

Removal of chlorinated volatile organic compounds by fixed bed adsorption technique: Adsorption equilibrium and breakthrough analyses

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Abstract

The adsorption equilibrium and dynamic breakthrough behaviour of chlorinated volatile organic compounds (CVOCs), namely chloroform and carbon tetrachloride, were experimentally investigated by using pelleted activated carbon in a fixed bed. The experimental studies were carried out at atmospheric pressure, the temperature of 313 K, the gas flow rate of 3 L/min and various inlet gas phase concentration of CVOCs (250-1250 ppmv). The experimental adsorption equilibrium isotherms were obtained and compared with four model equations (Freundlich, Langmuir, DRK and BET) existing in literature. It was observed that the Freundlich and Langmuir isotherm models were in agreement with the experimental data obtained. It was also observed that K_F and q_m values of chloroform on the activated carbon used were greater than those values of carbon tetrachloride. The Yoon Nelson and deactivation models were used to describe the breakthrough curves of the CVOCs studied on the activated carbon by using the experimental data. It was found that the model results were in agreement with the experimental breakthrough curves.

Keywords: Air pollution, chlorinated volatile organic compounds, activated carbon, adsorption, fixed bed

1. Introduction

Chlorinated volatile organic compounds (CVOCs) are sub-group of volatile organic compounds (VOCs) which produced from sources such as organic solvents, degreasers, cleaners, lubricants, and liquid fuels. CVOCs are emitted into receiving environmental from their sources and may lead to serious environmental problems (water/groundwater, soil and air contamination) as well as healthy problems (poising, cancer and irritation). Due to these harmful effects, CVOCs emissions should be essentially limited and controlled [1-5].

There are two common techniques for controlling of CVOCs: The removal/recovery techniques (adsorption, absorption, condensation and membrane separation) and the destruction techniques (oxidation and bio-filtration). The latter, especially oxidation, has some disadvantages such as the formation of undesirable by-products and sensitive operation conditions. In contrast, among the removal/recovery techniques, the adsorption processes is the most selected one because of its advantages of lower operation cost, temperature, and its use also in very low CVOC concentrations [6-10].

The adsorption processes are widely carried out by using porous solid materials (adsorbents) which have highly surface area in a fixed bed adsorber. Due to its hydrophobic and organophilic surface properties and its large surface area and pore volume as a result of its vast of pores and micro-pores, activated carbon is commonly used as adsorbent material for VOCs recovery [8, 9, 11-13].

To design of fixed-bed adsorbers, there are two important properties that are needed to understand: knowledge of adsorption equilibrium and dynamic breakthrough behaviour between the adsorbent and adsorbate. Numerous models have been developed to define the knowledge of adsorption equilibrium and to predict breakthrough curves of fixed bed adsorption of activated carbon [14-16]. Some important adsorption isotherms used to account for knowledge of adsorption equilibrium are Freundlich, Langmuir, Brauner-Emmet-Teller (BET) and Dubinin-Radushkevitch-Kaganer (DRK) models.

There are also different model equations such as Yoon and Nelson developed as empirical, Wheeler equation and deactivation model for breakthrough analysis of fixed bed adsorption systems. The deactivation model has been mainly applied to breakthrough curve analysis of gas (especially acidic gases such as SO₂, H₂S and CO₂)-solid (silica gel, calcined limestone, soda ash and zeolite) systems in a fixed bed reactors [12, 15-20]. Park et al. [16], Suyadal et al. [21], and Suyadal [22] have showed that the deactivation model has been successfully applied to VOCs adsorption/desorption on an activated carbon bed.

This study aims to explore CVOCs (chloroform and carbon tetrachloride) adsorption capacity on pelleted activated carbon and to predict breakthrough curves by using the experimental data fitted to Yoon Nelson and deactivation models in a fixed bed adsorber.

