

Equilibrium and Kinetic Study of Benzene Removal from Aqueous Solution by Granular Dead Activated Sludge

Mudhaffer S. Al-Zuhairy¹, Ali H. Al-Aboodi ², Risalah A. Mohammed³

¹Professor, Chancellor of Southern Technical University, STU

²Assistant Professor, Civil Engineering Department, College of Engineering/ Basrah

³ Ph. D. student, Environmental Engineering Department /Basrah Engineering Technical College

Corresponding email: resala.75@gmail.com

Abstract

Benzene is one of the biggest challenges of groundwater pollution due to its toxicity, motility in the environment, and solubility in groundwater. Granular dead activated sludge (GDAS) was investigated as low-cost, and locally available as a sorbent material for removing benzene from aqueous solution. The experimental results show that the removal efficiency has improved, with increasing both of GDAS amount and the time of contact and decreasing the initial concentration of the contaminant. Batch investigations demonstrated that the GDAS efficiency removal for benzene is ranged from 55%-76% while, the maximum uptake (q_m) is 14.835 mg/g, at sorbent dose 5 g/100 mL and contact time 5 hours. Langmuir and Freundlich isotherm model gives a good fitting for the sorption process with high determination coefficient greater than 0.998. The parameter of this model shows favorable sorption for removing benzene by GDAS. Intra-particle diffusion model data fitting shows two separate regions; the first severe portion attributed to the immediate sorption step and another portion is the intraparticle diffusion rate is dominated. The parameters of the model illustrate the external mass transport mechanisms must be considered with intra-particle diffusion.

Keyword: Benzene, GDAS, isotherm model, kinetics model, mechanism of removal, sorption.

بواسطة الحمأة المنشطة الحبيبية الميتة دراسة توازنه وحركية لإزالة البنزين من المحلول المائي

مظفر صادق الزهيري¹، علي حسن دهيم²، رسالة عبدالاله محمد³

¹رئيس الجامعة التقنية الجنوبية،²كلية الهندسة/جامعة بصرة،³الكلية التقنية الهندسية/الجامعة التقنية الجنوبية

يعتبر البنزين أحد أكبر تحديات ملوث المياه الجوفية بسبب سميته، سهولة حركته في البيئة، وقابليته للذوبان في المياه الجوفية. في هذه الدراسة تم فحص الحمأة المنشطة الحبيبية الميتة (GDAS) على أنها مادة منخفضة التكلفة ومتوفرة محلياً كمادة مازة لإزالة البنزين من محلول مائي. وتبينت النتائج التجريبية أن كفاءة الإزالة قد تحسنت، مع زيادة كل من كمية GDAS ووقت التماس وخفض التركيز الأولي للملوثات. وأظهرت نتائج تجارب الدفعة أن كفاءة إزالة الـ GDAS للبنزين تراوحت بين 55 % - 76 % في حين أن أقصى امتزاز (q_m) هو 14.835 ملغم / غرام، باستخدام كمية المادة المازة 5 غم / 100 مل ووقت الاتصال 5 ساعات. موديلات Langmuir و Freundlich أعطيت تمثيل جيد لعملية الامتزاز مع معامل تحديد أكبر 0.998. أما آلية إزالة البنزين بواسطة الـ GDAS يُظهر هناك منطقتين منفصلتين؛ الجزء الحاد الأول يعزى إلى خطوة الامتزاز الفوري وجزء آخر هو معدل الانتشار. النماذج الحركية توضح أن الامتزاز الخارجي هو الآلية المسيطرة لميكانيكية الإزالة مع الأخذ بنظر الاعتبار آلية الانتشار كمحفز ثانوي للإزالة.

الكلمات الدالة: البنزين، الحمأة المنشطة الحبيبية الميتة، الامتزاز، نماذج الامتزاز التوازني، النماذج الحركية، الية الإزالة.

1. INTRODUCTION

Benzene is one of the most challenges for groundwater pollution due to its toxicity, motility in the environment, and solubility in groundwater [1]. According to the International Agency for Research on Cancer (IARC), the benzene was classified as carcinogenic to humans [2] (IARC. 1989c).

