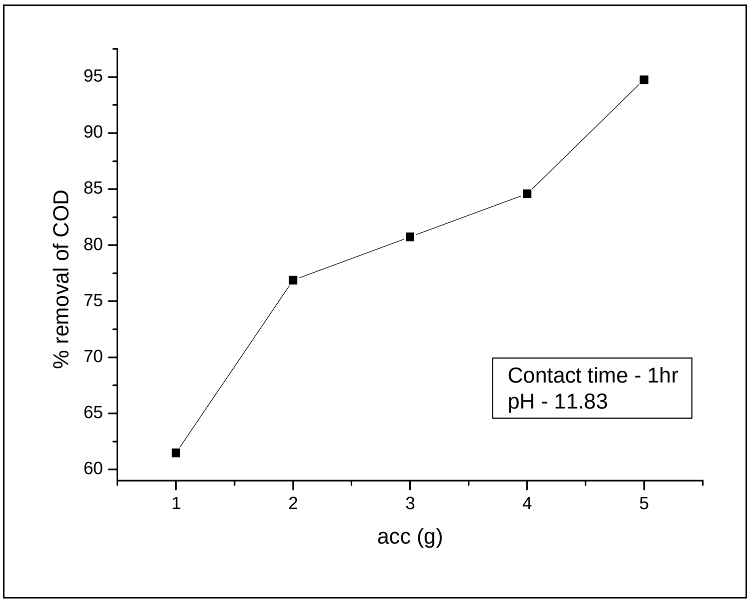

Fig. 1. Effect of carbon dosage on the reduction of COD

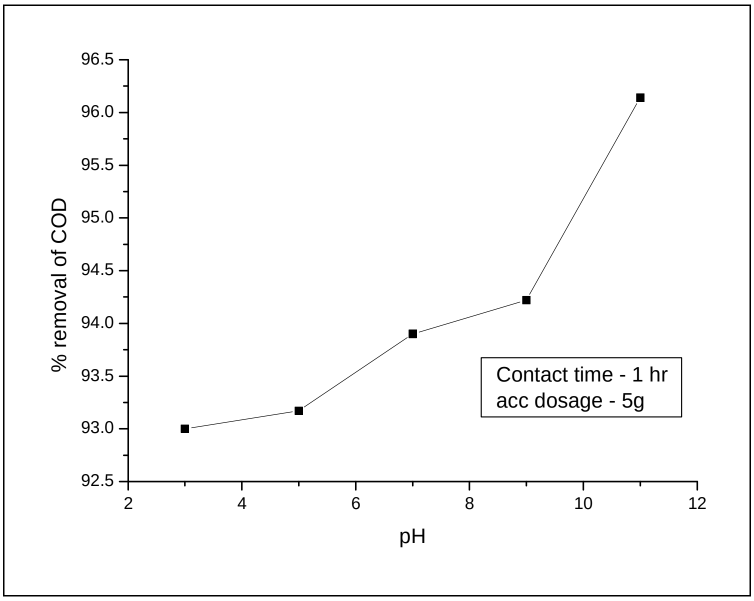

Fig. 2. Effect of pH on the reduction of COD

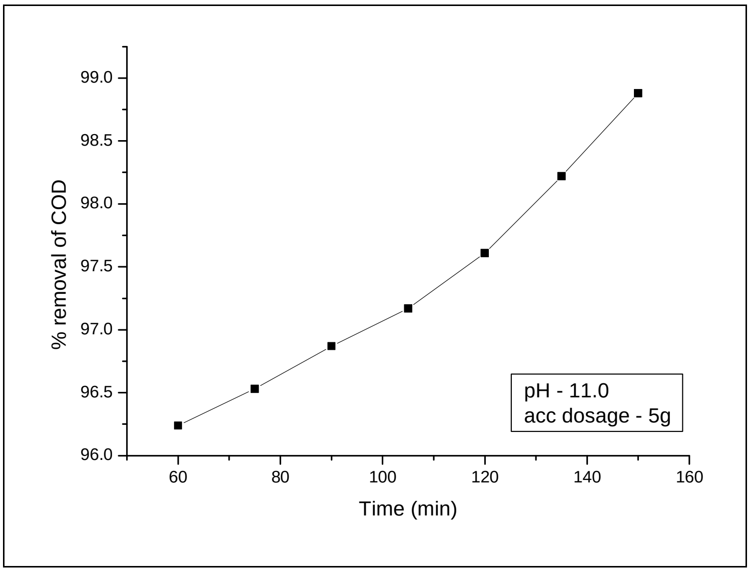

Fig.3. Effect of contact time on the reduction of COD

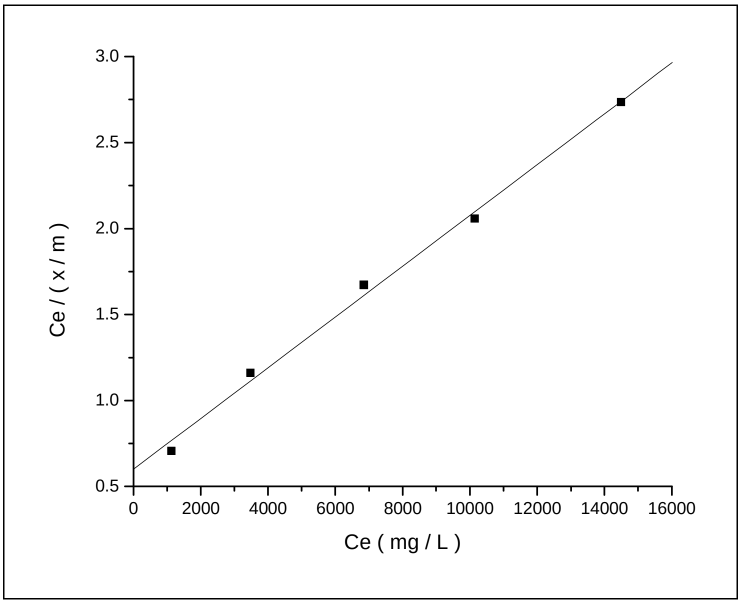

Fig. 4. Langmuir isotherm for fenvalerate process wastewater

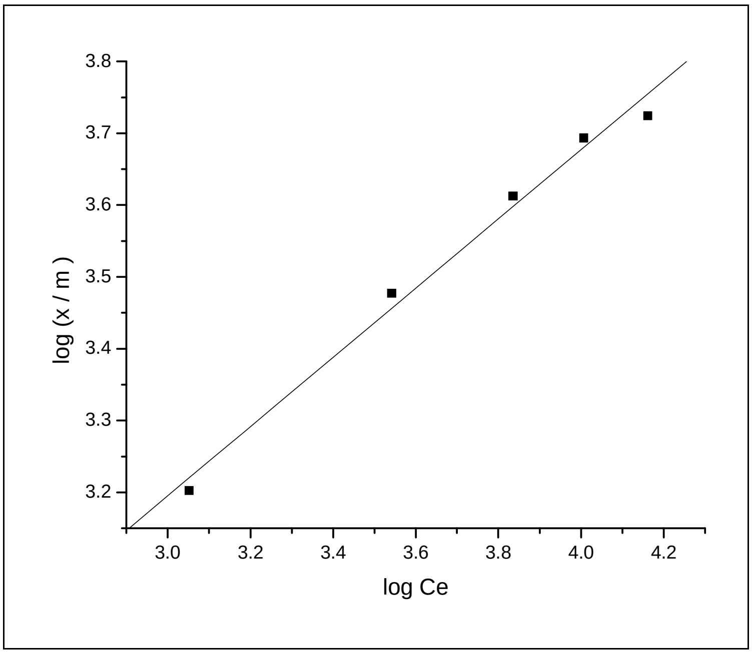

Fig. 5. Freundlich isotherm for fenvalerate process wastewater

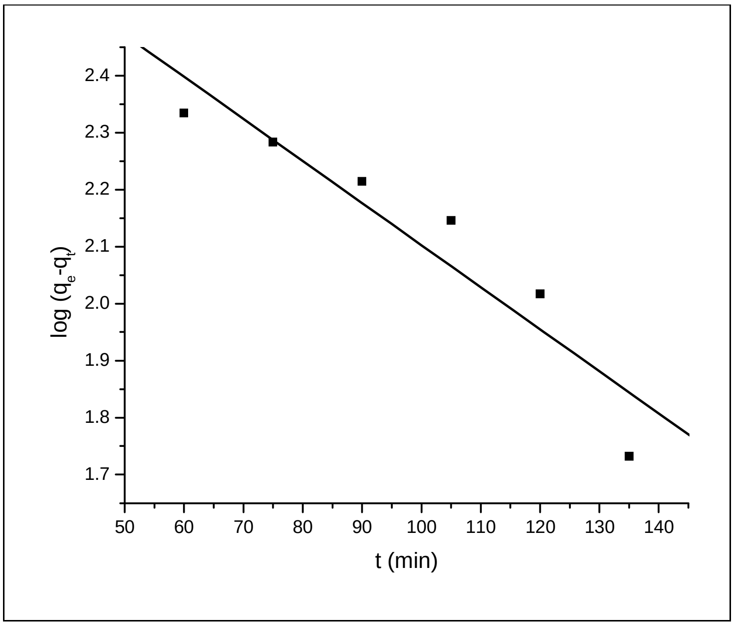

Fig. 6. Pseudo first-order adsorption kinetics of fenvalerate process wastewater