2. Theory

There have been many mathematical models developed as adsorption isotherm equation to account for the knowledge of adsorption equilibrium in the literature. Some of these equations commonly used are Freundlich, Langmuir, Brauner-Emmet-Teller (BET) and Dubinin-Radushkevitch-Kaganer (DRK) equations. These isotherms were used in order to apply the experimental adsorption data in this study.

The Freundlich equation is one of the earliest empirical equations for modeling adsorption equilibrium data and expressed as [15, 23, 24].

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

where q_e is the equilibrium adsorption capacity, C_e is the equilibrium concentration, K_F and n are the Freundlich isotherm parameters.

The Langmuir equation is a monolayer adsorption isotherm and written as

$$\frac{q_e}{q_m} = \frac{bC_e}{1 + bC_e} \quad (2)$$

where q_m and b are the Langmuir isotherm parameters.

The BET equation is derived by using the same assumptions as those used in the Langmuir isotherm for multilayer adsorption isotherm. The mathematical expression of BET equation is defined as follows

$$\frac{C_e}{q_e(1 - C_e)} = \frac{1}{q_0 c} + \frac{c-1}{q_0 c} C_e \quad (3)$$

where q_0 and c are the BET isotherm parameters.

It has been showed that the adsorption of inorganic gases and organic vapours on porous and microporous adsorbent materials such as activated carbon and molecular sieve can be described by the DRK equation [18, 19, 21, 25]:

$$q_e = a \exp[-b \ln^2(C_e)] \quad (4)$$

where a and b are the DRK isotherm constants.

The effluent concentration of pollutant in the fixed beds varies from 0% to 100% with changing time. When the concentration reaches degree of saturation, the pollutant in the gas stream sent out to the adsorption column cannot be adsorbed any longer. This moment is called as “breakpoint”. The plot (time-the effluent concentration or dimensionless concentration, C^* , that is the ratio of the effluent concentration to the inlet concentration) obtained from the concentration history (for the elapsed time from initial to the breakpoint) of the pollutant in the gas stream is called as “breakthrough curve” [26].

The adsorption capacity, q , of the fixed bed adsorption can be calculated from the breakthrough curve expressed as

$$q = \frac{Q \int_0^t (C_0 - C) dt}{m} \quad (5)$$

where C_0 and C are the inlet and effluent concentrations of CVOCs respectively, Q is the volumetric flow rate, m is the mass of adsorbent material, and t is the time. The value of adsorption capacity in the state of equilibrium is defined as the equilibrium adsorption capacity (q_e) and can be written

$$q_e = \frac{Q \int_0^{t_r} (C_0 - C) dt}{m} \quad (6)$$

where t_r is the time when the adsorption breakthrough is reached [18, 27].

In order to obtain the breakthrough curve by using the experimental data, one of the empirical expressions commonly used is the Yoon and Nelson equation [12, 15, 17, 24]:

$$\frac{C}{C_0} = \frac{1}{1 + e^{k'(t^* - t)}} \quad (7)$$

where k' is the adsorption rate constant, t is the breakthrough time, t^* is the time required for 50% adsorbate breakthrough called as the stoichiometric breakthrough time.

Another theoretical expression used to obtain the breakthrough curve is deactivation model equation written as [16, 18-22]

$$\frac{C}{C_0} = \exp[-k_s \tau \exp(-k_d t)] \quad (8)$$

where τ is the surface-time (S_0/Q_0); k_s is the observed adsorption rate constant, S_0 is initial surface area of the adsorbent, Q_0 is volumetric flow rate of the tracer-rich carrier gas stream introduced to the fixed bed adsorber, and k_d is first-order deactivation rate constant.

3. Methodology

3.1. Materials

A commercial coal based pelleted activated carbon, namely Envirocarb AP4-50, was obtained from Chemviron Carbon Corporation. The surface area and micropore volume of activated carbon sample were measured by the BET and t-plot methods (Quantachrome AUTOSORB-1). The true density of activated carbon sample was determined by helium pycnometer (Quantachrome MVP-1). The particle size range of the pelleted activated carbon sample was 6-8 mesh. Some properties of the activated carbon used in the experimental studies are listed in Table 1. Before being used in the fixed bed experiments, the activated carbon was dried at 378 K in an oven for removing the moisture for at least 24 hours and it was stored in impermeable glass cap. Chloroform (CHCl_3 , 99.9% GC purity) and carbon tetrachloride (CCl_4 , 99.9% GC purity) were selected as CVOCs for using in the experiments. Some properties of CVOCs used in the experimental studies are given in Table 2.