Remediation of groundwater is the procedure, which used to eliminate contamination from groundwater. There is numerous way to confiscate contamination. This method can be approximately divided into two groups. "Permeable reactive barrier (PRB) which is an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provides a flow path through the reactive media, and transform the contaminants into environmentally acceptable forms to attain remediation concentration goals downgradient of the barrier" [3,4].

The great engineering challenges are a determination of appropriate sort and amounts of reactive materials in a permeable wall and good placement techniques. The availability and the cost are important criteria for selecting a reactive material. Therefore, the target of this study was to conduct batch test studies on locally, low-cost and readily available materials; Granular dead activated sludge (GDAS) to be used as a reactive material in a PRB.

2. MATERIALS AND METHODS

2.1. SORBENT AND SORBATE

Granular dead activated sludge (GDAS) was collected about 25 cm depth of dried bed in Hamdaan municipal treatment plant, Basrah/south of Iraq.

This slurry was air-dried for seven days and, then, sieved into (2.36- 0.075) mm diameter mesh.

However, this fraction was repeatedly washed in distilled water and dried at 70°C for 6 hours prior to use. Energy-Dispersive X-ray Spectroscopy (EDS) is used for analysis of GDAS; the percentage of the chemical inorganic component for the selected section of reactive media is shown in Table 1 and Fig. 1.

Table 1

The percentage for chemical composition of GDAS by EDS test

Element	Atomic Concentration%
Carbon	76.05
Oxygen	21.99
Bromine	0.21
Silicon	0.50
Aluminum	0.75
Calcium	0.20
Copper	0.05
Magnesium	0.11
Sulfur	0.01

Potassium	0.01
Iron	0.12

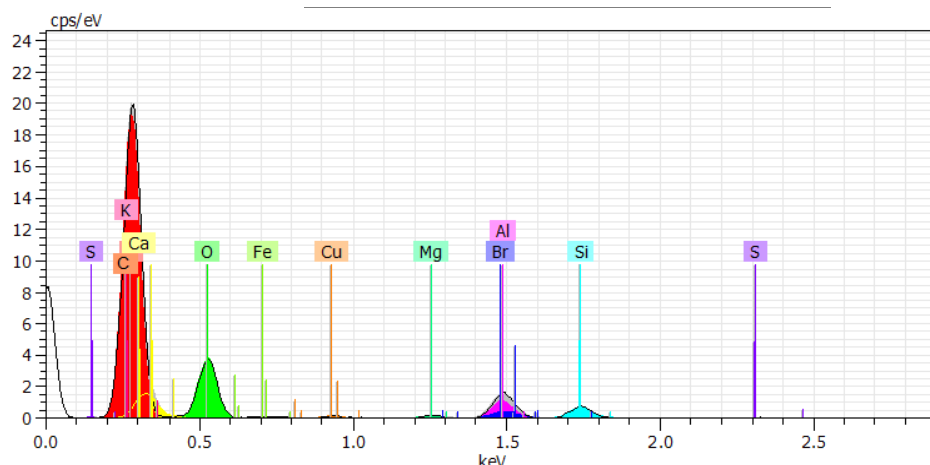


Fig. 1. EDS analysis for GDAS.

Scanning electron microscopy (SEM) has been used to assess the characteristics of the surface morphology and surface physical properties for the sorbent [5, 6]. SEM was used for examining the surface texture of GDAS by ZEISS Supra 55vp, 2013, Germany. Fig.2 shows that the SEM of GDAS before sorption of BTEX, it is clear that the presence of hole and a small opening on the surface, also a microporous network structure can be seen, thereby growing the contact area, which enables pore diffusion during the sorption/bio sorption process.

