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## ADSORPTION OF HYDROGEN FLUORIDE ONTO ACTIVATED CARBON UNDER VACUUM CONDITIONS: EQUILIBRIUM, KINETIC AND THERMODYNAMIC INVESTIGATIONS

*In this study, the adsorption of HF gas by three types of activated carbon has been investigated under vacuum conditions. The effects of experimental parameters such as initial pressure of the HF gas, contact time and temperature on adsorption process have been investigated. The results showed that the adsorption of the HF gas onto activated carbon increased by increasing the initial pressure of gas, while it decreased with increase in temperature. The Freundlich isotherm model fitted the equilibrium data better than the other isotherm models. Using the Langmuir isotherm model, the maximum adsorption capacities of the first type, the second type and third type of activated carbon were 226.4, 268.8 and 258.9 mg/g, respectively. Experimental data were also evaluated in terms of kinetic characteristics of adsorption and it was found that the adsorption process followed well pseudo-second-order kinetics. Thermodynamic parameters, the change of free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of adsorption were calculated at the temperature range of 28–55 °C. The results showed that the adsorption of HF on activated carbon is feasible, spontaneous and exothermic.*

*Keywords: activated carbon; hydrogen fluoride; adsorption; kinetic; thermodynamic.*

Hydrogen fluoride is a colorless, fuming liquid or gas with a strong, irritating odor. Hydrogen fluoride readily dissolves in water to form colorless hydrofluoric acid solutions; dilute solutions are visibly indistinguishable from water. Hydrogen fluoride is primarily an industrial raw material. It is produced commercially by an action of sulfuric acid on the mineral fluorospar. Hydrogen fluoride is used in separation and purification of uranium isotopes, as a cracking catalyst in oil refineries, and also for etching glass and enamel, removing rust, and cleaning brass and crystal. Additionally, it is used in manufacturing silicon semiconductor chips and as a laboratory reagent.

Throughout the global nuclear industry, uranium is enriched by one of two methods: gaseous diffusion or gas centrifuge. The gas centrifuge process uses a large number of rotating cylinders interconnected to form cascades. The  $\text{UF}_6$  gas is placed in the cylinder, which is then rotated at a high speed. The rotation creates a strong centrifugal force that draws more of the heavier gas molecules toward the wall of the cylinder, while the lighter gas molecules tend to collect closer to the center. The stream that is slightly enriched in  $\text{U}^{235}$  is withdrawn and fed into the next higher stage, while the slightly depleted stream is recycled back into the next lower stage. The inventory of  $\text{UF}_6$  in a centrifuge is limited by the condensation at the wall; the  $\text{UF}_6$  must remain in gas form in order to the rotor will not become unbalanced and crash. For this reason, uranium enrichment plants are operated under vacuum conditions. The vacuum pressure increases result in the accumulation of inert or atmospheric gases within the enrichment plant from small leaks. Hydrogen fluoride is always produced in the uranium en-

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richment process during the reaction of uranium hexafluoride with atmospheric water vapor [1]. For this reason, it is of paramount importance to remove hydrogen fluoride from the uranium enrichment process, which is carried out under vacuum conditions.

Inhalation of hydrogen fluoride gas may cause immediate or delayed-onset pulmonary edema after a 1-hour exposure. In addition, exposure to high concentrations of the vapors of hydrofluoric acid characteristically results in ulcerative tracheobronchitis and hemorrhagic pulmonary edema; this local reaction is equivalent to gaseous hydrogen chloride. From accidental, occupational, and volunteer exposures, it is estimated that the lowest lethal concentration for a 5-min human exposure to hydrogen fluoride is in the range of 50 to 250 ppm. The significant exposures by dermal or inhalation route may cause hypocalcemia and hypomagnesemia; cardiac arrhythmias may follow. Acute renal failure has also been documented after an ultimately fatal inhalation exposure. Repeated exposure to excessive concentrations of fluoride over a period of years results in increasing density of bone and eventually may cause crippling fluorosis (osteosclerosis caused by the deposition of fluoride in bone).

As a means to treat gaseous emissions, adsorption has achieved prominence for being efficient even at low pollutant concentration levels and for making it possible the discretionary recovery of the pollutant through adsorption [1]. The adsorption of polluting gases can be attained by using a number of adsorbents [3-5]. Activated carbon is the most popular and versatile adsorbent, have traditionally been used in the removal of scent, taste, and color caused by the presence of the pollutants in gaseous or liquid mixtures [6-8].

The treatment of the hydrogen fluoride found in effluents by using adsorption in alumina. Therefore, some other researchers [9-14] have studied on other adsorbent materials, while there is no data available on the adsorption of hydrogen fluoride by using activated carbon under vacuum conditions.

In the present work, the adsorption of hydrogen fluoride onto activated carbon has been investigated in vacuum conditions for absolute pressures less than 60 mbar. The Langmuir, Freundlich and Henry adsorption models are used to determine the isotherm parameters associated with the adsorption process. The adsorption mechanism of HF onto activated carbon is evaluated in terms of kinetics and thermodynamics.

## Mathematical description

### Adsorption isotherms

The study of equilibrium isotherms is fundamental in supplying the essential information required for

the design of sorption design. Several correlations have been presented for the equilibrium modeling of the adsorption systems. In this work, the Langmuir, Freundlich and Henry isotherm models have been used to describe the adsorption process [15]. Langmuir theoretically examined the adsorption of gases on solid surfaces and considered sorption as a chemical phenomenon. Basically, the Langmuir isotherm equation is in the form of hyperbolic function as follows:

$$q_e = \frac{q_m K_L P}{1 + K_L P} \quad (1)$$

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

where  $q_m$  and  $K_L$  can be determined from the linear plot of  $P/q_e$  versus  $P$  [16-19]. When the amount of adsorbate adsorbed is insignificant compared with the adsorption capacity of the adsorbent, the Langmuir equation is reduced to the following equation (Henry Equation):

$$q_e = HP \quad (3)$$

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface and is commonly presented as follows:

$$q_e = K_F P^{1/n} \quad (4)$$

where  $K_F$  and  $n$  can be determined from the linear plot of  $\log q_e$  versus  $\log P$ .

### Adsorption kinetic models

Adsorption kinetics is another basic requirement for the design of the adsorption systems. Several kinetic models have been presented for the adsorption kinetic modeling. In this study, we have used the pseudo-first-order and pseudo-second-order models to test the experimental data of the HF gas adsorption by activated carbon. The pseudo-first-order equation, developed by Lagergren, is expressed as follows [20,21]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (5)$$

In this model, the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. Integration of Eq. 5 with respect to  $t$  gives:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

where  $k_1$  and  $q_e$  can be determined from the linear plot of  $\log(q_e - q_t)$  versus  $t$ . The pseudo-second-order equation, the Ho and McKay model, is expressed as follows:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (7)$$

In this model, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. Integration of Eq. (7) with respect to  $t$  gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where  $k_2$  and  $q_e$  can be determined from the linear plot of  $t/q$  versus  $t$ .

