

Adsorption of Humic Acid From Aqueous Solution
Onto Fe₃O₄ Coated Carbon: Effect of Temperature

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ABSTRACT

The sorption of humic acid from aqueous solution onto Fe₃O₄ coated carbon under the influence of temperature has been investigated. Batch adsorption experiments were carried out using humic acid (HA) as an adsorbate. It was observed that the amount of humic acid adsorbed increase with increasing temperature. Thermodynamic parameters data indicated that the humic acid adsorption was non-spontaneous and endothermic under the experimental conditions, with the enthalpy (ΔH) and entropy (ΔS) of +29,44 J mol⁻¹ and +74.96 J mol⁻¹, respectively.

Key Words: Adsorption; endotherm; Fe₃O₄; humic acid; temperature

1. INTRODUCTION

Humic substance, which are present in peat water, adversely affect water quality in several ways: causing undesirable color and taste, binding with heavy metals and biocides and reacting with chlorine during water treatment to produce trihalomethanes (Ngah et al., 2011; Rojas et al., 2011; Sun et al., 2011), which affect human health very seriously and can even cause cancer (Ngah et al., 2011). Therefore, the presence of humic acid in peat water has been a great concern and measures have to be taken to minimize the presence of humic acid in peat water and in other water resources.

Among the many existing methods, adsorption has shown to be a promising technique to remove these organic matters from aqueous solution, which has great importance due to the ease of operation and comparable low cost of application in the adsorption process. Among these adsorbents, clay minerals have been shown to be the most promising alternatives due to their local availability, technical feasibility, easy engineering applications, highly specific surfaces area, and cost effectiveness (Dogan et al., 2007; Sheng et al., 2009).

Nowday, Fe₃O₄ nano-particles materials are in focus as powerful adsorbents due to their large specific surface area and small internal diffusion resistance (Mohammadi et al., 2014). These magnetic nano-particles can adsorb pollutants from aqueous solutions and then be separated from the water with a simple magnetic process. Many researchers have been focused on modification of the Fe₃O₄ nano-particles to provide a better surface specificity to removal of different pollutants from aqueous solutions. In the present work, we investigated the effect of temperature on adsorption of humic acid onto Fe₃O₄ coated carbon to be used as an adsorbent. In addition, thermodynamic parameters were also studied.

2. EXPERIMENT

2.1. Materials

Fe₃O₄ coated carbon was obtained from Analytical Chemistry Laboratory. Sodium hydroxide and hydrochloric acid used to adjust pH was purchased from Merck. Water used was generated from aqua demineralization system. All materials were used without further purification. The humic acid sample was obtained from Merck. Before mixing the humic acid sample with adsorbent, its pH value was adjusted using sodium hydroxide and hydrochloric acid. The pH value was measured using 300 Hanna Instrument pH meter.

2.2. Method

Adsorption experiments were carried out by mixing respectively of 0.3 g Fe₃O₄ coated carbon with 50 mL of humic acid 100 mg/L at 25 °C, 45 °C and 65 °C in thermostatic shaker bath for 2, 5, 10, 15, 20, 25, 30, 45, 60, 75, 120 and 180 minutes. At the end of the predetermined time interval, the suspension was extracted and then separated by using magnet force. The clear solution was analysed for the remaining HA concentration by an ultraviolet-visible spectrophotometer model UV-Vis 1601 (Agilent 8453, USA) at the λ 254 nm. The percent of humic acid adsorption was calculated using the following equation:

$$\text{Adsorption (\%)} = \frac{C_i - C_e}{C_i} \times 100$$

(1)

where:

$$\begin{aligned} C_i &= \text{initial concentration of humic acid (mg/L)} \\ C_e &= \text{final concentration of humic acid after adsorption (mg/L)} \end{aligned}$$

The adsorption capacity of an adsorbent at equilibrium with solution volume V (L) and adsorbent dosage m (g), was calculated using the following equation:

$$q_e \text{ (mg/g)} = \frac{C_i - C_e}{m} \times V$$

(2)

3. RESULTS AND DISCUSSION

The effect of contact time on humic acid adsorption onto Fe_3O_4 coated carbon at different temperature is shown in Figure 1. Based on the plot, humic acid adsorption was relatively fast with more than 50% adsorbed in 30 minutes first. After that, the sorption increases gradually with increasing contact time. At 90 minute, it can be observed that the humic acid adsorption remained constant and this indicating the equilibrium has been established.