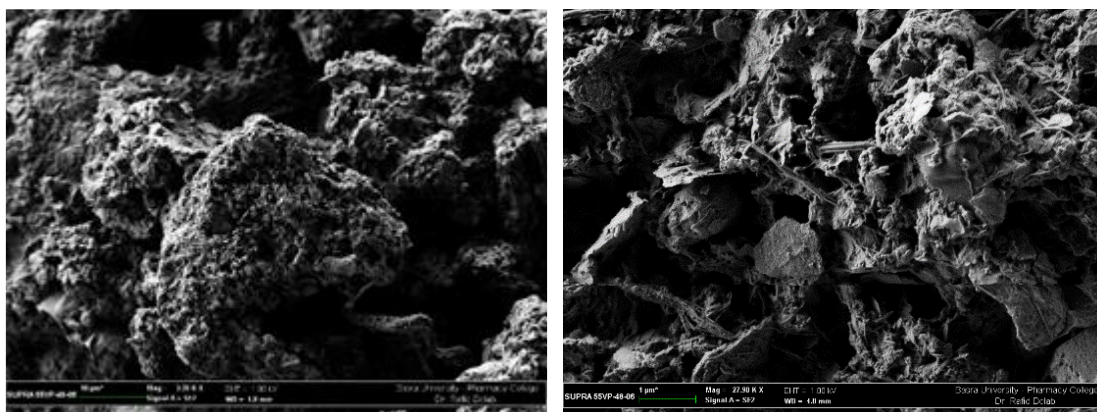


Fig.2. SEM images of GDAS.

The tested chemicals were benzene, from ROMIL-SA, with purity 99.5%. The contaminant was dissolved in the distilled water to prepare the required concentration at room temperature.

2.2. ANALYSIS

A high-performance liquid chromatography (HPLC) with UV-VIS detector was used to analyze the aqueous solution of benzene [7]. C18 (250×4.5mm, BK0033) was used as stationary phase. The mobile stage is usually a combination of solvents that can be combined in certain ratios, acetonitrile/water with ratio 80/20 used as a mobile phase that carried analytic with flow rate 1 ml/min and pressure of 14 MPa.

2.3. SORPTION EXPERIMENT

Batch experiments were conducted to obtain the equilibrium data and to specify the best conditions for the treatment process. Several factors were investigated which affect the sorption efficiency, such as; sorbent dose, contact time and initial contaminant concentration.

2.4. VALIDITY OF MODELS

In the sorption equilibrium and kinetic isotherm studies, the optimal process needs an error function to be evaluated the fit of the isotherm to the investigational equilibrium data. The common error function for determining the optimum isotherm parameter was, the determination coefficient (R^2), and the sum of squared errors (SSE) which are defined as [8]:

$$R^2 = \frac{\sum (q_{cal.} - q_{m,exp.})^2}{\sum (q_{cal.} - q_{m,exp.})^2 + (q_{cal.} - q_{exp.})^2} \quad (1)$$

$$SSE = \sum_{i=1}^n (q_{cal.} - q_{exp.})^2 \quad (2)$$

where q_{exp} is the amount of sorbate sorbed by sorbent during the experiment, q_{cal} is the amount of sorbate obtained by isotherm models, $q_{m,exp}$ is average of q_{exp} and n is number of data points.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF ADSORBENT DOSE

The dependency of benzene sorption on GDAS dosage was calculated by using various amounts of granular dead biomass from 0.2 to 10 g are added to 100 ml of polluted solution for batch tests. Fig.3 shows the benzene removal efficiency as a function of various quantities of sorbent dose. It is obvious that effectiveness improved, with increasing GDAS from 0.2 g to 10 g, and then it fixed after a certain period of time. This was expected because of the greater dosage of sorbents in the solutions, the larger accessibility of sorption places. In addition, the results show that after a certain dosage of sorbent about 5 g/100 ml, the maximum sorption sets in and hence the amount of benzene bound to the sorbent and the amount of this contaminant in solution remain constant even with the additional amount of the sorbent dosage. Fig.3 shows with increasing sorbent dose, the quantity sorbed per unit mass (q_e), reductions. The dwindling in sorption density with an excess in the sorbent dosage is mainly since of a sorption site stay unsaturated during the sorption reactions whilst the number of sites obtainable for sorption site growths by growing the sorbent dosage [9, 10].

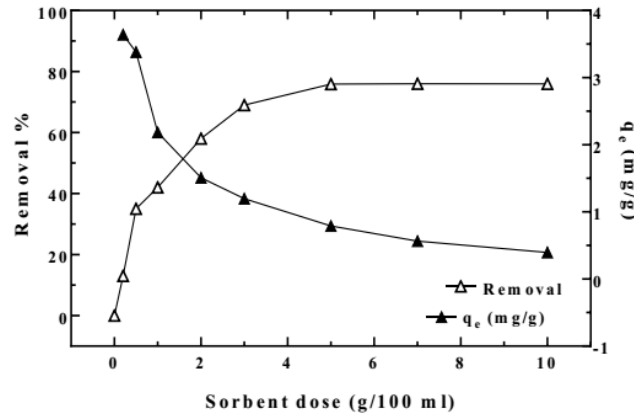


Fig. 3. Dependency of sorption on sorbent dose.