#### Adsorption thermodynamics

In engineering practice, entropy and Gibbs free energy factors should be considered in order to determine which process will occur simultaneously. Thermodynamic parameters such as enthalpy change ( $\Delta H^\circ$ ), Gibbs free energy ( $\Delta G^\circ$ ) and entropy change ( $\Delta S^\circ$ ) can be estimated by using equilibrium constant changing with temperature. The values of standard Gibbs free energy change for the adsorption process are evaluated by using  $K_L$  values obtained from the Langmuir model at different temperatures. Thermodynamic parameters are determined using the following equation:

$$\Delta G^\circ = -RT \ln K_L \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

where  $R$  is the universal gas constant (8.314 J/mol K),  $T$  is the temperature (K) and  $K_L$  is the Langmuir adsorption isotherm constant. The enthalpy change ( $\Delta H^\circ$ ) and the entropy change ( $\Delta S^\circ$ ) of adsorption are obtained from the following equation:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

According to Eq. (11), ( $\Delta H^\circ$ ) and ( $\Delta S^\circ$ ) parameters can be calculated from the slope and intercept of a plot of  $\ln K_L$  versus  $1/T$ , respectively.

## EXPERIMENTAL

In this work, three types of cylindrical activated carbons were used as adsorbent, and they were provided by the Norit and Jacobi companies. The characteristics of adsorbents are listed in Table 1. Figure 1 shows a schematic diagram of the experimental setup. As seen in this figure, three solenoid valves (specified as SV<sub>1</sub>, SV<sub>2</sub> and SV<sub>3</sub>) are used to isolate the reservoir tank and also to connect it to the other parts of the system in vacuum conditions. A needle valve was used to control the rate of HF feeding and a micro-valve was used for controlling the rate of N<sub>2</sub> feeding.

Table 1. Characteristics of the activated carbons used

| Activated carbon | $d$<br>mm | Density<br>kg/m <sup>3</sup> | BET-surface area<br>m <sup>2</sup> /g |
|------------------|-----------|------------------------------|---------------------------------------|
| First type       | 3         | 505                          | 1100                                  |
| Second type      | 4         | 385                          | 1100                                  |
| Third type       | 4         | 365                          | 1200                                  |

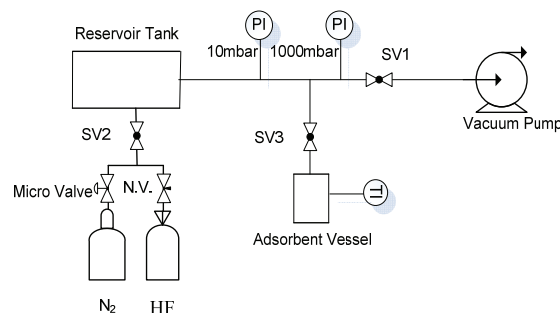


Figure 1. A schematic diagram of the experimental setup.

The pressure was measured by two pressure gages at ranges of 0-10 mbar (with a precision of  $\pm 0.001$  mbar) and 0-1000 mbar (with a precision of  $\pm 0.1$  mbar). The temperature was measured by a thermometer (Pt-100) with a precision of  $\pm 0.1$  °C. Each experiment was carried out at three temperatures (28, 40 and 55 °C) to determine the effect of temperature and study of the adsorption thermodynamic parameters. In this paper, we used the bath technique [12] and each experiment included the following five steps:

1. In the first step, one gram of activated carbon was weighed by a balance with a precision of  $\pm 0.001$  g and then placed in the adsorbent vessel.
2. At the second step, the needle and micro valves were first closed and the valves of SV<sub>1</sub>, SV<sub>2</sub> and SV<sub>3</sub> were then opened. The vacuum pump creates vacuum conditions so that the reached pressure was less than 0.01 mbar. After achieving vacuum conditions, the SV<sub>1</sub> valve was closed and the static leak test was performed on system.
3. At the third step, the SV<sub>3</sub> valve was first closed and hydrogen fluoride (HF) was sent into the reservoir tank, then the initial absolute pressure of reservoir tank was fixed by needle valve on 5, 10, 20, 30, 40 and 60 mbar for each experiment.
4. At the fourth step, the SV<sub>2</sub> valve was first closed and the SV<sub>3</sub> valve was then opened. The pressure was also measured with respect time by pressure gage. This measurement continued until achieving equilibrium conditions.
5. At the fifth step, the SV<sub>1</sub> valve and micro valve were first opened and all hydrogen fluorides was discharged from system by nitrogen gas then adsorbent was weighed by balance. In this step, the amount of HF adsorbed on carbon can be measured.

As all experiments were carried out at vacuum pressure, so the amount of hydrogen fluoride can be calculated from the ideal gas law [22]:

$$q = \frac{(P_0 - P) V}{MRT} \frac{V}{m} \quad (12)$$

The average absolute value of relative error, *AARE*, is used to compare the predicted results with the experimental data. It is defined as follows:

$$AARE = \frac{1}{NDP} \sum_{i=1}^{NDP} \frac{|\text{Predicted value} - \text{Experimental value}|}{\text{Experimental value}} \quad (13)$$

in which NDP is the number values of data points.

## RESULTS AND DISCUSSION

### Study of contact time

The rate of the adsorption is a very important factor in the design of an adsorption system. The effect of contact time on the equilibrium uptake of HF adsorbed by three types of carbons at initial pressures of 5, 10, 20, 30, 40 and 60 mbar were studied at temperatures of 28, 40 and 55 °C. For example, the plot of *q* (mg/g) *versus* *t* for the second type of carbon is shown in Figure 2. According to this figure, the adsorption capacity increases by increasing contact time. The equilibrium is reached after of 60, 70, 80, 200 and 250 min for initial absolute pressures of 5,

