



## INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

### ADSORPTION OF PERCHLORATE BY GFH AND GAC IN WATER

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#### ABSTRACT

This study aims to remove perchlorate when using granular ferric hydroxide (GFH) and granular activated carbon (GAC) in water. Dynamic and equilibrium adsorption experiments were performed to evaluate the thermodynamic behaviour of perchlorate on GFH and GAC. The experimental results showed that two dynamic adsorption experiments achieved equilibrium in approximately forty minutes and eight hours. The maximal adsorption capacities of GAC and GFH were 33.8 - 28.2 mg/g and 2.7 - 3.5 mg/g, respectively, at a constant temperature between 5 °C and 45 °C. The thermodynamic parameters, such as the equilibrium constant ( $K_0$ ), the standard free energy changes ( $\Delta G^\circ$ ), the standard enthalpy change ( $\Delta H^\circ$ ) and the standard entropy change ( $\Delta S^\circ$ ), were obtained.

**KEYWORDS:** Adsorption, granular ferric hydroxide, granular activated carbon, kinetics, perchlorate, thermodynamics

#### INTRODUCTION

Aqueous perchlorate in its monovalent anion form ( $\text{ClO}_4^-$ ) is nonreactive and stable; it does not precipitate with cationic irons and is not removed by typical sediments in aquifers (Brown and Gu 2006). Humans can be exposed to perchlorate through food, water contamination, or other sources that exist in the environment (Craig et al. 2013). Numerous studies have found that perchlorate poses a potential threat to human health. The U.S. Environmental Protection Agency has set a reference dose standard of 0.7  $\mu\text{g}$  of perchlorate/kg/day to protect the safety of the public (USEPA 2004).

Currently, three methods are employed to remove perchlorate or remediate perchlorate pollution: physical remediation (ion exchange, membrane separation, and adsorption using adsorbents), chemical remediation (advanced chemical or electrochemical restoration), and biological remediation (phytoremediation and microorganism biodegradation) (Yang et al. 2013). To date, researchers from numerous countries have tested the efficacy of various adsorbents in removing perchlorate

such as surfactant loaded activated carbons, ion-exchange membranes, synthetic-layered double hydroxides, and organic-clay minerals (Parette et al. 2005; Srinivasan and Sorial 2009; Kim et al. 2011).

Adsorption studies were conducted to remove contaminants from aqueous solution by using low-cost materials as an alternative to GAC (Weng et al. 2009; Weng et al. 2013; Weng et al. 2012; Weng et al. 2008). A quaternary amine-modified reed adsorbed perchlorate was reported (Baidas et al. 2011). Such performance is suitable for the Langmuir–Freundlich model, and its adsorption is most efficient between pH 3.5 and pH 7.0. The adsorption capacity of granular ferric hydroxide showed it is applicable for perchlorate with pH values ranging from 6.0 to 6.5; it is also suitable for use in the Langmuir model (Kumar et al. 2010). The acidified, zero-valent aluminium and aluminium hydroxide removed 95% of perchlorate when the concentration of perchlorate was 10 mg/L (Lien et al. 2010). In summary, these methods demonstrate the adsorption of organics or perchlorate on various adsorbents. Presently, there is a lack of

adsorption results and model analyses for comparing the removal of perchlorate adsorption when using GFH.

With the concern of perchlorate polluting drinking water and degrading its quality, innovative treatment technologies are of particular interest. Because of cost factors, the strong demand for safe drinking water warrants research into the ability of GFH-adsorption to remove perchlorate from surface water or groundwater. GAC is firm and has high levels of chemical stability with a specific surface area. The surface complexion of activated carbon and static electricity are used to adsorb perchlorate onto the activated carbon.

To better understanding the kinetics and performance of perchlorate adsorbing to GFH and GAC, this study compared the adsorption properties of GFH and GAC, including the kinetics and thermodynamics by which the adsorbents remove the perchlorate from the water. Additionally, the model that best fits the physicochemical and surface properties of GFH and GAC was explored. The results of this study highlight the importance of physical and chemical conditions of the solution on the adsorption behaviour of perchlorate onto GFH and GAC in water treatment and purification systems.

## MATERIALS AND METHODS

### Preparations of GFH, GAC and Perchlorate

GFH (GEH Wasserchemie GmbH & Co., Osnabrück, Germany) were prewashed using  $\text{HNO}_3$ . The GFH were dried to remove the water content. Particles with a 0.2- 2 mm size and with  $\beta\text{-FeOOH}$  and  $\text{Fe}(\text{OH})_3$  were used in the adsorption studies. The appearance of the GFH is similar to the granular activated carbon. Table 1 summarizes the basic properties of GFH, including specific surface area, pore volume, and particle size.

GAC for the experiment was prewashed using nitric acid. Next, the GAC was washed with deionized water, after which the GAC was dried in a well-ventilated area. The carbon purity of the GAC was 87%, and its specific surface area was  $940 \text{ m}^2/\text{g}$ . Table 1 shows the physical data of the GAC and includes its specific surface area, average pore diameter, and pore volume. The GAC was manufactured by Calgon Carbon Co. located in Tianjin, China, and the activated carbon material employed was prepared using coconut shells. Moreover, given the price of U.S. \$3/kg of

GAC is expensive compared to the price of U.S. \$1/kg of GFH.

The perchlorate solution was prepared by the authors; deionized water and nitric acid were added to sodium perchlorate, producing water samples of varying concentrations of perchlorate.

### Analysis of Perchlorate

The perchlorate concentration in the water samples was quantitatively analysed using an ion chromatograph; the water samples were first filtered using  $0.20 \mu\text{m}$  Advantec (Japan) glass fiber filter papers before being injected into the ion chromatograph (Metrohm 861 Advanced Compact IC, Switzerland).

### Adsorption of Time

The objective of the dynamic adsorption experiment was to understand the changes in the adsorption capacity over time to derive the time required to achieve equilibrium. The results were used as the basis for selecting the times of subsequent adsorption equilibrium and calculating the dynamic parameters. The experimental procedures are as follows:

A mixed solution containing  $\text{NO}_3^-$  (ionic strength) and perchlorate was prepared with the concentration levels required. The volume of deionized water was fixed at 1 L, and the mixture was distributed in 100 mL portions into a series of 125 mL brown bottles. Subsequently, aliquots of 0.1 M  $\text{H}_2\text{SO}_4$  and 0.1 M NaOH were added to adjust the pH level of the solution. Then, 0.5 g/L of GFH and GAC were added. The brown bottles were placed inside a reciprocating oscillator and agitated at 300 rpm at a constant temperature of  $25^\circ\text{C}$ . The brown bottles were removed from the oscillator in sequence at fixed time intervals, and the pH values of the solutions were recorded. Next, 20 mL of each solution was extracted from the brown bottles and filtered using  $0.20 \mu\text{m}$  Advantec filter papers. Finally, the residual perchlorate concentration of the filtrate was measured using an ion chromatograph.