3.2 DEPENDENCY OF SORPTION ON CONTACT TIME

An important aspect of the efficient and cost-effective implementation of the remediation treatment process is the equilibrium contact time. Shorter equilibrium contact time enhances the efficiency of the separation process [11]. Fig.4 shows the effect of contact time on efficiency removal using optimal sorbent dose of GDAS (5 g/100 mL). This figure demonstrates that the percentage of removal of these pollutants increased significantly with increase in interaction time. The sorption rate was fast in the first phase and progressively slowed down then. The slower sorption was probably because of the diminution in sorptions site on the surface of the GDAS. The kinetic data show that 75% of benzene was removed mainly within 5 hr. There was no significant change in residual concentrations after these equilibrium times.

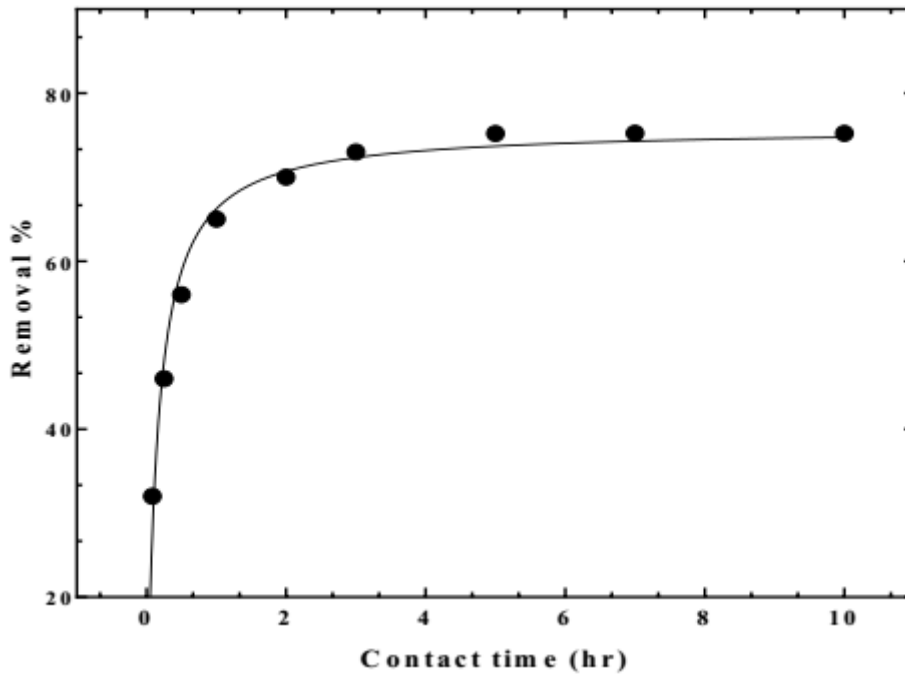


Fig.4. Dependency of sorption on contact time.

3.4. DEPENDENCY OF INITIAL CONCENTRATION OF CONTAMINANTS ON SORPTION EFFICIENCY

The effects of initial contaminate concentration on the sorption efficiency were examined under equilibrium conditions with GDAS dosage of 5 g /100 ml of benzene solution with concentrations ranged from 25 to 700 mg/L. The results were shown in Fig5; it could be seen that by growing the concentrations of contaminant, the removal efficiency would decrease and the uptake sorption q_e (mg/g) would increase. By way of a rule, growing the initial concentrations of contaminating results is an increase in the sorption capacity because it provides an important driving force to overcome all resistance of the benzene between the aqueous and solid phase, thus growing the uptake. Furthermore, increasing the initial benzene concentrations increase the number of collision between benzene and the sorbent, which enhance the sorption procedure. However, the sorption effectiveness decrease since the sorbent has a restricted number of active site, which saturates at a certain concentration. This denotes that the sorption capacity will grow with the increase of initial concentrations mostly due to the increases in the mass transfer from the concentrations gradient. Yet, the concentrations will in reverse impact on the sorption efficiency because of the restricted sorption sites available for the uptake of contaminants [12-14].