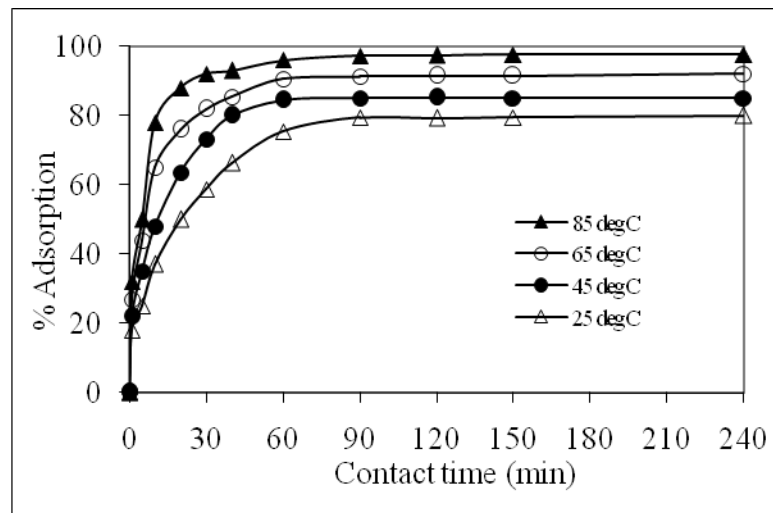


Figure 1. Effect of temperature on humic acid adsorption onto Fe_3O_4 coated carbon

From Figure 1, it also shows that the amount of humic acid adsorbed onto Fe_3O_4 coated carbon is enhanced with increasing temperature. Increasing of temperature is known to increase the diffusion rate of the humic acid molecule across the external boundary layer and the internal pores of the adsorbent particles. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the adsorbent enabling large humic acid to penetrate further (Amran and Zulfikar, 2010; Mohammadi et al., 2014; Wang and Zhu, 2007; Zulfikar et al., 2014a).

The thermodynamic parameters such as Gibbs free energy, enthalpy and entropy changes for humic acid sorption on pyrophyllite are calculated from the temperature dependent sorption isotherms. The Gibbs free energy change (ΔG°) of the sorption reaction is given by:

$$\Delta G^\circ = - RT \ln K_L \quad (3)$$

where:

$$\begin{aligned} R &= \text{gas constant (8.314 J/mol K)} \\ T &= \text{absolute temperature (K)} \\ K_L &= \text{Langmuir isotherm constant (L/mg)} \end{aligned}$$

The Gibbs free energy change indicates the degree of spontaneity of the adsorption process and the higher value reflects a more energetically favourable adsorption (Yeddou and Bensmaili, 2007). The Gibbs free energy change (ΔG°) is also calculated as:

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (4)$$

Combining equation (3) and (4) and rearranging:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

where:

$$\begin{aligned} \Delta H^\circ &= \text{enthalpy change (kJ/mol)} \\ \Delta S^\circ &= \text{entropy change (J/mol)} \end{aligned}$$

The value enthalpy (ΔH°) and entropy (ΔS°) can be evaluated from the slope and intercept of the linear plot of $\ln K_L$ vs $1/T$. The parameter values obtained from the slope and intercept of the linear plot of $\ln K_L$ vs $1/T$ are tabulated in Table 1. A positive value of the standard enthalpy change indicates that the sorption process is endothermic and thus the adsorption of humic acid onto Fe_3O_4 coated carbon is entropy driven (Salman et al., 2007).

The positive values of Gibbs free energy (ΔG°) obtained indicate the non-spontaneous nature of adsorption process at the range of temperatures being studied. It can also noted that the value of ΔG° become more negative with the increase of temperature, which indicates that the reaction is more favorable at high temperatures.

Table 1. Thermodynamic parameters of adsorption process

| Temperature (°C) | K_L (L/mg) | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (J/mol) |
|---------------------|-----------------|------------------------------|------------------------------|-----------------------------|
| 25 | 0.05 | 7.42 | | |
| 45 | 0.12 | 5.61 | | |
| 65 | 0.23 | 4.13 | 34.39 | 90.50 |
| 85 | 0.45 | 2.38 | | |

The positive value of entropy change (ΔS°) indicates the increased randomness at the solid-solution interface during the adsorption of HA onto Fe_3O_4 nanoparticles (Liang et al., 2011; Lin and Zhan, 2012; Wang et al., 2013; Zulfikar et al., 2014). The enthalpy change (ΔH°) for chemisorption is in the range 40-120 kJ/mol (Lin and Zhan, 2012). Since the value of ΔH° observed in the system is lower than 40 kJ/mol, the adsorption of humic acid onto Fe_3O_4 coated carbon by physisorption.

4. CONCLUSIONS

The main aim of this study was to investigate the effect of temperature on humic acid adsorption using Fe_3O_4 coated carbon as an adsorbent. The result from this work showed that the temperature has an important role in the adsorption of humic acid compounds onto Fe_3O_4 coated carbon. Thermodynamic parameters data indicated that the humic acid sorption process was non-spontaneous and endothermic under the experimental conditions, with the Gibbs free energy (ΔG°) in the range of 7.42-2.38 kJ mol⁻¹, enthalpy (ΔH°) and entropy (ΔS°) of 34.39 kJ mol⁻¹ and 90.50 J mol⁻¹, respectively.

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