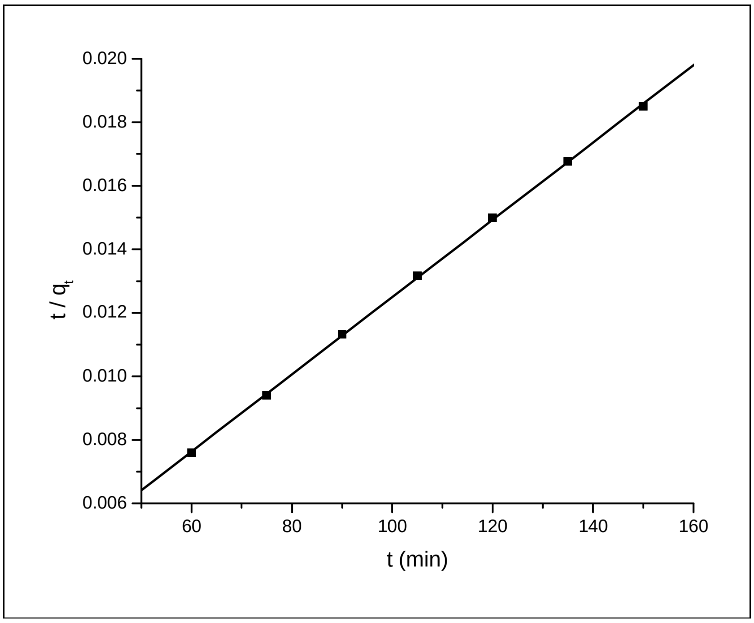

Fig. 7. Pseudo second-order adsorption kinetics of fenvalerate process wastewater

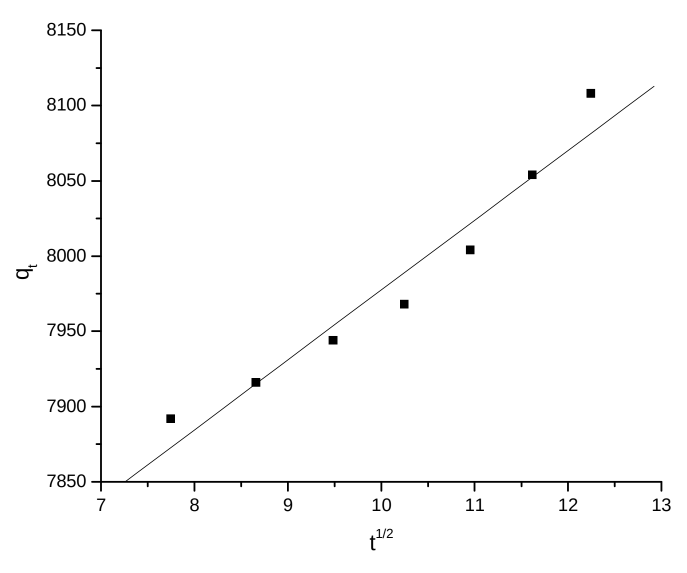

Fig. 8. Intraparticle diffusion adsorption kinetics of fenvalerate process wastewater

CONCLUSION

The physicochemical parameters of wastewaters from fenvalerate manufacturing process were determined. Treatment of the wastewater was carried out using acc as adsorbent. Maximum COD reduction of 98.90% was obtained for fenvalerate process wastewaters under optimal conditions of 5g of acc per 100ml of wastewater at pH 11.0 and at a contact time of 150 min. complete color removal was achieved under these conditions. Equilibrium studies also revealed that acc could be used as a potential adsorbent for the removal of organic matter from fenvalerate process wastewaters. The experimental data obtained was well fitted into Langmuir and Freundlich adsorption isotherm models. It was observed that the experimental data was well fitted in Langmuir and Freundlich adsorption models. Studies on the applicability of kinetic models indicated that pseudo second-order kinetic model was the best fit and was the rate-determining step among the three models studied.

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