3.2. Methods

The adsorption experiments were performed in a fixed bed experimental set up illustrated in Figure 1. The system consists of a fixed bed adsorption column made of glass with 0.3 m length and 0.025 m ID, an evaporator unit, a constant temperature controlling units, rotameters, and a gas chromatography (GC) device with a thermal conductivity detector (SRI-8610). About 5 g of the pelleted activated carbon sample was used in the experimental studies. Nitrogen was used as the carrier gas in the experiments.

The carrier gas stream at the out of nitrogen cylinder was divided into two lines. One line was passed through the CVOCs evaporator to make a stream saturated with CVOCs. Then, the CVOCs-saturated stream and the other line were mixed at the out of the evaporator system with a "T" pipe to obtain gas streams with different CVOCs concentrations. The evaporator was heated by a water bath and the desired amount of CVOCs in gas streams were adjusted by varying both the temperature of the water bath and the rates of stream lines. The pipe line made of glass with 0.01 m ID through from the evaporator to the fixed bed column was heated by a heating band consisting of electrically resistant controlled by a digital thermostat to prevent from condensation of CVOCs. The carrier gas containing desired concentration of CVOCs was passed through the column. The gas samples of 1 ml were taken from at effluent stream and were analysed by GC to determine the concentration of CVOCs at different time intervals. The fixed bed experiments were ended that the effluent concentration of CVOCs equalled the inlet concentration. The fixed bed adsorption column was heated by a heating jacket made of glass. Hot water was supplied to the jacket by using a Grant series of water bath and re-circulator providing accurate temperature control in range of 253 to 373 K.

In order to obtain vapour standard samples for GC analysis, different volumes of the liquid samples for CVOCs were evaporated in 50 ml impermeable glass vials by using an oven at the temperature of the boiling point of CVOCs for several hours. Then, the vapour samples of 1 ml were taken from the vials by using head-space technique and analysed by GC. In this way, standard curve (the peak area vs. known concentration) obtained was used in determining unknown concentrations of the gas streams containing CVOCs. The GC analyses were performed by using a stainless steel packed column (Carbowax, 6-ft x 1/8-in). The temperatures of column and detector were 80 °C and 100 °C, respectively. The injection temperature was same as the column temperature. The experimental studies were carried out at atmospheric pressure, the temperature of 313 K, the gas flow rate of 3 L/min and varying initial gas phase concentration of CVOCs (250-1250 ppmv).

4. Results and Discussion

4.1. Adsorption Equilibrium

The experimental data for breakthrough curves and adsorption isotherms have been obtained from the fixed bed experimental studies. The data were compared with the theoretical adsorption isotherms and the breakthrough model equations discussed in chapter 1.

Figure 2 illustrates typical experimental breakthrough curves showing change in dimensionless concentration (C^*) with time for chloroform (a) and carbon tetrachloride (b) in different inlet concentrations. As seen from Figure 2, the breakpoint times of both CVOCs studied have been decreased with increasing inlet concentration. However, the breakthrough time values of chloroform are larger than those obtained with carbon tetrachloride. This result reflects that the adsorption of chloroform is greater than carbon tetrachloride.

The experimental adsorption capacity (q) values of both CVOCs studied were calculated from Eq. 5 by using the experimental breakthrough curves data shown in Figure 2. Figure 3 shows changes in the experimental adsorption capacities of both CVOCs with time for different inlet concentrations. As seen Figure 3, the adsorption capacity values of chloroform are greater than those of carbon tetrachloride for all inlet concentrations. It is also observed that the adsorption capacity values of the CVOCs used increase with increasing time. After a while (t_r), the state of equilibrium when no change in these values occurs with time is established. The experimental equilibrium adsorption capacity (q_e) values were then calculated by using Eq. 6.