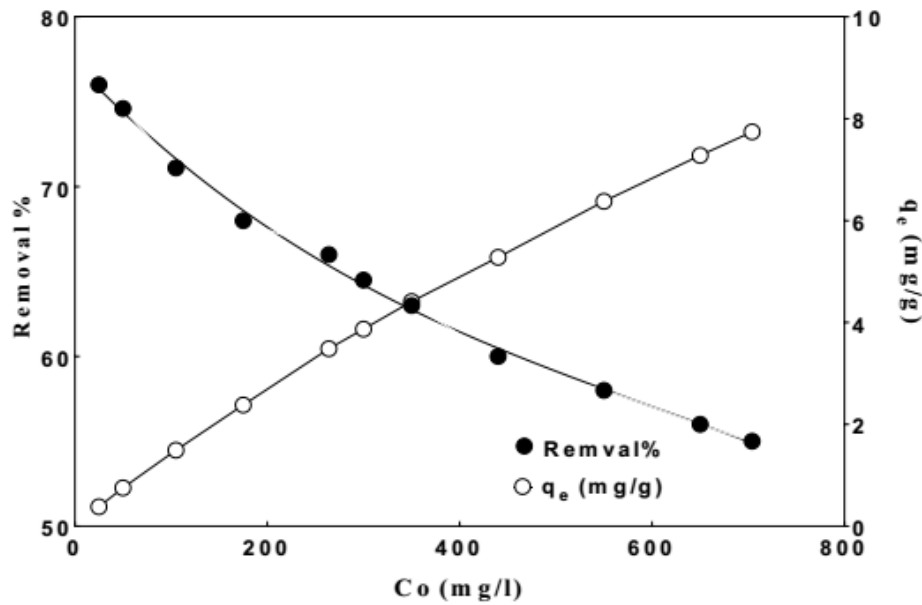


Fig. 5. The dependency of sorption on of initial solute concentration

3.5. EQUILIBRIA ISOTHERM MODELS

Sorption isotherms are a mathematic model that define the distribution of the sorbate species among liquid and sorbent; sorption data are described by Langmuir and Freundlich isotherm model. These isotherms related metal uptake (q_e) per unit mass (m) of sorbent to the equilibrium sorbate concentrations in the bulk fluid stage (C_i).

$$q_e = \frac{V(C_o - C_i)}{m} \quad (3)$$

Where V is the volume of solution in L.

3.5.1. THE LANGMUIR ISOTHERM

The Langmuir model based on the hypothesis that the maximum sorption occurs when a saturated mono-layer of solute molecule is current on the sorbent surface. The Langmuir isotherm is given by [15]:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

Where q_m and b are the Langmuir constant, represent the maximum sorption capacity for the solid phases loading, and the energy constant relates to the heat of sorption correspondingly.

It can be seen from Fig.6 that the isotherm data have a good fitting to the Langmuir equation with ($R^2=0.998$) and SSE 0.123. The values of q_m and b were determined from non-linear regression are listed in Table 2 were found to be 14.835 mg/g and 0.0033 L/mg, respectively.

3.5.2. THE FREUNDLICH ISOTHERM

The Freundlich isotherm model is an experiential relationship describe the sorption of solute from a liquid to solid surfaces and assume that different site with some sorption energy is complicated. Freundlich sorption isotherm is the association between the amount of benzene sorbed per unit mass of GDAS, q_e , and the concentrations of the benzene at equilibrium, C_e [16].

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where K_F and n are the Freundlich constant, the characteristic of the system.

K_F and n are the indicator of the sorption capability and sorption strength, respectively. The ability of the Freundlich model to fit the experimental data was shown in the Fig6 with a determination coefficient (0.9982) and SSE (0.1195). The Freundlich constants K_F and n were found to be 0.163 and 1.487 correspondingly, as seen from Table 2. The magnitude of K_F and n show indicate favorable sorption of benzene by GDAS.