### Isotherm adsorption experiment: pH effects

The purpose of the adsorption equilibrium experiments using perchlorate in varying pH levels was to investigate how varying pH levels affect

adsorption. The experimental procedures are as follows:

A mixed solution containing  $\text{NO}_3^-$  (ionic strength) and perchlorate was prepared with the concentration levels required. The volume of the deionized water was fixed at 1 L, and the mixture was distributed in 100 mL portions into a series of 125 mL brown bottles. The pH of the solutions was adjusted (2.0 to 12.0), and 0.5 g/L of GFH and GAC were added to each brown bottle. The bottles were placed inside a reciprocating oscillator and agitated at 300 rpm for eight hours (the dynamic adsorption equilibrium time) at a constant temperature of 25°C. Next, the pH value of the solutions was recorded, and 20 mL of each solution was extracted from the bottles and filtered using 0.20  $\mu\text{m}$  Advantec filter papers. Finally, the residual perchlorate concentration of the filtrate was measured using an ion chromatograph.

#### **Isotherm adsorption experiment: Temperature effects**

The isothermal adsorption experiments varying temperature were conducted to investigate the changes in the adsorption capacity of GFH and GAC when the temperature changes. In addition, the thermodynamic parameters were obtained. The experimental procedures are as follows:

A mixed solution containing  $\text{NO}_3^-$  (ionic strength) and perchlorate was prepared with the concentration levels required. The volume of the deionized water was fixed at 1 L and the mixture was distributed in 100 mL portions into a series of 125 mL brown bottles. The temperatures of the solutions were adjusted, and 0.5 g/L of GFH and GAC were added to each brown bottle. The bottles were placed inside a reciprocating oscillator and agitated at 300 rpm for eight hours at a temperature ranging from 5 °C to 45 °C. Next, the pH values of the solutions were recorded, and 20 mL of solution was extracted from each bottle and filtered using 0.20  $\mu\text{m}$  Advantec filter papers. Finally, the residual perchlorate concentration of the filtrate was measured using an ion chromatograph.

## **RESULTS AND DISCUSSION**

### **Kinetic study**

To assess the time required to reach equilibrium during the experiment, a dynamic equilibrium experiment was conducted. To demonstrate the adsorption properties, 0.5 g/L of adsorbent was used. For this experiment, the perchlorate concentration,

oscillation rate, pH level, and temperature were fixed at 20 mg/L, 300 rpm, 3.0, and 25 °C, respectively, to determine the amount of time required for adsorption to reach equilibrium.

Figure 1 displays the adsorption equilibrium curve, comparing perchlorate adsorption capacity with time. Based on the diagram, when the initial perchlorate concentration is 20 mg/L, the time required for GFH and GAC adsorption to achieve equilibrium is approximately forty minutes and eight hours. The adsorption capacities of GFH and GAC are approximately 3 mg/g and 22 mg/g, respectively.

### **Effect of varying ionic strengths on adsorption capacity**

To investigate the effects of ionic strength ( $\text{NO}_3^-$ ) on the perchlorate adsorption capacity and contact time of GFH and GAC, the ionic strength was controlled at  $2 \times 10^{-4}$  M,  $1 \times 10^{-3}$  M, and  $5 \times 10^{-3}$  M. The perchlorate concentration and the pH were 20 mg/L and 3, respectively. Figure 2 shows the changes in adsorption capacity versus time at various ionic strengths. As the time increased, the adsorption capacity of GAC increased. The decrease in the equilibrium adsorption capacity from 20.9 mg/g (a removal rate of 52%) to 12.6 mg/g (a removal rate of 32%) indicates that the higher the ionic strength is, the lower the equilibrium adsorption capacity becomes. The results in Figure 2 were further simulated and analysed using three common dynamic adsorption models: the modified Freundlich, pseudo-1st-order, and pseudo-2nd-order models. Table 2 lists the related simulation parameter results for the GAC, which indicate the adsorption reaction rate, K, for the models. Compared to low ionic strengths, solutions with high ionic strengths have lower adsorption reaction rates: high ionic strengths compress the electric double layer, reducing the surface potential energy and electrostatic repulsion, and increase the number of neutral ions residing on the surface of the adsorbent, ultimately decreasing the capacity of GAC to adsorb perchlorate.

Figure 3 shows the changes in adsorption capacity versus time at various ionic strengths. As time increased, the adsorption capacity of the GFH increased. The decrease in equilibrium adsorption capacity from 2.2 mg/g (a removal rate of 5%) to 1.7 mg/g (a removal rate of 4%) indicates that the higher the ionic strength is, the lower the equilibrium adsorption capacity becomes. The results in Figure 3 were further simulated and analysed using three

common dynamic adsorption models: the modified Freundlich, pseudo-1st-order, and pseudo-2nd-order models. Table 3 lists the related simulation parameter results for GFH which indicate the adsorption reaction rate,  $K$ , for the models. Compared to low ionic strengths, solutions with high ionic strengths have lower adsorption reaction rates: high ionic strengths compress the electric double layer, reducing the surface potential energy and electrostatic repulsion, and increase the number of neutral ions residing on the surface of the adsorbent, ultimately decreasing the capacity of GFH to adsorb perchlorate.

### **Isotherm adsorption experiments**

#### ***Effect of various pH values on the perchlorate removal efficiency***

Figure 4 shows the effect of the pH level on the perchlorate adsorption of GAC and GFH. Based on the experimental results, when the pH value decreased from 12 to 2, the perchlorate adsorption capacity of GAC increased from 1.3 mg/L to 18.9 mg/L. The adsorption capacity of GFH increased from 2.0 mg/g to 3 mg/g when the pH decreased. Under high pH, the removal rate of perchlorate by GAC and GFH was less than 10%. Conversely, under low pH, the adsorption rate of perchlorate on GAC and GFH was enhanced. The experiment shows that the perchlorate removal rate is significantly correlated with pH values. When  $\text{pH} < \text{pH}_{\text{zpc}}$  (GAC in aqueous solution), perchlorate is negatively charged and the surface of the adsorbent, which is positively charged, attracts the negatively charged perchlorate. When  $\text{pH} > \text{pH}_{\text{zpc}}$ , the surface of the GAC, which is negatively charged, repels the negatively charged perchlorate. Therefore, solutions with low pH values facilitate the adsorption and removal of perchlorate.