Figure 4 shows comparison of the experimental adsorption isotherms of chloroform (a) and carbon tetrachloride (b) with the adsorption isotherm models used on the activated carbon sample. As shown in Figure 4, the equilibrium adsorption capacity of both CVOCs increases with increasing equilibrium concentration. The model parameters of Langmuir, Freundlich, DRK isotherms of the CVOCs studied were determined by the non-linear estimation methods (quasi-Newton and Hooke-Jeeves) by using the experimental adsorption capacity values. Because estimation process for the original form of BET isotherm did not converge, linearized form of this isotherm was used in estimation of the BET parameters. The model constants and correlation coefficients (R^2) of the isotherms used for chloroform and carbon tetrachloride are given in Tables 3 and 4, respectively.

From Tables 3 and 4, it was observed that the experimental adsorption equilibrium data of both chloroform and carbon tetrachloride on the activated carbon sample used were in agreement with the Freundlich and Langmuir isotherm equations. Correlation coefficients (R^2) values between these isotherm equations and the experimental data of both CVOCs studied were over 0.98 as given in Tables 3 and 4. q_m and K_F values obtained for chloroform were three times as much as these values obtained for carbon tetrachloride. This result could be explained by dipole moment and acentric factor values of chloroform as shown in Table 2, which is greater than those of carbon tetrachloride. One of the most important physical properties effecting on the CVOCs adsorption is the molecule polarity. The dipole moment is the measure of net molecular polarity. The larger the dipole moment, the higher the polarity and the adsorptivity. Because it is also the measure of molecule geometry, the acentric factor is more important parameter used in determining of the adsorptivity [28, 29].

The theory of DRK isotherm is based on a pore filling mechanism for adsorption on porous adsorbents such as activated carbon, zeolite and silica gel [18, 19]. The b constant of the DRK isotherm given in Eq. 4 depends on the characteristic energy of the system. The characteristic energy relates to the average width of the micropores [30]. Thus the b parameter cannot be negative [18, 19, 30]. As seen Tables 3 and 4, the DRK model was also in agreement with the experimental data with R^2 values greater than 0.97 for CVOCs studied

on the activated carbon, but the value of b parameter for this model was determined as negative which was an unexpected result. Similar result was also obtained for the BET model; on the other hands, among the models used the BET equation was the model with the lowest correlation coefficient values.

4.2. Modelling of Adsorption Breakthrough

To determine the dynamic behaviour of the fixed bed used in this study, the experimental breakthrough curves obtained for both CVOCs studied adsorption on the activated carbon sample were fitted to the Yoon Nelson and the deactivation model equations. Figure 5 illustrates the breakthrough curves obtained from the experimental and the Yoon Nelson (a) and deactivation (b) models for different inlet chloroform concentrations. Comparisons of the experimental data and results of Yoon Nelson and deactivation models for different inlet carbon tetrachloride concentrations are shown in Figure 6. The parameters of Yoon Nelson and deactivation models for both CVOCs studied were calculated by non-linear estimation by using the experimental breakthrough data obtained. Tables 5 and 6 tabulate the results for the Yoon Nelson and deactivation model parameters and the correlation coefficients (R^2) calculated of chloroform and carbon tetrachloride at various inlet concentrations, respectively. As seen Tables 5 and 6, the predictions of both Yoon Nelson and deactivation models are well fit to the experimental data because of the high value of the correlation coefficient (R^2). As expected, it was observed that the stoichiometric breakthrough time (t^*) values of both CVOCs given in Tables 5 and 6 were decreased with increasing the inlet concentration [24]. It was also found that, in general, the rate constant values of Yoon Nelson (k') and deactivation (k_d) models for chloroform given in Table 5 were independent of the inlet concentration. It was observed that, on the other hand, the values of k' and k_d for carbon tetrachloride given in Table 6 was increased with increasing the inlet concentration. These results were in agreement with previous studies in the literature [21, 22, 31].