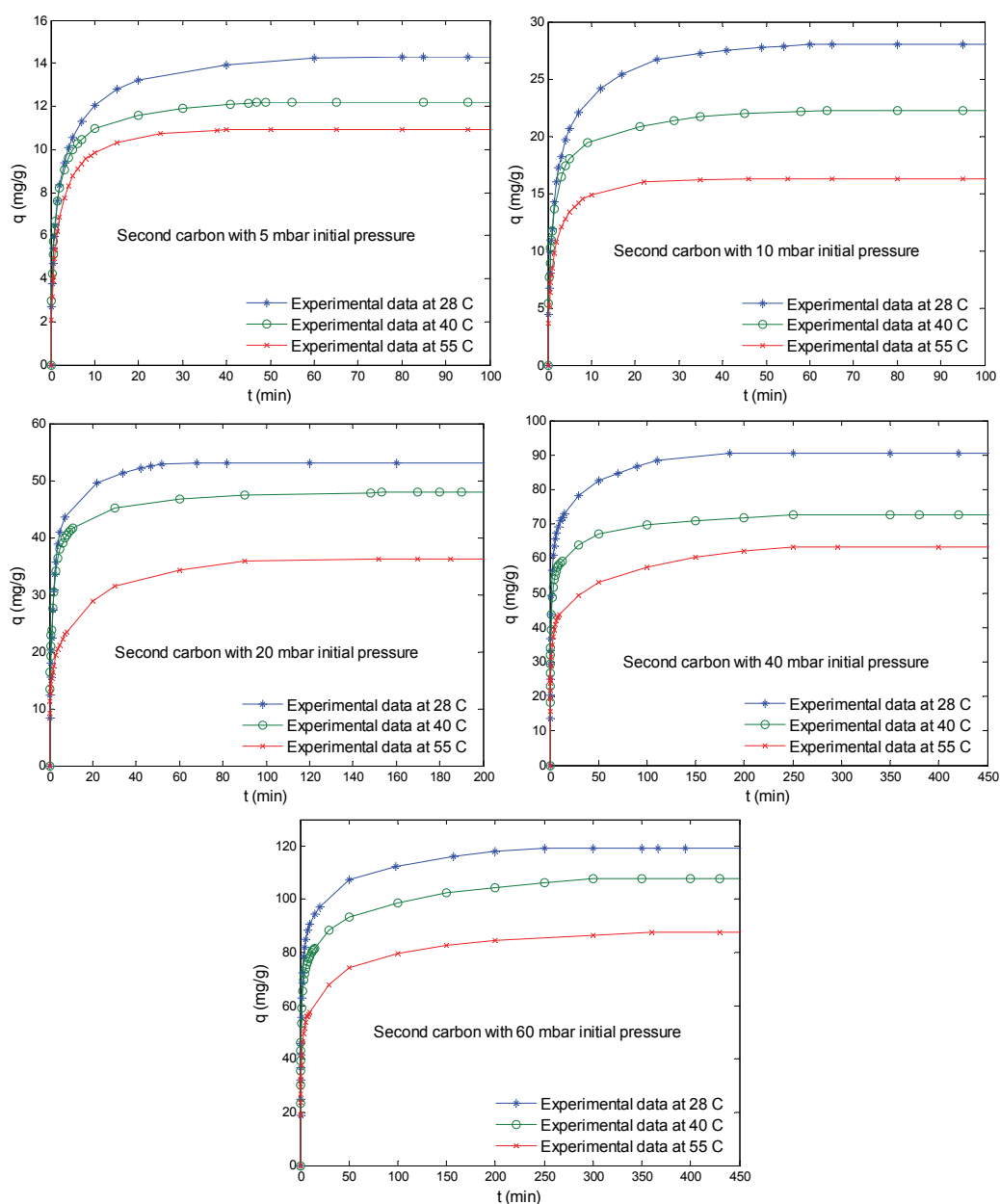


Figure 2. Effect of contact time on the HF gas adsorption by the activated carbon at temperatures of 28, 40 and 55 °C.

10, 20, 20, 40 and 60 mbar, respectively. This figure also shows that the sorption takes place in two stages. The first stage can be attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surface. The second stage may be attributed to very slow diffusion of the adsorbate from the surface site into the inner pores. Thus, the initial part of HF adsorption by activated carbon may be governed by the initial interparticle transport of HF controlled by surface diffusion process and the second part controlled by pore diffusion [23].

#### Study of the effect of initial pressure and temperature

Table 2 shows the adsorption of the HF gas onto activated carbons as a function of initial pressure of the HF gas and temperature at equilibrium conditions. According to this table, the adsorption of the HF gas decreases by increasing temperature up to 55 °C. This shows that the adsorption of the HF gas on all activated carbons is controlled by an exothermic process. The sorption of the HF gas onto activated carbons may involve not only a physical but also a chemical sorption. This effect may be due to the fact that at higher temperature a decrease in active sites occurs due to bond rupture.

The adsorption capacity also increases by an increase in initial gas pressure because it provides a driving force to overcome mass transfer resistance between adsorbent and adsorption medium. So higher sorption capacities are obtained at higher initial pressures of the HF gas at all temperature studied.

#### Study of adsorption isotherms

The analysis of experimental equilibrium data is important for developing an equation that can be ap-

plied for the design purposes. In this investigation, in order to get the equilibrium data, initial pressures of the HF gas were changed while the absorbent weight in each experiment was kept constant.

The Langmuir, Freundlich, and Henry adsorption models were used to determine the isotherm parameters associated with the adsorption process. The constants of these models as well as the values of  $R^2$  and  $AARE\%$  are given in Table 3. From  $R^2$  and  $AARE\%$  values in Table 3, it is clear that the Freundlich model predicts experimental data better than the other models. Figure 3 also shows the comparison of experimental data with the  $q_e$  values obtained by applying these models.

The maximum capacity,  $q_m$ , determined from the Langmuir equation defines the total capacity of the adsorption for the HF gas. The  $q_m$  decreases with an increase in temperature. The value of  $q_m$  obtained at 28 °C appears to be higher in comparison with uptake obtained at other temperatures. The higher value of  $K_L$  also implied strong bonding of HF to activated carbon at this temperature.

#### Study of kinetic models

In order to clarify the adsorption kinetics of HF onto activated carbon Lagergren pseudo-first-order and pseudo-second-order kinetic models are applied to the experimental data.

For example, Figure 4 shows the experimental data fitted to the pseudo-first-order model for the first type activated carbon and Figure 5 indicates the experimental data fitted to the pseudo-second-order model for the second type activated carbon. The obtained results were shown in Tables 4-6. As it can

Table 2. Effect of initial pressure on the adsorption capacity at different temperatures

| Initial pressure, mbar | Temperature, °C | $q_e / \text{mg g}^{-1}$ |                   |                  |
|------------------------|-----------------|--------------------------|-------------------|------------------|
|                        |                 | The first carbon         | The second carbon | The third carbon |
| 5                      | 28              | 14.52                    | 14.28             | 14.21            |
| 10                     | 28              | 27.41                    | 28                | 26.00            |
| 20                     | 28              | 58.87                    | 53.09             | 52.38            |
| 30                     | 28              | 85.95                    | 78                | 73.88            |
| 40                     | 28              | 90.38                    | 90.38             | 94.58            |
| 60                     | 28              | 124.62                   | 119.05            | 121.04           |
| 5                      | 40              | 12.4                     | 12.18             | 12.16            |
| 10                     | 40              | 21.2                     | 22.19             | 21.03            |
| 20                     | 40              | 48.26                    | 47.95             | 45.22            |
| 40                     | 40              | 82.28                    | 72.71             | 79.99            |
| 60                     | 40              | 107.54                   | 107.92            | 109.45           |
| 5                      | 55              | 10.4                     | 10.91             | 10.37            |
| 10                     | 55              | 17.96                    | 16.29             | 17.13            |
| 20                     | 55              | 38.56                    | 36.25             | 36.34            |
| 40                     | 55              | 60.26                    | 63.18             | 69.39            |
| 60                     | 55              | 88.57                    | 87.65             | 86.92            |