#### ***Effect of various temperatures on the perchlorate removal efficiency***

Figure 5 shows the perchlorate adsorption isotherm curve for GAC at varying temperatures. After calculating the results from Figure 5 by using the Langmuir-Freundlich models, the equilibrium parameters and correlation coefficients were obtained and listed in Table 4. The results from the Langmuir model (Table 4) indicate that the maximal GAC adsorption capacity decreases as temperature increases. At 5 °C, 25 °C, and 45 °C, the maximal GAC adsorption capacity ( $q_m$ ) for perchlorate was about 33.8 mg/g, 30.4 mg/g, and 28.2 mg/g, respectively. Figure 6 shows the perchlorate adsorption isotherm curve of GFH at varying temperatures. After

calculating the results from Figure 6 by using the Langmuir-Freundlich models, the equilibrium parameters and correlation coefficients were obtained and listed in Table 5. The results from the Langmuir model (Table 5) indicate that the maximal GFH adsorption capacity decreases as temperature increases. At 5 °C, 25 °C, and 45 °C, the maximal GFH adsorption capacity ( $q_m$ ) for perchlorate was about 2.6 mg/g, 3 mg/g, and 3.5 mg/g, respectively.

Because the constant  $K_L$  and adsorption strength  $n$  both decrease as temperature increases, at low temperatures, GAC possesses higher adsorption affinity than GFH for perchlorate. In addition, the Freundlich constant ( $K_F$ ) also decreases as temperature increases. The  $q_m$  and  $K_F$  values from the two common adsorption isotherm models coincide, in which the values of  $n$  related to the adsorption strength are all greater than one, indicating the effective adsorption of perchlorate by GAC.

Based on the parameter values obtained from the experimental data and the adsorption isotherm curve, the authors contend that an increase in temperature affects the surface properties of adsorbents, resulting in the accelerated desorption rate of GAC and GFH, which causes a reduction in adsorption capacity. The correlation coefficient  $R^2$  from Table 4 and Table 5, the high  $R^2$  in the Langmuir ( $R^2$ : over 0.97) and Freundlich ( $R^2$ : over 0.99) models indicates that the two models are suitable for describing the isothermal equilibrium for GAC and GFH in the removal of perchlorate.

#### ***Calculation of thermodynamic parameters***

Based on the equilibrium constant  $K_0$  with the change in temperature, a straight line is fitted to the points by a least-squares analysis. Its intercept with the vertical axis gives the values of  $K_0$  (Lou et al. 2014). The adsorption standard free energy changes ( $\Delta G^\circ$ ) can be calculated according to  $K_0$  by plotting  $\ln K_0$  vs.  $1/T$  (See Figures 7 and 8). The average standard enthalpy change ( $\Delta H^\circ$ ) is obtained from the van't Hoff equation with different temperatures. The standard entropy change ( $\Delta S^\circ$ ) can be obtained by as a function of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and temperature.

The thermodynamic parameters of perchlorate adsorbing to GFH and GAC are listed in Tables 6 and 7. From the results of Tables 6 and 7, a positive and negative standard enthalpy change suggests the interaction of perchlorate by GFH is endothermic and GAC is exothermic. That supports the increasing

adsorption of perchlorate when using GFH with the increase in temperature. A negative adsorption standard free energy change and a positive standard entropy change shows that the adsorption reaction of perchlorate is a spontaneous process when using GFH or GAC. The positive standard entropy change is because of the release of water molecules produced by an ion exchange reaction between the adsorbate and the functional groups on the surface of adsorbents (Li et al.2001).

## CONCLUSION

The adsorption thermodynamics and kinetics of perchlorate adsorbing to GFH and GAC have been studied and compared. The dynamic adsorption showed that the adsorption capacity increases as the perchlorate concentration increases or as the ionic strength decreases. Concerning the correlation of the data, the kinetic adsorption process can be well described by the modified Freundlich model.

The isothermal equilibrium adsorption showed that a low pH improves the ability of GFH and GAC to adsorb perchlorate. A positive and negative standard enthalpy change suggests that the interaction of perchlorate when using GFH or GAC is endothermic and exothermic, respectively. The negative adsorption standard free energy change and a positive standard entropy change shows that the adsorption reaction is a spontaneous process.

Perchlorate can be removed from GFH and GAC by adjusting the solution pH; therefore, GFH and GAC are promising adsorbents in water treatment.

## ACKNOWLEDGEMENTS

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financial partially supporting this research under Contract No. NSC-101-2221-E-110-059.

## REFERENCES

1. Brown, G.M.; Gu, B. The chemistry of perchlorate in the environment. In B. Gu and J.D. Coates, Eds. (2006) Perchlorate Environmental Occurrence, Interactions and Treatment. New York: Springer, 17-42.
2. Craig S.; Mark D.M.; Lara C.; Benjamin C. B.; Allan H. S. (2013) Combined effects of perchlorate, thiocyanate, and iodine on thyroid function in the National Health and

- Nutrition Examination Survey 2007-08. Environmental Research 123, 17-24.
3. USEPA. (2004) Public Health Goal for Chemicals in Drinking Water, Perchlorate, Office of Environmental Health Hazard Assessment, Environmental Protection Agency.
4. Yang, Z.; Xiao O.; Chen B.; Zhang L.; Zhang H.; Niu X.; Zhou S. (2013) Perchlorate adsorption from aqueous solution on inorganic-pillared bentonites. Chemical Engineering Journal, 223, 31-39.
5. Parette, R.; Cannon, F.S.; Weeks, K. (2005) Removing low ppb level perchlorate, RDX, and HMX from groundwater with cetyltrimethylammonium chloride (CTAC) preloaded activated carbon. Water Research 39, 4683-4692.
6. Srinivasan, R.; Sorial, G.A. (2009) Treatment of perchlorate in drinking water: a critical review. Separation and Purification Technology, 69, 7-21.
7. Kim, J.Y.; Komarneni, S.; Parette, R.; Cannon, F.S.; Katsuki, H. (2011) Perchlorate uptake by synthetic layered double hydroxides and organo-clay minerals. Applied Clay Science 51, 158-164.
8. Weng, C.H.; Lin, Y.T.; Tzeng, T.W. (2009) Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder. Journal of Hazardous Materials, 170, 417-424.
9. Weng, C.H.; Lin, Y.T.; Chen, Y.J.; Sharma, Y.C. (2013) Spent green tea leaves for decolorization of raw textile industry wastewater. Coloration Technology 129, 298-304.
10. Weng, C.H.; Wu, Y.C. (2012) Potential Low-cost Biosorbent for Copper Removal: Pineapple Leaf Powder. Journal of Environmental Engineering-ASCE, 138, 286-292.
11. Weng, C.H.; Sharma, Y.C.; Chu, S.H. (2008) Adsorption of Cr (VI) from Aqueous Solution by Spent Activated Clay. Journal of Hazardous Materials, 155, 65-75.
12. Baidas, S.; Gao, B.; Meng, X. (2011) Perchlorate removal by quaternary amine modified reed. Journal of Hazardous Materials 189, 54-61.
13. Kumar, E.; Amit, B.; Choi, J.A.; Kumar, U.; Min, B.; Kim, Y.; Song, H.; Paeng, K.J.;

Jung, Y.M; Abou-Shanab, R.A.I.; Jeon, B.H. (2010) Perchlorate removal from aqueous solutions by granular ferric hydroxide (GFH). Chem. Eng. J. 159, 84-90.