5. Conclusions

The adsorption characteristics and breakthrough analysis of the CVOCs, namely chloroform and carbon tetrachloride, on the pelleted activated carbon were investigated in a fixed bed adsorber at the temperature of 313 K. The experimental adsorption isotherms of CVOCs were compared with four adsorption isotherms (Freundlich, Langmuir, DRK and BET). The experimental adsorption capacity data of both CVOCs were in agreement with the results obtained from solutions of Freundlich and Langmuir isotherms. The DRK and BET model results did not fit to the experimental adsorption capacity data, because some parameters such as b and q_0 of these models were negative. K_F and q_m values (6.98 and 137.90) of chloroform on the activated carbon used were greater than those values (2.06, 43.41) of carbon tetrachloride. The experimental breakthrough curves obtained for CVOCs studied were in good agreement with the Yoon Nelson and deactivation model equations. The values of the t^* , k' and k_d for chloroform ranged from 83.44, 0.0706 and 0.0486 to 32.03, 0.0799 and 0.0557 at the temperature of 313 K, whereas for carbon tetrachloride, the values ranged from 19.20, 0.1437 and 0.0949 to 6.99, 0.2606 and 0.1829 at the temperature of 313 K, respectively.

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Nomenclature

- a : constant in the DRK isotherm
 b : constants in Langmuir and DRK isotherms
 c : constant in the BET isotherm
 C : effluent gas phase concentration (ppmv)
 C_e : equilibrium gas phase concentration (ppmv)
 C_0 : inlet gas phase concentration (ppmv)
 C^* : dimensionless effluent gas phase concentration (-)
 k_d : first-order deactivation rate constant for the deactivation model (min^{-1})
 k_s : observed adsorption rate constant (m min^{-1})
 K_F : constant in the Freundlich isotherm
 k' : adsorption rate constant in the Yoon Nelson equation (min^{-1})
 m : mass of adsorbent (g)
 n : Freundlich exponent
 q : adsorption capacity (mg g^{-1})
 q_e : equilibrium adsorption capacity (mg g^{-1})
 q_m : constant in the BET isotherm (maximum adsorption capacity) (mg g^{-1})
 q_0 : constant in the BET isotherm
 Q : volumetric flow rate (L min^{-1})
 Q_0 : volumetric flow rate of the tracer-rich carrier gas stream introduced to the fixed bed adsorber defined in the deactivation model (L min^{-1})
 S_0 : initial surface area of the adsorbent defined in the deactivation model ($\text{m}^2 \text{g}^{-1}$)
 S_g : BET surface area of the adsorbent ($\text{m}^2 \text{g}^{-1}$)
 t : time or breakthrough time, min
 t_r : time when the adsorption breakthrough is reached (min)
 t^* : stoichiometric breakthrough time (min)

Greek letters

- ρ_{bad} : bed density (g cm^{-3})
 ρ_s : true density (g cm^{-3})
 τ : surface-time (S_0/Q_0) defined in the deactivation model ($\text{min m}^{-1} \text{g}^{-1}$)

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Table 1. Some properties of the activated carbon used in this study

| Parameters | Activated carbon AP4-50 |
|---|-------------------------|
| Raw material | Coal based |
| BET surface area, S_g (m ² /g) | 838.80 |
| t-method micropore volume (ml/g) | 0.324 |
| Bed density, ρ_{bed} (g/ml) | 0.48 |
| True density, ρ_s (g/ml) | 1.12 |
| Moisture content (%W/W) | 5.00 |
| Particle size, mesh (95%) | 6-8 |