Table 3. The constants obtained for Freundlich, Langmuir and Henry equations

| Model      | Model constant  | First activated carbon |        |        | Second activated carbon |        |        | Third activated carbon |        |        |
|------------|-----------------|------------------------|--------|--------|-------------------------|--------|--------|------------------------|--------|--------|
|            |                 | Temperature, °C        |        |        |                         |        |        |                        |        |        |
|            |                 | 28                     | 40     | 55     | 28                      | 40     | 55     | 28                     | 40     | 55     |
| Langmuir   | $K_L$           | 0.0476                 | 0.0326 | 0.0236 | 0.0351                  | 0.0266 | 0.0196 | 0.0451                 | 0.0288 | 0.0244 |
|            | $q_m$           | 226.4                  | 199.8  | 164.3  | 268.8                   | 237.1  | 200.6  | 258.9                  | 235.6  | 213.9  |
|            | $R^2$           | 0.989                  | 0.994  | 0.989  | 0.992                   | 0.995  | 0.989  | 0.997                  | 0.992  | 0.986  |
|            | $AARE\%$        | 14.53                  | 13.21  | 15.76  | 17.02                   | 13.10  | 15.41  | 10.71                  | 12.15  | 14.64  |
| Freundlich | $K_F$           | 0.0162                 | 0.0094 | 0.0054 | 0.0152                  | 0.0109 | 0.0055 | 0.0158                 | 0.0082 | 0.0059 |
|            | $n$             | 1.588                  | 1.443  | 1.356  | 1.523                   | 1.453  | 1.249  | 1.516                  | 1.31   | 1.278  |
|            | $R^2$           | 0.994                  | 0.996  | 0.992  | 0.998                   | 0.987  | 0.992  | 0.984                  | 0.989  | 0.990  |
|            | $AARE\%$        | 3.54                   | 6.20   | 11.35  | 5.13                    | 3.30   | 12.58  | 3.48                   | 8.82   | 11.38  |
| Henry      | $H \times 10^3$ | 6.79                   | 4.10   | 2.37   | 5.08                    | 4.30   | 2.76   | 6.80                   | 4.52   | 2.816  |
|            | $R^2$           | 0.972                  | 0.980  | 0.988  | 0.982                   | 0.987  | 0.992  | 0.984                  | 0.989  | 0.990  |
|            | $AARE\%$        | 33.44                  | 24.84  | 24.02  | 37.29                   | 24.27  | 22.57  | 27.74                  | 22.12  | 23.03  |

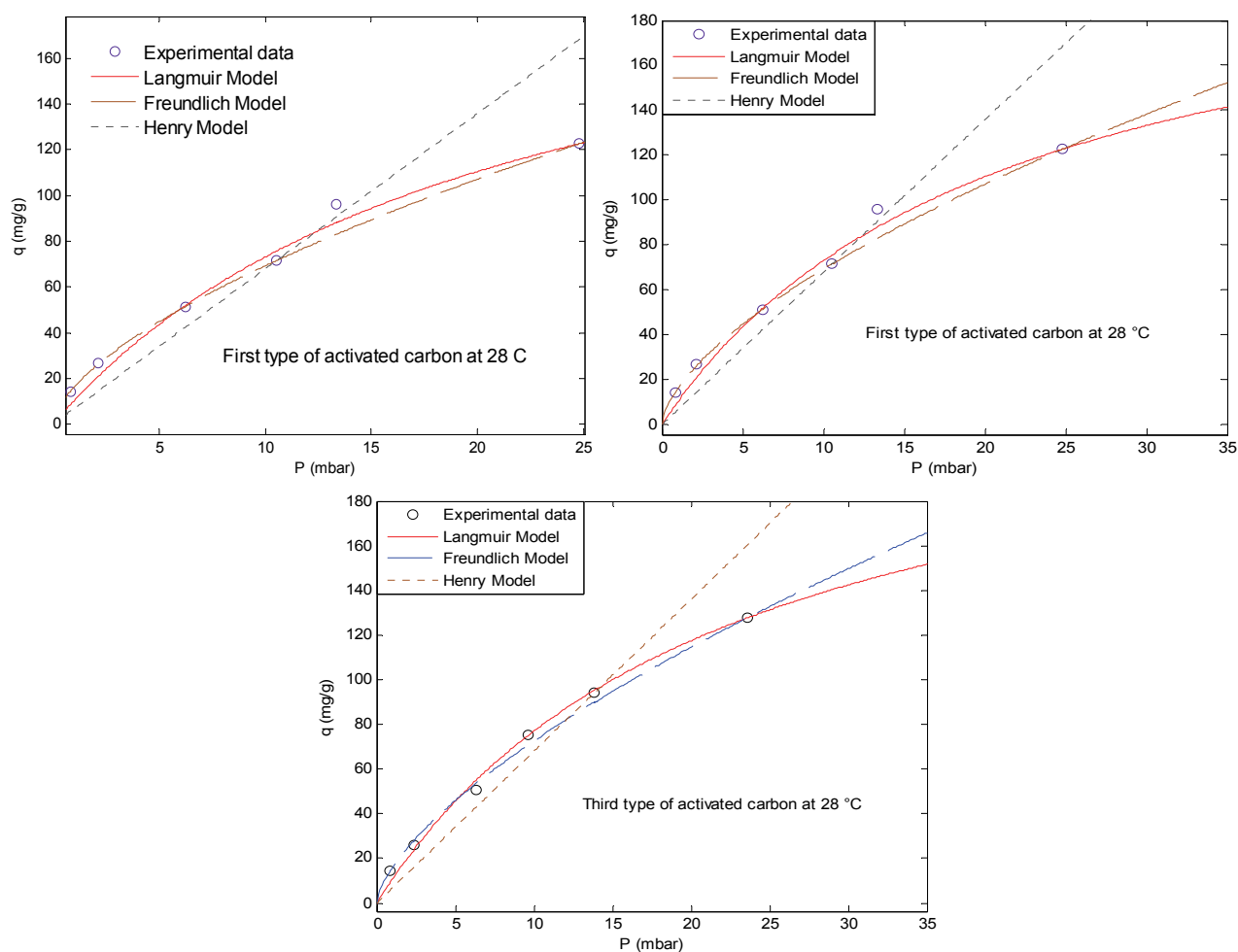


Figure 3. Comparison between adsorption isotherms of Freundlich, Langmuir and Henry with experimental data.