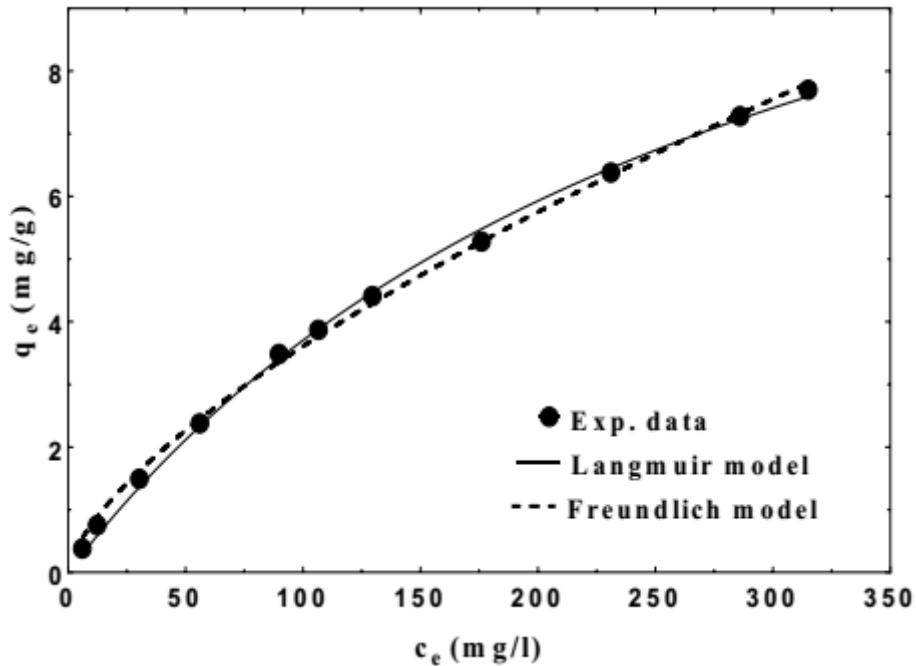


Fig. 6. Sorption isotherm model for benzene removal onto GDAS.

Table 2
Isotherm Equilibrium Data

Langmuir Model	
q_m	14.8350
b	0.00333
R^2	0.99810
SSE	0.12290
Freundlich Model	
K_F	0.16340
n	1.48720
R^2	0.99820
SSE	0.11950

3.6. KINETIC MODELS

In order to examine the controlling mechanism of sorption processes, the “Pseudo-first-order” (PFM) and “Pseudo-second order” (PSM) equations are applied to model the kinetics of benzene sorption onto GDAS. The pseudo-first-order rate equation is given as [17, 18]:

$$q_t = q_e(1 - e^{-K_1 t}) \quad (6)$$

Where q_t and q_e (mg/g) are the amounts of sorbate remove from the aqueous solutions at time t and at equilibrium correspondingly, and K_1 is the “Pseudo first order” rate constants (1/min).

Pseudo-second order model assume that; the mono-layer of sorbate attach to the sorbent surface, the energy of sorption is the same for each sorbent, and there are no interactions between sorbed species. The kinetic forms of this model are showed in the following appearance [19]:

$$q_t = \frac{K_2 q_e^2 t}{(1 + K_2 q_e t)} \quad (7)$$

Where K_2 is the Pseudo-second order rates constants (g/mg min).

Kinetic results data was well analyzed by the Pseudo first- order and Pseudo-second-order kinetic models (Fig.7) and gave the best fitting for data depending on statistical error, where (R^2) was greater than 0.95 and the calculated sorption capacity q_e (mg/g) values were consistent very well with those obtained from experiments. The constant of this model was determined by using non-linear regression methods as listed in Table 3.