Table 2. Some physical properties of CVOCs
used in this study [32, 33]

| Compound | Molecule formula | Molecule weight (g/mol) | Melting point (°C) | Boiling point (°C) | Liquid density (g/ml) | Vapour density (g/L) | Dipole moment (Debyes) | Pitzer's acentric factor |
|-----------------------------|-------------------|-------------------------|--------------------|--------------------|-----------------------|----------------------|------------------------|--------------------------|
| Chloroform | CHCl ₃ | 119.40 | -63.50 | 61.20 | 1.489 | 4.36 | 1.1 | 0.216 |
| Carbon tetrachloride | CCl ₄ | 153.80 | -22.60 | 76.70 | 1.595 | 5.36 | 0 | 0.194 |

Table 3. Adsorption parameters of selected adsorption isotherms
for chloroform adsorption on the activated carbon

| Isotherm | Parameters |
|------------|--|
| Freundlich | $K_F = 6.98$ $n = 2.60$ $R^2 = 0.9880$ |
| Langmuir | $q_m = 137.90$ $b = 0.0027$ $R^2 = 0.9960$ |
| DRK | $a = 24.00$ $b = -0.029741$ $R^2 = 0.9274$ |
| BET | $q_0 = -53.79$ $c = 0.999570$ $R^2 = 0.7056$ |

Table 4. Adsorption parameters of selected adsorption isotherms for carbon tetrachloride adsorption on the activated carbon

| Isotherm | Parameters |
|------------|--|
| Freundlich | $K_F = 2.06$ $n = 2.56$ $R^2 = 0.9960$ |
| Langmuir | $q_m = 43.41$ $b = 0.0024$ $R^2 = 0.9920$ |
| DRK | $a = 7.24$ $b = -0.029989$ $R^2 = 0.9801$ |
| BET | $q_0 = -17.76$ $c = 0.999645$ $R^2 = 0.9216$ |

Table 5. Parameters of Yoon Nelson and deactivation models for adsorption of chloroform on the activated carbon at various inlet concentrations

| Inlet concentrations (ppmv) of CHCl ₃ | Yoon Nelson parameters | | | Deactivation model parameters | | |
|--|------------------------|---------------------------|--------|-------------------------------|----------------------------|--------|
| | t^* (min) | k' (min ⁻¹) | R^2 | $k_s \tau$ | k_d (min ⁻¹) | R^2 |
| 250 | 83.44 | 0.0706 | 0.9982 | 35.79 | 0.0486 | 0.9954 |
| 500 | 68.02 | 0.0799 | 0.9979 | 27.57 | 0.0557 | 0.9939 |
| 750 | 46.20 | 0.0739 | 0.9982 | 6.26 | 0.0501 | 0.9978 |
| 1250 | 32.03 | 0.0701 | 0.9896 | 2.91 | 0.0491 | 0.9918 |

Table 6. Parameters of Yoon Nelson and deactivation models for adsorption of carbon tetrachloride on the activated carbon at various inlet concentrations

| Inlet concentrations (ppmv) of CCl ₄ | Yoon Nelson parameters | | | Deactivation model parameters | | |
|---|------------------------|---------------------------|--------|-------------------------------|----------------------------|--------|
| | t^* (min) | k' (min ⁻¹) | R^2 | $k_s \tau$ | k_d (min ⁻¹) | R^2 |
| 300 | 19.20 | 0.1437 | 0.9955 | 3.86 | 0.0949 | 0.9977 |
| 500 | 14.61 | 0.1556 | 0.9961 | 3.00 | 0.1075 | 0.9976 |
| 750 | 10.75 | 0.1807 | 0.9908 | 2.58 | 0.1308 | 0.9946 |
| 1250 | 6.99 | 0.2606 | 0.9897 | 2.34 | 0.1829 | 0.9942 |

Captions

Figure 1. Experimental set up: (1) nitrogen gas cylinder, (2) rotameters, (3) constant temperature water bath, (4) evaporator, (5) heating jacket, (6) fixed bed adsorption column, (7) gas chromatography, (8) computer.

Figure 2. Variation of dimensionless concentration in the effluent gas phase with time for chloroform (a) and carbon tetrachloride (b) at different inlet concentrations.