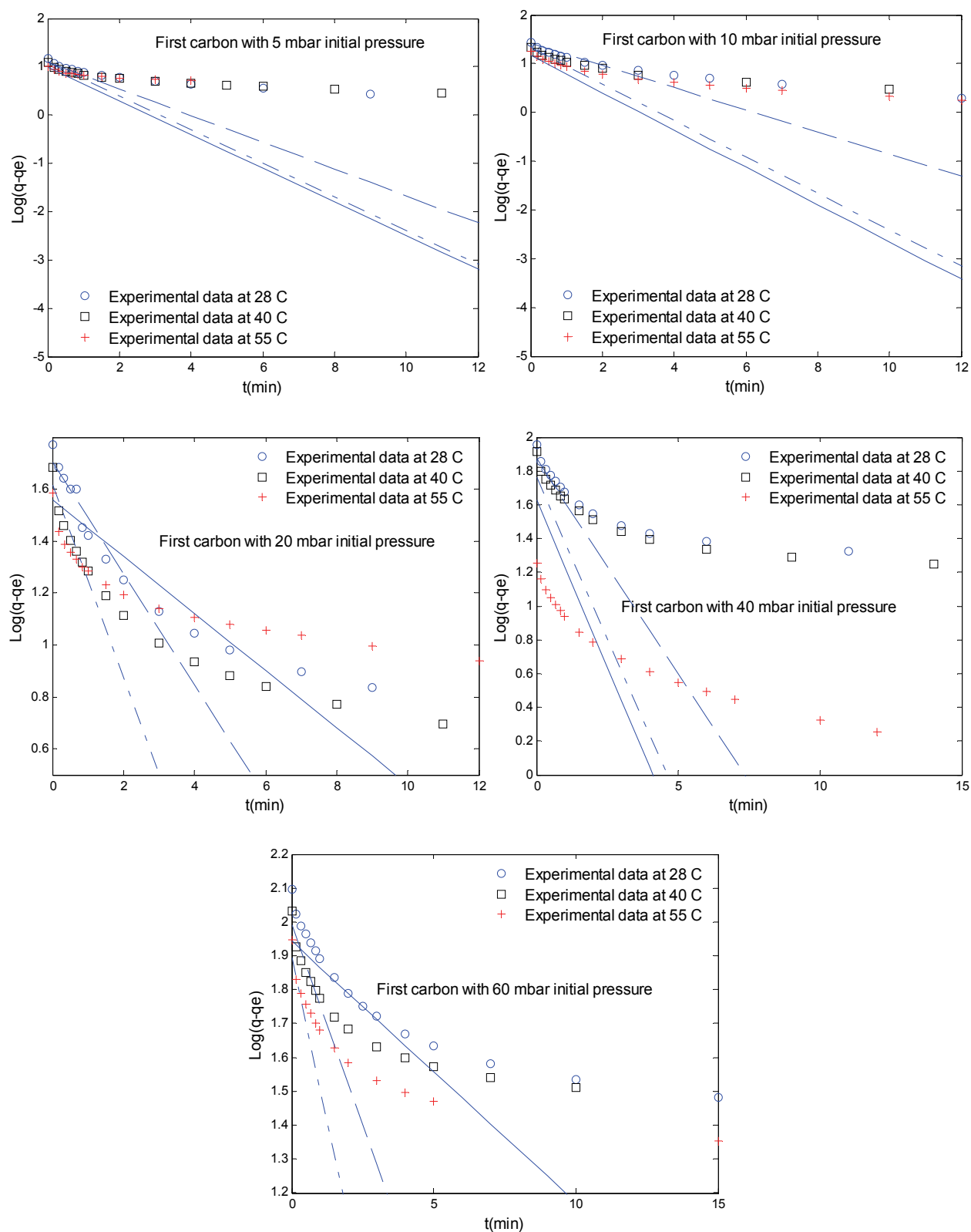


Figure 4. Pseudo-first-order kinetic plots for the HF gas adsorption onto activated carbon.

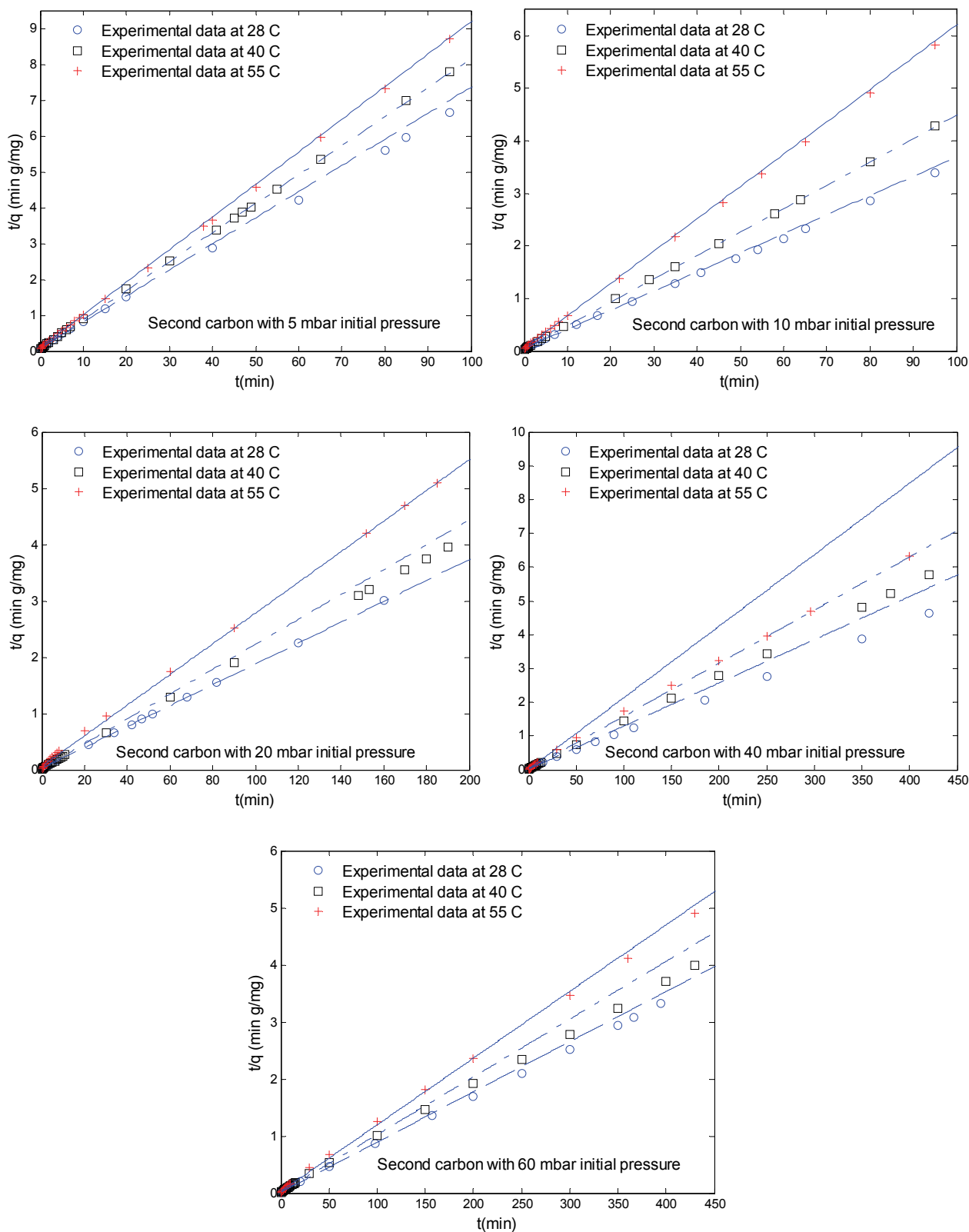


Figure 5. Plot of  $t/q$  versus  $t$  for the HF gas adsorption onto activated carbon (the pseudo-first-order kinetic model).