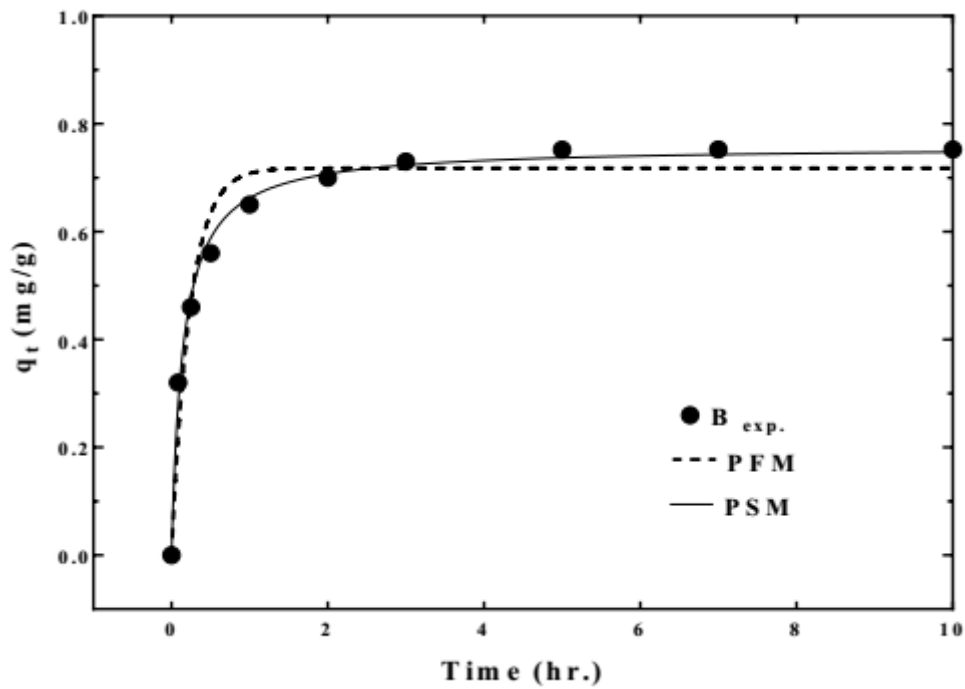


Fig. 7. Kinetic models for sorption of benzene onto GDAS

Table 3

Constants of kinetic models.

Pseudo-first order	$q_e^{EXP.}$ (mg/g)	0.7823
	q_e (mg/g)	0.7177
	K_1 (hr. ⁻¹)	4.283
	R^2	0.9563
	SSE	0.028
Pseudo-second order	q_e (mg/g)	0.7583
	K_2 (g/mg hr)	9.082
	R^2	0.993
	SSE	0.0037

3.7. MECHANISM OF REMOVAL

Usually, the “intra-particle diffusion model” (IPD) was used to recognize the mechanisms of the sorption processes. This model assume that intra-particle diffusion is the rates-controlling steps that are normally the case for the well-mix solution. The “intra-particle diffusion” model is a sole - fighting model in nature and might be described by Weber and Morris, which is based on Fick’s second law [20]. The sorbed amounts q_t should differ linearly with the square root of time. The “intra-particle diffusion” model can be defined by the following equation [21]:

$$q_t = k_{di}t^{1/2} + I_i \quad (8)$$

Where k_{di} (mg/g h^{1/2}) is the rate constants of phase i and it is equal to the grade of relationship relate q_t with $t^{1/2}$. In addition, the interrupt of phase i is signified by the values of I_i (mg/g) and it reflect the width of boundary layer.

This means that the larger effects of the boundary layer can be predictable with the larger value of interrupt. If the relationships connected between q_t versus $t^{1/2}$ is linear, the intra-particle diffusion occurs. If the linear plot passes through the origin, the only intra-particle diffusion is represented the rate-limiting procedure. Then, another mechanism must be considered with intra-particle diffusion [22, 23].

An intra-particle diffusion model has fitted the kinetic data. The results show in the Fig.8 two separate region; the first severe portion attributed to the immediate sorption step and another portion is the intraparticle diffusion rate is dominated. The intra-particle diffusion coefficient for the sorption was listed in Table (4). It is clear that the I_i for all stages is larger than zero and regression line didn't pass through the origin. This means the external mass transport mechanisms must be considered with intra-particle diffusion [24].

Also, the results shown the constant rate k_{1B} for the initial stage (surface sorption) is larger than of k_{2B} which obtain from second stage (internal diffusion), that's mean the sorption was governed by external sorption rather than intraparticle diffusion.