Figure 3. Variation of the experimental adsorption capacity of chloroform (a) and carbon tetrachloride (b) on the activated carbon with time at different inlet concentrations.

Figure 4. Adsorption equilibrium data for chloroform (a) and carbon tetrachloride (b) on the activated carbon.

Figure 5. Comparison of the experimental breakthrough curves with the Yoon Nelson (a) and deactivation (b) models for chloroform adsorption on the activated carbon at various inlet concentrations.

Figure 6. Comparison of the experimental breakthrough curves with the Yoon Nelson (a) and deactivation (b) models for carbon tetrachloride adsorption on the activated carbon at various inlet concentrations.

Figure 1.

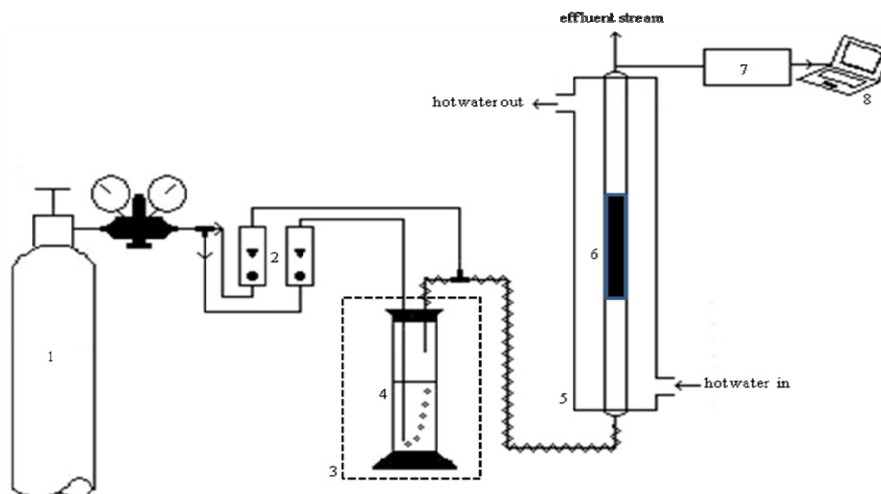


Figure 2.

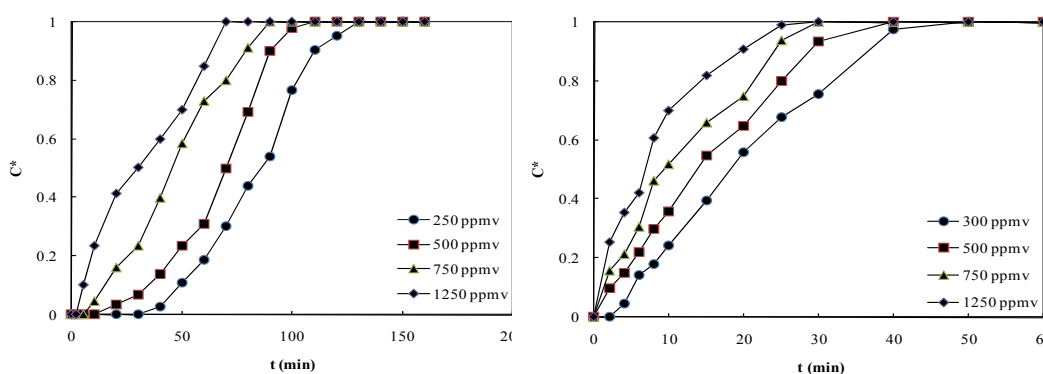


Figure 3.