Table 4. Kinetic parameters obtained for HF adsorption onto the first type of activated carbon

| Initial $P$<br>mbar | $T / ^\circ\text{C}$ | $q_{e,\text{exp}}$<br>mg/g | Pseudo-first-order kinetic equation |                                     |       |         | Pseudo-second-order kinetic equation |                                          |       |         |
|---------------------|----------------------|----------------------------|-------------------------------------|-------------------------------------|-------|---------|--------------------------------------|------------------------------------------|-------|---------|
|                     |                      |                            | $q_e / \text{mg g}^{-1}$            | $k_1 \times 10^2 / \text{min}^{-1}$ | $R^2$ | AARE, % | $q_{e,2} / \text{mg g}^{-1}$         | $k_2 \times 10^3 / \text{g mg min}^{-1}$ | $R^2$ | AARE, % |
| 5                   | 28                   | 14.52                      | 13.29                               | 72.39                               | 96.03 | 13.88   | 14.51                                | 61.6                                     | 99.23 | 7.65    |
| 10                  | 28                   | 27.41                      | 26.44                               | 76.82                               | 98.16 | 10.51   | 27.8                                 | 37.41                                    | 99.89 | 3.83    |
| 20                  | 28                   | 58.87                      | 57.21                               | 70.92                               | 98.22 | 7.90    | 58.98                                | 18.08                                    | 99.83 | 3.47    |
| 30                  | 28                   | 85.95                      | 74.69                               | 50.59                               | 94.50 | 12.20   | 80.94                                | 8.648                                    | 99.14 | 5.92    |
| 40                  | 28                   | 90.38                      | 87.2                                | 67.95                               | 97.73 | 12.82   | 87.51                                | 11.04                                    | 98.94 | 6.59    |
| 60                  | 28                   | 124.62                     | 99.54                               | 49.98                               | 93.44 | 16.04   | 123.6                                | 4.196                                    | 98.31 | 10.32   |
| 5                   | 40                   | 12.4                       | 9.036                               | 96.33                               | 94.06 | 15.85   | 12.56                                | 52.98                                    | 98.45 | 14.07   |
| 10                  | 40                   | 21.2                       | 20.48                               | 70.22                               | 98.09 | 11.93   | 21.4                                 | 54.55                                    | 99.67 | 6.79    |
| 20                  | 40                   | 48.26                      | 47.12                               | 104.7                               | 97.79 | 7.47    | 47.79                                | 32.11                                    | 99.38 | 3.45    |
| 40                  | 40                   | 82.28                      | 66.59                               | 89.64                               | 94.69 | 13.58   | 75.38                                | 14.54                                    | 97.62 | 8.15    |
| 60                  | 40                   | 107.54                     | 75.01                               | 109.5                               | 95.31 | 14.79   | 108.1                                | 6.42                                     | 98.51 | 13.90   |
| 5                   | 55                   | 10.4                       | 9.572                               | 38.06                               | 95.22 | 18.38   | 9.982                                | 47.79                                    | 97.51 | 13.59   |
| 10                  | 55                   | 17.96                      | 17.1                                | 78.17                               | 97.48 | 10.16   | 17.79                                | 61.3                                     | 99.55 | 3.66    |
| 20                  | 55                   | 38.56                      | 36.57                               | 75.36                               | 91.63 | 15.82   | 37.56                                | 23.89                                    | 97.67 | 10.55   |
| 40                  | 55                   | 60.26                      | 60.26                               | 68.71                               | 96.88 | 17.77   | 60.44                                | 16.25                                    | 98.67 | 11.58   |
| 60                  | 55                   | 88.57                      | 88.75                               | 49.3                                | 96.63 | 20.59   | 89                                   | 9.556                                    | 98.94 | 11.35   |

Table 5. Kinetic parameters obtained for HF adsorption onto the second type of activated carbon

| Initial $P$<br>mbar | $T / ^\circ\text{C}$ | $q_{e,\text{exp}}$<br>mg/g | First order kinetic equation |                                     |       |         | Second order kinetic equation |                                          |       |         |
|---------------------|----------------------|----------------------------|------------------------------|-------------------------------------|-------|---------|-------------------------------|------------------------------------------|-------|---------|
|                     |                      |                            | $q_e / \text{mg g}^{-1}$     | $k_1 \times 10^2 / \text{min}^{-1}$ | $R^2$ | AARE, % | $q_{e,2} / \text{mg g}^{-1}$  | $k_2 \times 10^3 / \text{g mg min}^{-1}$ | $R^2$ | AARE, % |
| 5                   | 28                   | 14.28                      | 12.54                        | 63.82                               | 92.62 | 14.17   | 13.74                         | 64.73                                    | 99.33 | 6.36    |
| 10                  | 28                   | 28                         | 25.58                        | 51.91                               | 94.25 | 13.81   | 27.51                         | 26.22                                    | 99.56 | 5.78    |
| 20                  | 28                   | 53.09                      | 50.38                        | 49.24                               | 96.26 | 12.02   | 53.98                         | 12.61                                    | 99.90 | 4.29    |
| 30                  | 28                   | 78                         | 66.97                        | 53.78                               | 93.65 | 13.31   | 69.57                         | 11.06                                    | 99.62 | 5.78    |
| 40                  | 28                   | 90.38                      | 75.01                        | 58.78                               | 92.21 | 12.80   | 78.2                          | 11.27                                    | 99.72 | 4.00    |
| 60                  | 28                   | 119.05                     | 98                           | 54.04                               | 91.80 | 13.64   | 102.2                         | 7.941                                    | 99.66 | 4.58    |
| 5                   | 40                   | 12.18                      | 12.11                        | 79.84                               | 97.35 | 11.82   | 12.37                         | 94.23                                    | 99.77 | 5.14    |
| 10                  | 40                   | 22.19                      | 21.32                        | 86.01                               | 98.18 | 10.70   | 22.49                         | 50.24                                    | 99.61 | 5.93    |
| 20                  | 40                   | 47.95                      | 41.35                        | 85.28                               | 93.87 | 11.99   | 45.29                         | 23.19                                    | 99.63 | 6.55    |
| 40                  | 40                   | 72.71                      | 58.19                        | 88.02                               | 96.20 | 12.31   | 63.64                         | 18.1                                     | 99.32 | 6.85    |
| 60                  | 40                   | 107.92                     | 78.47                        | 89.2                                | 94.51 | 12.19   | 85.65                         | 13.74                                    | 98.84 | 7.06    |
| 5                   | 55                   | 10.91                      | 9.729                        | 80.25                               | 95.79 | 9.97    | 11.01                         | 78.16                                    | 99.75 | 4.89    |
| 10                  | 55                   | 16.29                      | 14.49                        | 87.85                               | 96.03 | 10.55   | 16.26                         | 66.88                                    | 99.62 | 4.61    |
| 20                  | 55                   | 36.25                      | 36.25                        | 25.24                               | 94.62 | 27.92   | 36.73                         | 12.43                                    | 97.37 | 19.36   |
| 40                  | 55                   | 63.18                      | 42.76                        | 91.1                                | 92.82 | 16.89   | 47.26                         | 24.93                                    | 97.98 | 11.72   |
| 60                  | 55                   | 87.65                      | 87.65                        | 17.71                               | 94.28 | 29.79   | 87.97                         | 4.227                                    | 97.64 | 19.63   |