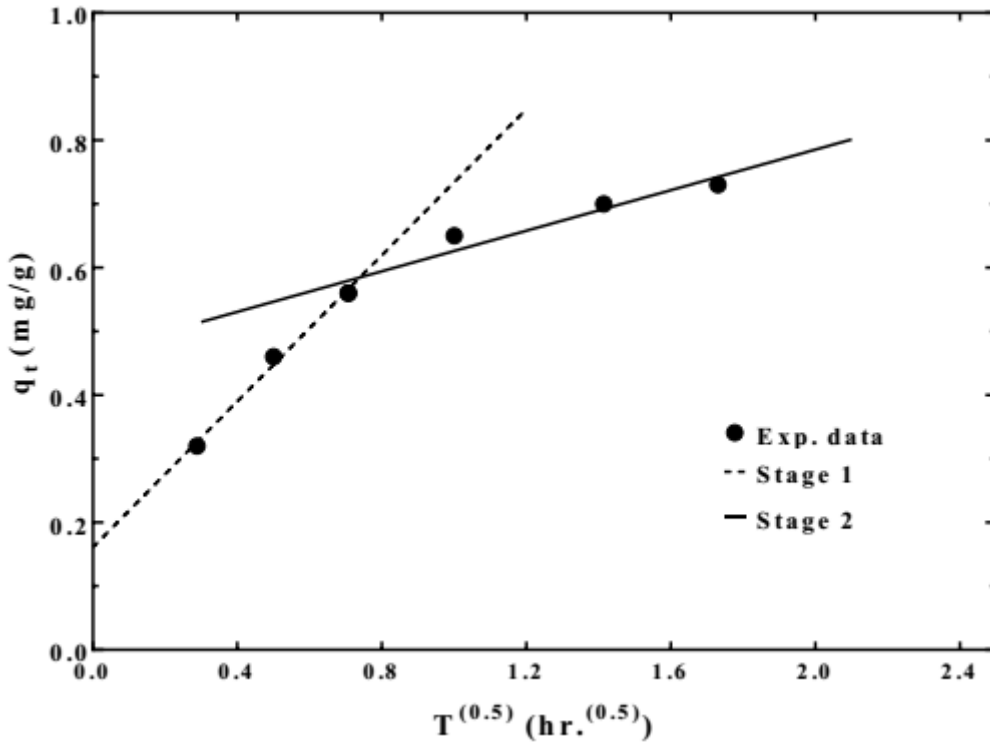


Fig. 8. IPD model of benzene sorption from aqueous solution onto GDAS

Table 4

Constants of Intraparticle diffusion model

Portion	Parameter	value
1	k_{1B} (mg/g h ^{1/2})	0.4580
	I_{1B} (mg/g)	0.2155
	R^2	0.9921
	SSE	0.0152
2	k_{2B} (mg/g h ^{1/2})	0.1592
	I_{2B} (mg/g)	0.4669
	R^2	0.9298
	SSE	0.0241

4. CONCLUSIONS

The GDAS sorption of benzene aqueous solution was investigated at different conditions. Results show the benzene removal efficiency as a function of various quantities of sorbent dose. It is obvious that effectiveness improved, with increasing GDAS from 0.2 g to 10 g, and then it fixed after a certain period of time. When increasing the sorbent dose the sorption density and the quantity sorbed per unit mass (q_e) are reduced.

The effects of contact time on efficiency removal shows that the percentage of removal of these pollutants increased significantly with growth in interaction time. The sorption rate was fast in the first phase and progressively slowed down then. Also, it could be seen that by growing the initial concentrations of contaminant the removal efficiency would decrease and the uptake sorption would increase. Batch investigations demonstrated that the GDAS efficiency removal for benzene is ranged from 55%-76% at sorbent dose 5 g/100 mL and contact time 5 hours.

The Langmuir and Freundlich isotherm model gave a good representation for the sorption process with high determination coefficient.

The values of maximum uptake (q_m) about 14.835 mg/g and Freundlich constants (K_F) and (n) were found to be 0.163 and 1.487 respectively which indicate favorable sorption of benzene onto GDAS.

Kinetic results data analyzed by the Pseudo first- order and Pseudo-second-order kinetic models and gave the best fitting for data depending on a statistical error, where (R^2) was greater than 0.95. The calculated sorption capacity q_e (mg/g) values agreed well with those obtained from experiments.

Intra-particle diffusion data consisted from two separated region; the first severe portion recognized to the immediate sorption step, and another portion is the intraparticle diffusion rate is dominated.

It is clear that the I_i for all stages is larger than zero and regression line didn't pass through the origin. This means the external mass transport mechanisms must be considered with intra-particle diffusion.

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