14. Lien, H.L.; Yu, C.C.; Lee, Y.C. (2010) Perchlorate removal by acidified zero-valent aluminum and aluminum hydroxide, Chemosphere 80, 888-893.

15. Lou, J.C.; Lee, R.H.; Chen, W.H.; Chang, C.J.; Hsu, K.L.; Han, J.Y. (2014) Adsorption kinetics and thermodynamics of perchlorate on carbon nanotubes in water, J. Environ. Eng. 140(11), 04014038-1-04014038-6.

16. Li, Y.H.; Wang, S.G.; Cao, A.Y.; Zhao, D.; Zhang, X.F.; Xu, C.L.; Luan, Z.K.; Ruan, D.B.; Liang, J.; Wu, D.H.; Wei, B.Q. (2001) Adsorption of fluoride from water by amorphous alumina supported on carbon nanotubes. Chem. Phys. Lett, 350, 412-416.

**Table Captions**

- Table 1. GFH and GAC specific surface area, pore volume, pore diameter and particle size.
- Table 2. Parameters of the GAC adsorption obtained using different models to simulate sorption at different ionic strengths.
- Table 3. Parameters of the GFH adsorption obtained using different models to simulate sorption at different ionic strengths.
- Table 4. The Langmuir and Freundlich model constants for the equilibrium condition for the adsorption of perchlorate onto GAC.
- Table 5. The Langmuir and Freundlich model constants for the equilibrium condition for the adsorption of perchlorate onto GFH.
- Table 6. Values of the thermodynamic parameters for the adsorption of perchlorate onto GFH.
- Table 7. Values of the thermodynamic parameters for the adsorption of perchlorate onto GAC.

**Table 1. GFH and GAC specific surface area, pore volume, pore diameter and particle size**

Adsorbent	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Particle Size(mm) or Average Pore Diameter(nm)
GFH	300	0.87	0.2-2(mm)
GAC	940	0.48	1.55(nm)

**Table 2. Parameters of the GAC adsorption obtained using different models to simulate sorption at different ionic strengths.**

HNO <sub>3</sub>	2×10 <sup>-4</sup> M	1×10 <sup>-3</sup> M	5×10 <sup>-3</sup> M
<i>q<sub>e</sub></i> (mg/g)	20.9	18.7	12.6
Removal (%)	52	47	32
Model	Modified Freundlich equation		
<i>K</i> (L/g-min)	0.8	0.7	0.4
R <sup>2</sup>	0.997	0.999	0.993

Model		Pseudo-1 <sup>st</sup> -order	
$k_1$ (min <sup>-1</sup> )	1.21	1.44	0.93
R <sup>2</sup>	0.978	0.984	0.979
Model		Pseudo-2 <sup>nd</sup> -order	
$k_2$ (g/mg-min)	0.15	0.22	0.17
R <sup>2</sup>	0.993	0.998	0.988

**Table 3. Parameters of the GFH adsorption obtained using different models to simulate sorption at different ionic strengths.**

HNO <sub>3</sub>	2×10 <sup>-4</sup> M	1×10 <sup>-3</sup> M	5×10 <sup>-3</sup> M
$q_e$ (mg/g)	2.15	1.9	1.7
removal (%)	5	5	4
Model		Modified Freundlich equation	
$K$ (L/g-min)	0.05	0.04	0.04
R <sup>2</sup>	0.993	0.992	0.990
Model		Pseudo-1 <sup>st</sup> -order	
$k_1$ (min <sup>-1</sup> )	0.11	0.11	0.11
R <sup>2</sup>	0.996	0.995	0.993
Model		Pseudo-2 <sup>nd</sup> -order	
$k_2$ (g/mg-min)	0.15	0.16	0.22
R <sup>2</sup>	0.986	0.982	0.973

**Table 4. The Langmuir and Freundlich model constants for the equilibrium condition for the adsorption of perchlorate onto GAC.**

Temp. (°C)	Langmuir model			Freundlich model		
	$q_m$ (mg/g)	$K_L$ (L/mg)	R <sup>2</sup>	$K_F$	$n$	R <sup>2</sup>
4	33.8	3.0	0.997	24.9	8.7	0.999
25	30.4	2.8	0.985	21.9	8.1	0.997
45	28.2	2.3	0.987	19.8	7.5	0.998

**Table 5. The Langmuir and Freundlich model constants for the equilibrium condition for the adsorption of perchlorate onto GFH**

Temp. (°C)	Langmuir model			Freundlich model		
	$q_m$ (mg/g)	$K_L$ (L/mg)	R <sup>2</sup>	$K_F$	$n$	R <sup>2</sup>
5	2.6	4.17	0.976	2.05	9.7	0.991
25	2.9	3.93	0.986	2.33	10.4	0.996
45	3.5	4.45	0.986	2.82	12.0	0.995

**Table 6. Values of the thermodynamic parameters for the adsorption of perchlorate onto GFH**

Temp (°C)	$K_0$	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta S^\circ$
		(1000 cal mol <sup>-1</sup> )	(1000 cal mol <sup>-1</sup> )	(cal mol <sup>-1</sup> K <sup>-1</sup> )
5	17.6	-6.6	15	0.08
25	22.4	-7.7	15	0.08
45	39.2	-9.7	15	0.08

**Table 7. Values of the thermodynamic parameters for the adsorption of perchlorate onto GAC**

Temp (°C)	$K_0$	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta S^\circ$
		(1000 cal mol <sup>-1</sup> )	(1000 cal mol <sup>-1</sup> )	(cal mol <sup>-1</sup> K <sup>-1</sup> )
5	7.5	-1.11	-0.6	1.84
25	6.6	-1.04	-0.6	1.47
45	5.9	-0.99	-0.6	1.21