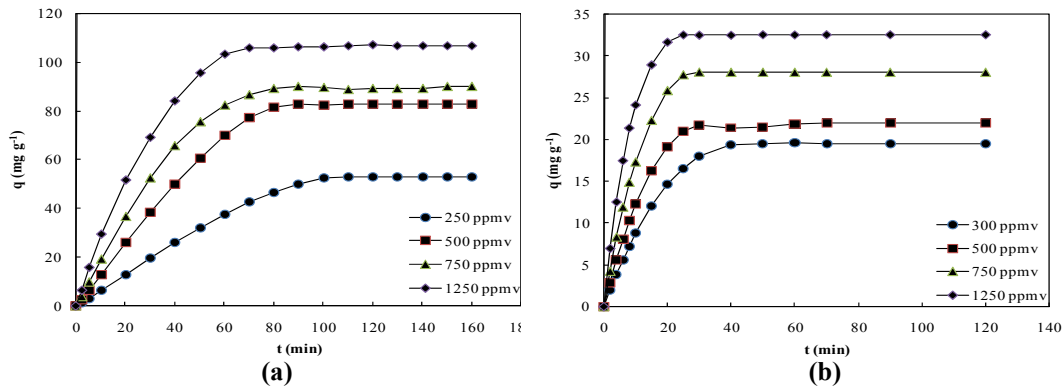


Figure 4.

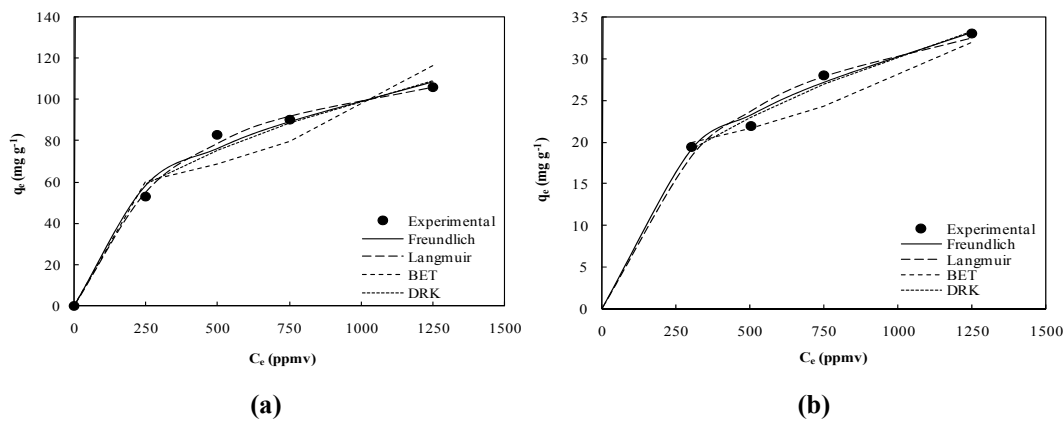


Figure 5.

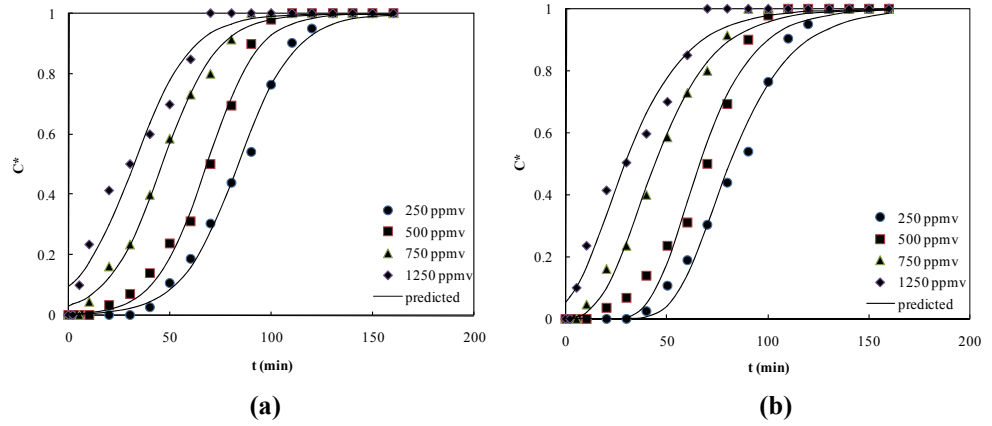


Figure 6.