Table 6. Kinetic parameters obtained for HF adsorption onto the third type of activated carbon

| Initial $P$<br>mbar | $T / ^\circ\text{C}$ | $q_{e,\text{exp}}$<br>mg/g | First order kinetic equation |                                     |       |         | Second order kinetic equation |                                          |       |         |
|---------------------|----------------------|----------------------------|------------------------------|-------------------------------------|-------|---------|-------------------------------|------------------------------------------|-------|---------|
|                     |                      |                            | $q_e / \text{mg g}^{-1}$     | $k_1 \times 10^2 / \text{min}^{-1}$ | $R^2$ | AARE, % | $q_{e,2} / \text{mg g}^{-1}$  | $k_2 \times 10^3 / \text{g mg min}^{-1}$ | $R^2$ | AARE, % |
| 5                   | 28                   | 14.21                      | 12.98                        | 56.61                               | 96.43 | 10.73   | 14.1                          | 58.93                                    | 99.27 | 5.41    |
| 10                  | 28                   | 26.00                      | 23.88                        | 104.1                               | 98.17 | 9.89    | 26.08                         | 52.07                                    | 99.82 | 3.98    |
| 20                  | 28                   | 52.38                      | 45.31                        | 63.78                               | 97.2  | 11.58   | 50.81                         | 16.24                                    | 99.83 | 4.41    |
| 30                  | 28                   | 73.88                      | 64.14                        | 57.41                               | 97.92 | 13.60   | 70.56                         | 10.43                                    | 99.14 | 6.91    |
| 40                  | 28                   | 94.58                      | 92.03                        | 41.33                               | 97.28 | 14.30   | 92.66                         | 7.4                                      | 99.02 | 7.42    |
| 60                  | 28                   | 121.04                     | 115.9                        | 68.29                               | 97.06 | 15.34   | 116.8                         | 8.253                                    | 98.74 | 7.94    |
| 5                   | 40                   | 12.16                      | 12.16                        | 118.1                               | 98.51 | 10.24   | 12.31                         | 158.1                                    | 99.82 | 3.57    |

Table 6. Continued

| Initial $P$<br>mbar | $T/^\circ\text{C}$ | $q_{e,\text{exp}}$<br>mg/g | First order kinetic equation |                                     |       |         | Second order kinetic equation |                                          |       |         |
|---------------------|--------------------|----------------------------|------------------------------|-------------------------------------|-------|---------|-------------------------------|------------------------------------------|-------|---------|
|                     |                    |                            | $q_e / \text{mg g}^{-1}$     | $k_1 \times 10^2 / \text{min}^{-1}$ | $R^2$ | AARE, % | $q_{e,2} / \text{mg g}^{-1}$  | $k_2 \times 10^3 / \text{g mg min}^{-1}$ | $R^2$ | AARE, % |
| 10                  | 40                 | 21.03                      | 20.69                        | 126.4                               | 98.72 | 8.50    | 21.16                         | 107.3                                    | 99.86 | 2.46    |
| 20                  | 40                 | 45.22                      | 40.32                        | 128                                 | 94.62 | 9.38    | 43.01                         | 44.56                                    | 99.63 | 4.30    |
| 40                  | 40                 | 79.99                      | 58.18                        | 109.5                               | 94.42 | 13.44   | 63.3                          | 22.4                                     | 98.56 | 8.53    |
| 60                  | 40                 | 109.45                     | 75.78                        | 110.3                               | 94.25 | 12.56   | 81.32                         | 17.92                                    | 98.02 | 8.09    |
| 5                   | 55                 | 10.37                      | 9.92                         | 97.3                                | 90.33 | 13.67   | 10.48                         | 136.3                                    | 99.46 | 6.82    |
| 10                  | 55                 | 17.13                      | 16.13                        | 133.5                               | 91.78 | 10.25   | 17.24                         | 106.9                                    | 99.69 | 4.26    |
| 20                  | 55                 | 36.34                      | 30.67                        | 131.9                               | 92.53 | 11.11   | 32.7                          | 61.29                                    | 99.12 | 6.15    |
| 40                  | 55                 | 69.39                      | 48.21                        | 129.1                               | 95.01 | 12.04   | 51.03                         | 38.81                                    | 97.84 | 7.51    |
| 60                  | 55                 | 86.92                      | 59.16                        | 131.8                               | 94.47 | 11.69   | 62.1                          | 33.64                                    | 97.21 | 7.45    |

be seen from these tables, the correlation coefficient ( $R^2$ ) for the pseudo-first-order rate equation was found to be lower than 98.72 and for the pseudo-second-order was greater than 97.2. Also, the average absolute values of relative error (AARE%) for equations of the pseudo-first-order and the pseudo-second-order were 14.5 and 7.6%, respectively. Hence, it was concluded that the HF gas adsorption by activated carbon was better described by the pseudo-second-order rate equation than by the pseudo-first-order rate equation.

#### Study of adsorption thermodynamics

According to Eq. (11), ( $\Delta H^\circ$ ) and ( $\Delta S^\circ$ ) parameters can be calculated from the slope and intercept of a plot of  $\ln K_L$  versus  $1/T$ , respectively (Figure 6). The Gibbs free energy is also calculated from Eq.

(10). The values of thermodynamic parameters are given in Table 7. The negative  $\Delta G^\circ$  values indicate that thermodynamically feasible and spontaneous nature of adsorption of HF on activated carbon. The negative  $\Delta H^\circ$  values indicate the exothermic nature of the adsorption of HF onto activated carbon in the temperature range of 28–55  $^\circ\text{C}$ . For the first type activated carbon, the negative value of  $\Delta S^\circ$  suggests a decrease in randomness at solid/gas interface during the adsorption process, and positive  $\Delta S^\circ$  values were obtained for the second and third type of activated carbon.