Figure Captions

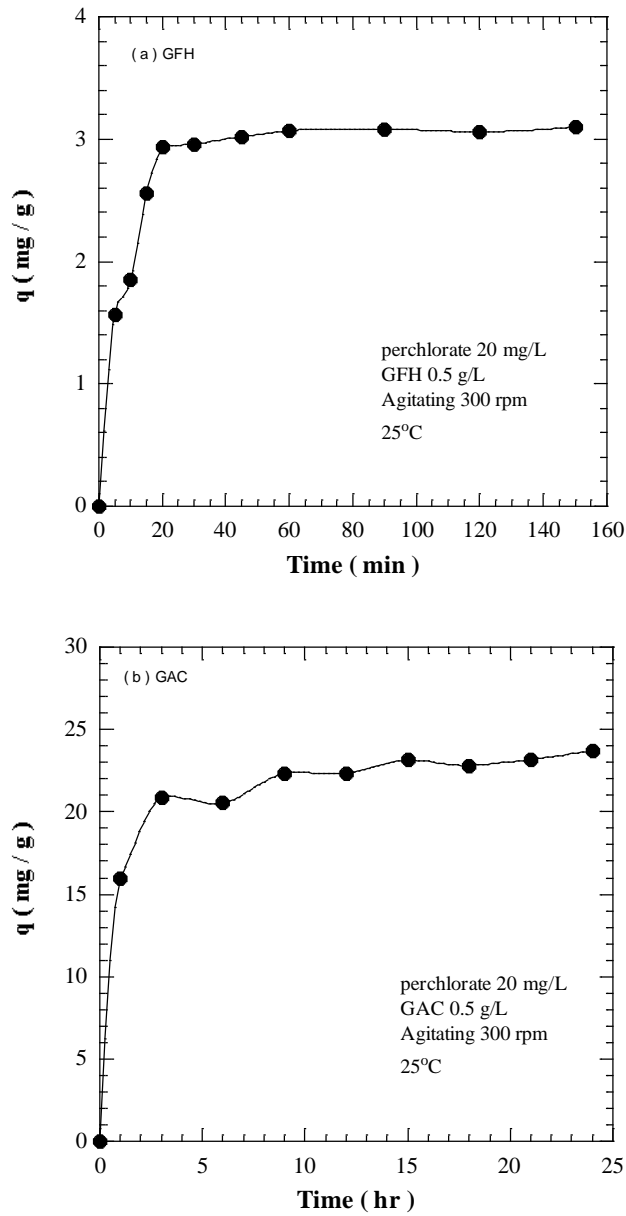


Figure 1. Changes in the perchlorate adsorption capacity of GFH and GAC over time.  
(a) GFH; (b) GAC.

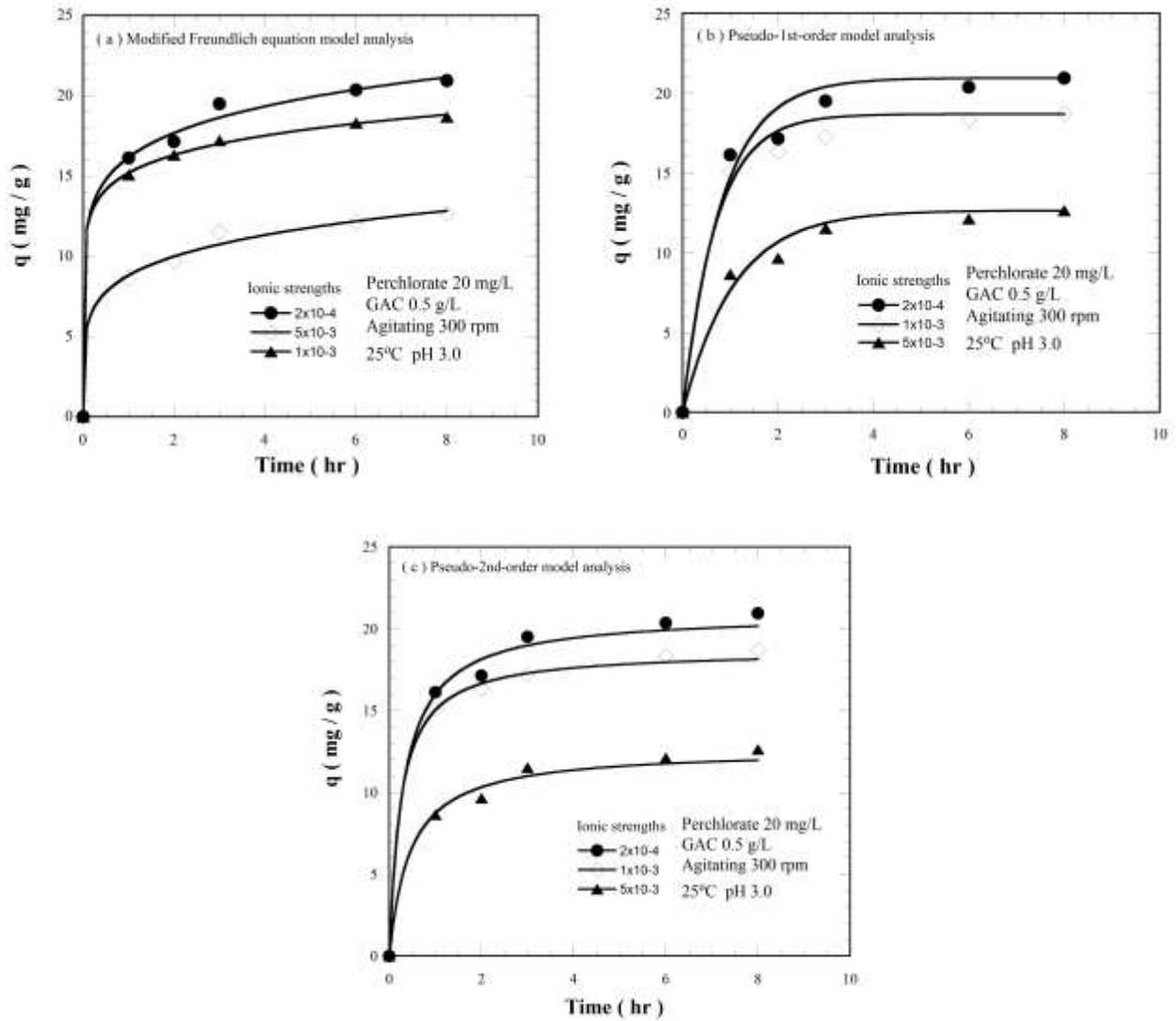


Figure 2. Perchlorate adsorption onto GAC as a function of time at different ionic strengths.  
 (a) Modified Freundlich equation model analysis; (b) Pseudo-1st-order model analysis; (c) Pseudo-2nd-order model analysis.

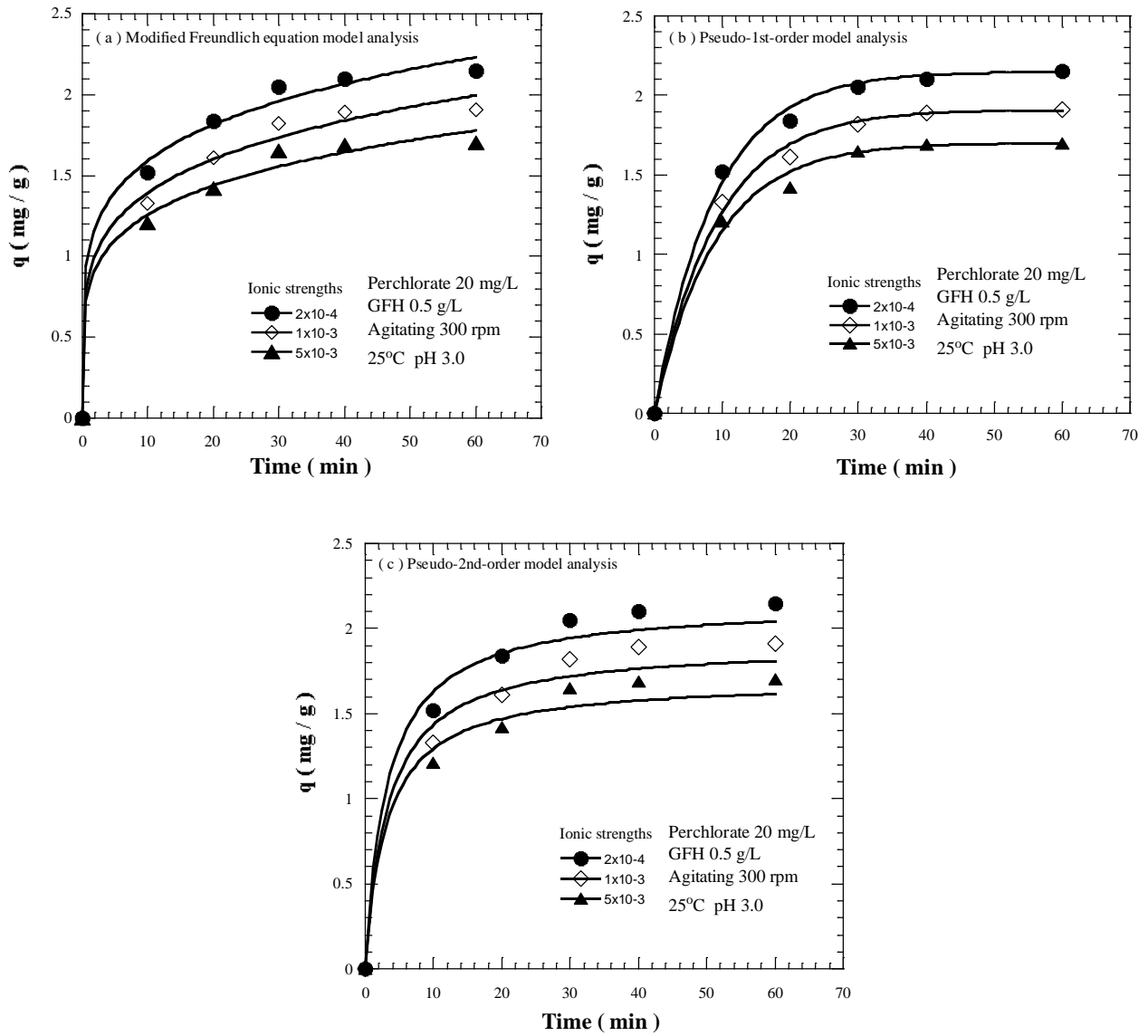


Figure 3. Perchlorate adsorption onto GFH as a function of time at different ionic strengths.  
 (a) Modified Freundlich equation model analysis; (b) Pseudo-1st-order model analysis; (c) Pseudo-2nd-order model analysis.

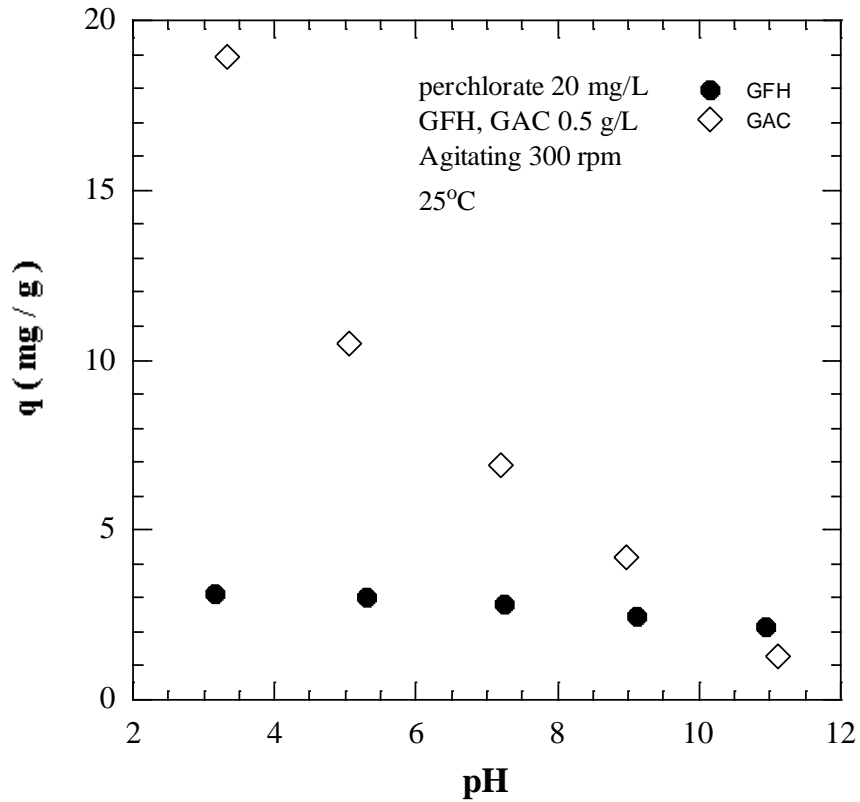


Figure 4. The effect of pH on the adsorption of perchlorate onto GFH and GAC.