#### CONCLUSIONS

The adsorption process of hydrogen fluoride on activated carbon was investigated under vacuum

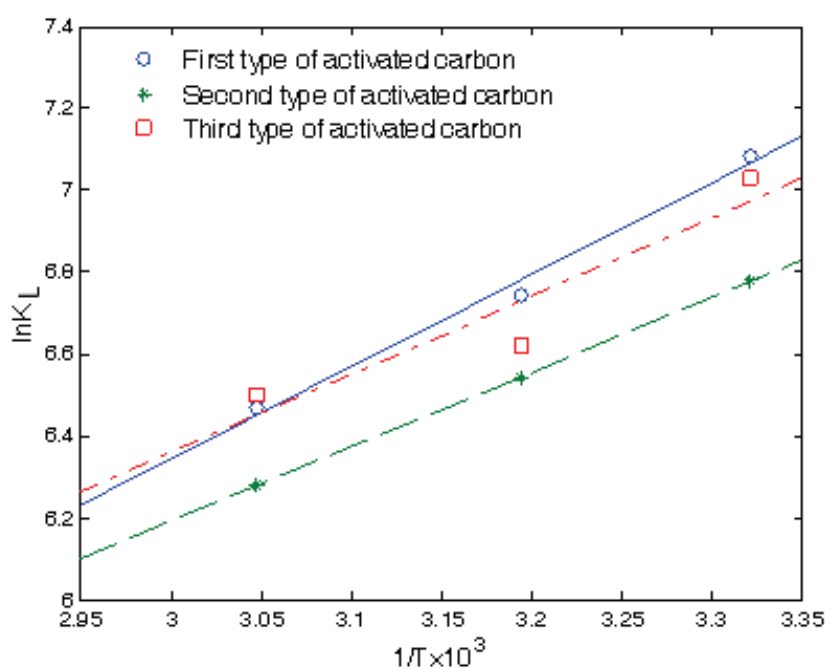
Figure 6. Plot of  $\ln K_L$  versus  $1/T$  (Van't Hoff Plot).

Table 7. Thermodynamic parameters obtained for the HF adsorption onto activated carbon

| Type of activated carbon as adsorbent | $T / ^\circ\text{C}$ | $K_L / \text{l mol}^{-1}$ | $\Delta G^\circ / \text{kJ mol}^{-1}$ | $\Delta H^\circ / \text{kJ mol}^{-1}$ | $\Delta S^\circ / \text{J mol}^{-1} \text{K}^{-1}$ |
|---------------------------------------|----------------------|---------------------------|---------------------------------------|---------------------------------------|----------------------------------------------------|
| First                                 | 28                   | 1191.8                    | -17.689                               | -18.665                               | -3.239                                             |
|                                       | 40                   | 848.8                     | -16.964                               |                                       |                                                    |
|                                       | 55                   | 643.9                     | -17.455                               |                                       |                                                    |
| Second                                | 28                   | 878.72                    | -17.651                               | -15.107                               | 6.168                                              |
|                                       | 40                   | 692.54                    | -17.038                               |                                       |                                                    |
|                                       | 55                   | 534.73                    | -17.519                               |                                       |                                                    |
| Third                                 | 28                   | 1129.2                    | -17.602                               | -15.855                               | 5.315                                              |
|                                       | 40                   | 749.8                     | -17.131                               |                                       |                                                    |
|                                       | 55                   | 665.7                     | -17.599                               |                                       |                                                    |

conditions. The equilibrium data were interpreted using Langmuir, Freundlich, and Henry isotherms. The Freundlich isotherm model gave better fittings than the other models. The maximum adsorption capacity was found to be 226.4, 268.8 and 247.8 mg/g for the first, second and third activated carbon, respectively. The results showed that the adsorption kinetic was well represented by the pseudo-second-order model. Thermodynamic calculations showed that the hydrogen fluoride sorption process by activated carbon was spontaneous and exothermic in nature with the HF removal capacity decreasing with increasing temperature. The results of the present study showed that activated carbon is an effective adsorbent for the removal of HF under vacuum conditions.

### Nomenclature

|                  |                                                              |
|------------------|--------------------------------------------------------------|
| $H$              | Henry constant (mg/g mbar)                                   |
| $\Delta H^\circ$ | Enthalpy change (J/mol)                                      |
| $k_1$            | The pseudo first-order rate constant ( $\text{min}^{-1}$ )   |
| $k_2$            | The pseudo second-order rate constant (g/mg min)             |
| $K_F$            | Constant of Eq.(9) ( $\text{mg g}^{-1} \text{mbar}^{-1/n}$ ) |
| $K_L$            | Langmuir isotherm constant ( $\text{mbar}^{-1}$ )            |
| $M$              | Molecular weight of the gas (g/gmol)                         |
| $m$              | Adsorbent mass (g)                                           |
| $n$              | Empirical parameter (-)                                      |
| $P_0$            | Initial pressure (Pa)                                        |
| $P$              | Final pressure (Pa)                                          |
| $q_e$            | The equilibrium adsorption capacity (mg/g)                   |
| $q_m$            | The monolayer adsorption capacity of the adsorbent (mg/g)    |
| $q_t$            | Amount of adsorbate absorbed at time $t$ (min)(mg/g)         |
| $R$              | The universal gas constant (8.314 J/mol.K)                   |
| $\Delta S^\circ$ | Entropy change (J/mol.K)                                     |
| $T$              | Absolute temperature (K)                                     |
| $t$              | Time (min)                                                   |
| $V$              | The volume of the gas (l)                                    |

### Subscript

e Equilibrium conditions

### Superscript

o Standard conditions

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NAUČNI RAD

## ADSORPCIJA FLUOROVODONIKA NA AKTIVNOM UGLJU U VAKUUMU: RAVNOTEŽNA, KINETIČKA I TERMODINAMIČKA ISTRAŽIVANJA

*U ovom radu je ispitivana adsorpcija gasa fluorovodonika na tri aktivna uglja u uslovima vakuuma. Ispitivani su uticaji eksperimentalnih parametara kao što su: početni pritisak fluorovodonika, kontaktno vreme i temperatura, na proces adsorpcije. Dobljeni rezultati su pokazali da se količina adsorbovanog fluorovodnika na aktivnom uglju povećava sa povećanjem početnog pritiska gasa, a da se smanjuje sa povećanjem temperature. Model Freund-lich-ove izoterme bolje fituje ravnotežne podatke nego drugi modeli. Koristeći model Langmuir-ove izoterme, maksimalni kapaciteti adsorpcije prvog, drugog i trećeg tipa aktivnog uglja iznose 226,4, 268,8 i 258,9 mg/g, redom. Eksperimentalni podaci su, takođe, iskorišćeni za dobijanje kinetičkih karakteristika adsorpcije, a nađeno je da ovaj adsorpcioni proces sledi kinetiku pseudo drugog reda. Termodinamički parametri adsorpcije: promene slobodne energije, entalpije i entropije, izračunati su za temperaturni interval 20-55 °C. Rezultati su pokazali da je adsorpcija fluorovodonika na aktivnom uglju izvodljiva, spontana i egzotermna.*

*Ključne reči: aktivni ugalj, fluorovodonik, adsorpcija, kinetika, termodinamika.*