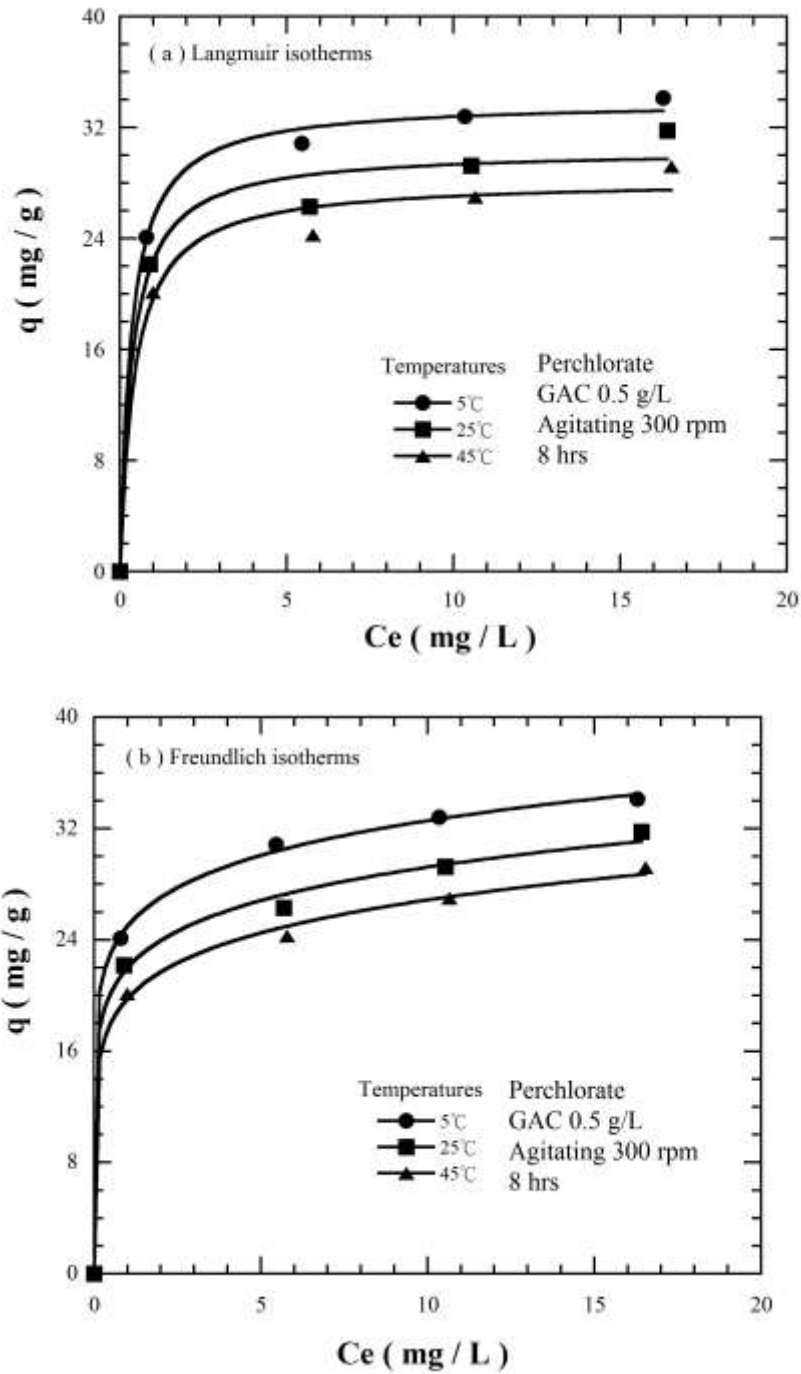


Figure 5. The equilibrium adsorption results from the Langmuir and the Freundlich adsorption model analysis.(a) Langmuir isotherms of GAC and (b) Freundlich isotherms of GAC; temperatures are at 5°C, 25°C and 45°C

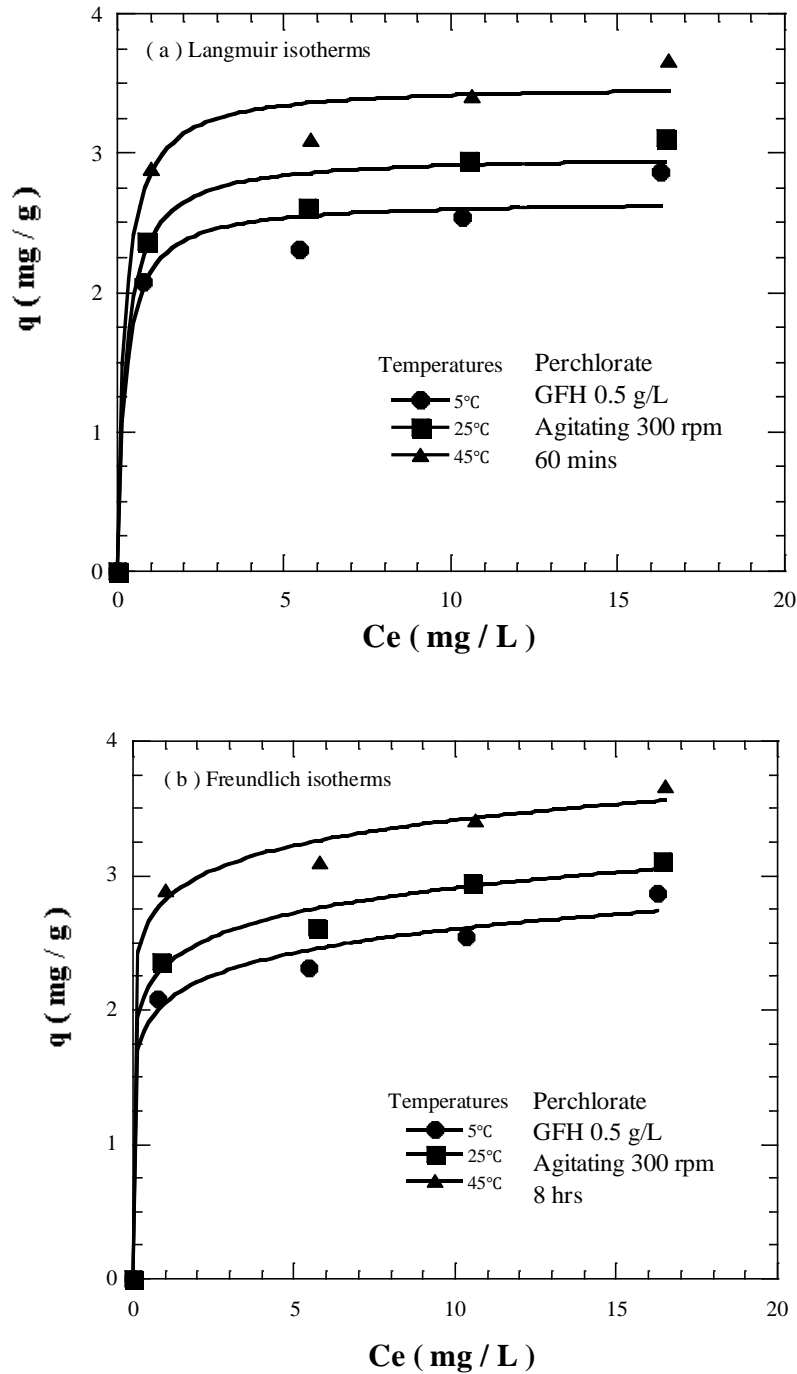


Figure 6. The equilibrium adsorption results from the Langmuir and the Freundlich adsorption model analysis. (a) Langmuir isotherms of GFH and (b) Freundlich isotherms of GFH; temperatures are at 5 °C, 25 °C and 45 °C

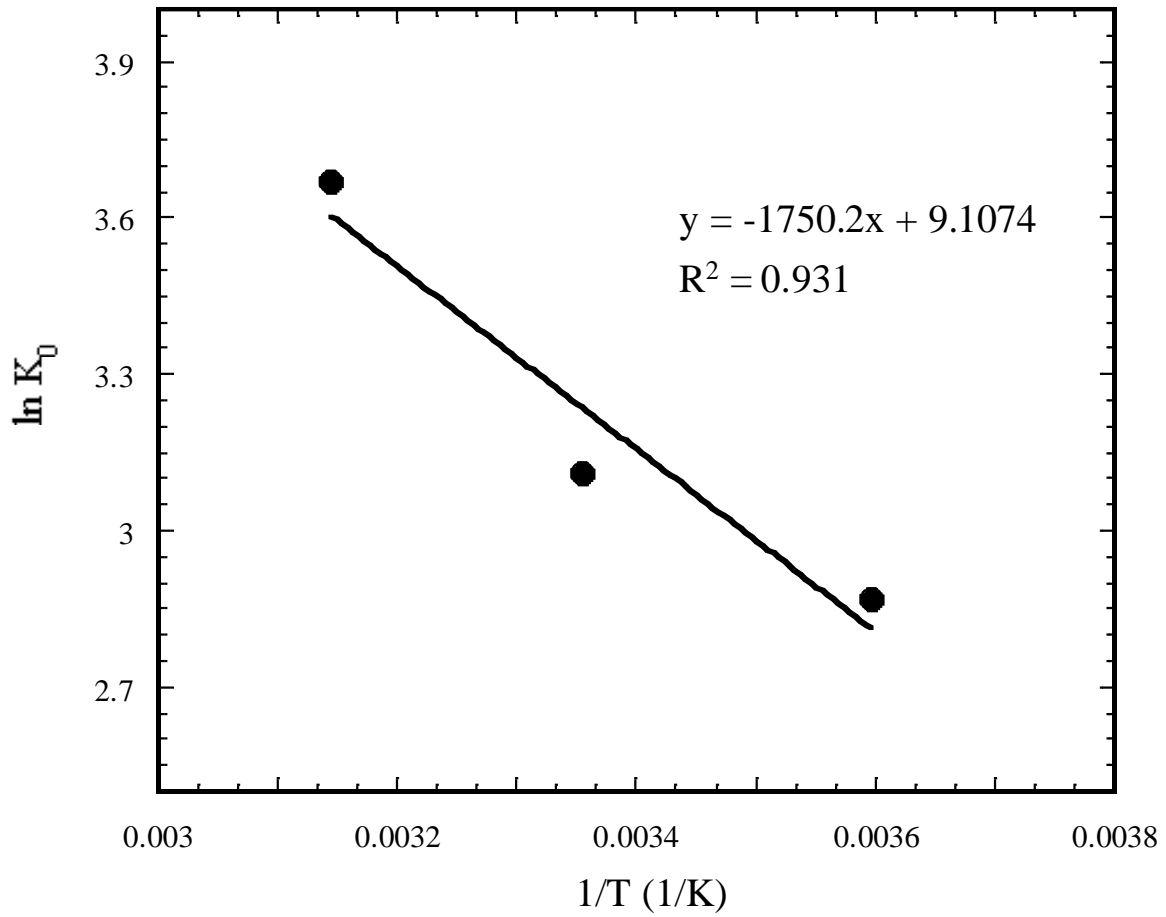


Figure 7. Plot of  $\ln K_0$  vs.  $1/T$  for perchlorate adsorbing onto GFH.

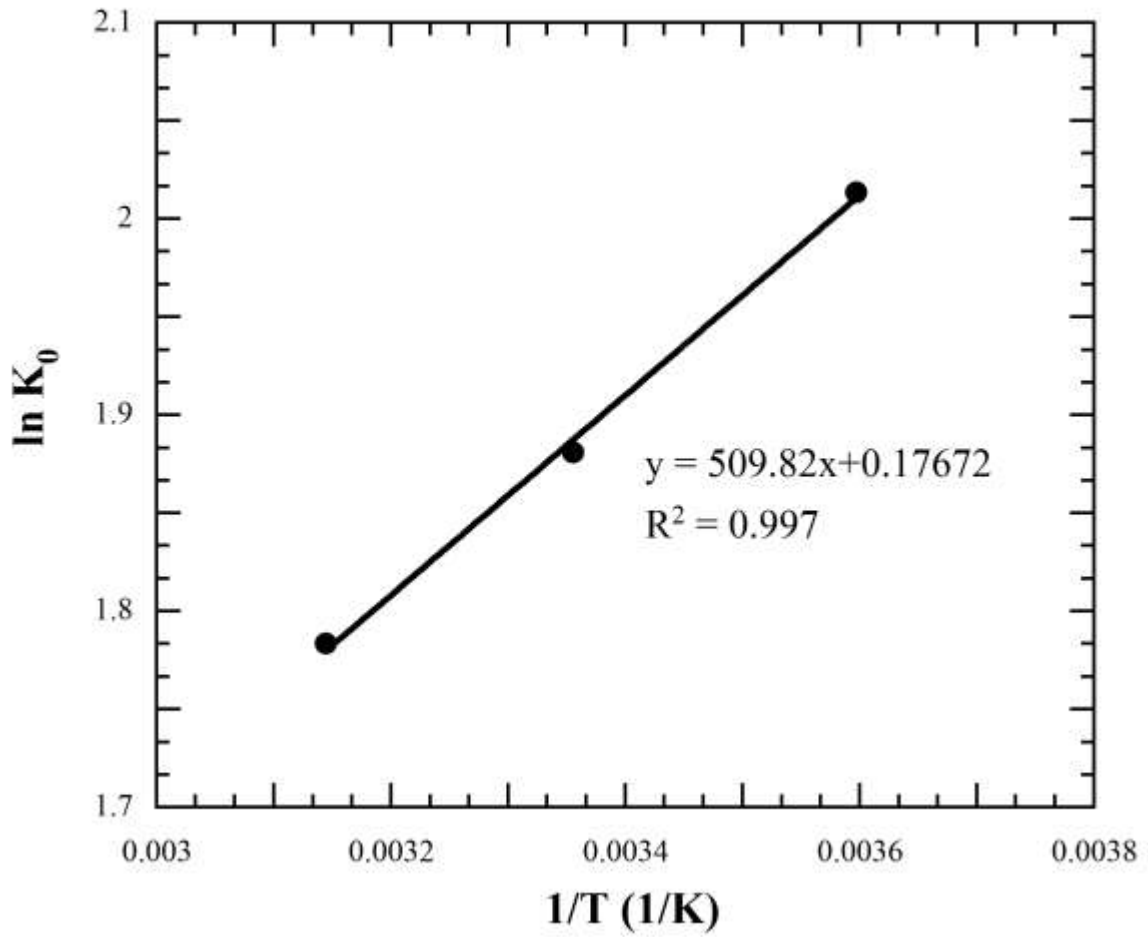


Figure 8. Plot of  $\ln K_0$  vs.  $1/T$  for perchlorate adsorbing onto GAC.