Studies on the Adsorption of p-Aminoazobenzene onto Kaolinite

Qingfeng Wu[1,2], Hanlie Hong[*,1] and Xiaoling Zhang[1]

[1]*Faculty of Earth Sciences, China University of Geosciences, Wuhan, Hubei 430074, China*

[2]*College of Physical Science and Technology, Yangtze University, Jingzhou, Hubei, 434100, China*

Abstract: As one of the most important soil components, kaolinite plays an important role in transport and fixation of organic pollutants in soils. P-Aminoazobenzene (PAAB) is a sort of the carcinogenic aromatic amine which is commonly used as the intermediates of azo dyes. It can cause mutations and cancer of aquatic biota as well as humans. In this study, adsorption of PAAB on kaolinite in aqueous solution under different pHs, temperature and ionic strength was examined. Adsorption kinetic experiments indicated that the adsorption of PAAB on kaolinite at pH 1.4 and 4.0 followed the Elovich kinetics. The adsorption isotherm of PAAB onto kaolinite was well described by the Langmuir model, with an adsorption capacity of 2.2 mg/g at pH 1.4 and 1.43mg/g at pH 4.0. Adsorption of PAAB increased with decreasing solution pH and ionic strength. The negative free energy change (ΔG) after adsorption indicated that the adsorption process is a spontaneous process. The enthalpy change (ΔH) at pH 1.4 and 4.0 was -6.93 and -4.72 kJ/mol, respectively, suggesting that PAAB adsorption was an exothermal process and the physical adsorption predominated in the adsorption of PAAB on kaolinite. The adsorption affinity of PAAB for kaolinite surface was attributed to the electrostatic attractive and van der Waals' forces.

Keywords: Adsorption, p-Aminoazobenzene, kaolinite.

1. INTRODUCTION

Azo dyes have been widely used in the printing and dyeing for textile, leather, and paper, etc. Due to incomplete utilization, up to 40% of dyes used during the dyeing process are discharged into municipal effluents. However, current wastewater treatment technology cannot remove dyes in the wastewater completely [1]. As a result, a large amount of dyes will pass through the wastewater treatment plants and enter the environment *via* different pathways. Although not strongly hazardous, the presence of dyes in the environment will lead to the increasing possibility of the occurrence of cancer [2]. P-Aminoazobenzene (PAAB) is a sort of the carcinogenic aromatic amine which is commonly used as the intermediates of azo dyes. And it has been recommended as an unsafe substance because it may cause cancer to people [3].

Clay minerals are important constituents of soils and sediments, which have large specific surface area and high cation exchange capacity (CEC). Organic compounds in soils tend to be taken up by clay minerals. Therefore, the clay minerals in soils may play an important role in controlling the transport of organic compounds in the environment. In addition, it is a fact that various clay minerals have been used to remove heavy metals and organic pollutants from aqueous solutions [4]. Therefore, it is necessary for us to carry out detailed investigation of the binding affinity of PAAB to the clay minerals. Investigations on sorptive removal of azo dyes employing the raw mineral materials were mainly focused on basic dyes. Basic dyes often exist in cationic form, while clay minerals are negatively charged [5-9]. Thus, the electrostatic attraction would increase the removal of basic dyes. On the other hand, acidic dyes could be removed by surfactant-modified clay minerals, as they are often in cationic form while surfactant-modified clay minerals surfaces are negatively charged [10-11].

Kaolinite is found as a common constituent of soils and sediments. In this work, we investigated the adsorption of PAAB on kaolinite as a function of PAAB concentration, pH, temperature and cation strength, and then discussed the mechanisms of PAAB adsorption onto kaolinite, which will provide a better understanding of the fate of PAAB in water and soil and guidance for wastewater remediation.

2. EXPERIMENTAL

2.1. Materials

The kaolinite used in this study was purchased from Maoming, Guangdong, China. XRD and FTIR analysis showed the purity of kaolinite was very high, only containing trace amount of feldspar. The mean particle size measured was 1.4 μm. The specific surface area (SSA) was 28-30 m^2/g, and the cation exchange capacity (CEC) was 3.6-3.8 cmol/kg determined by a spot methylene blue method [12].

The p-Aminoazobenzene (PAAB) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Its chemical formula is $C_{12}H_{11}N_3$ and structure is presented in Fig. (**1**). The dissociation constant (pKa) of PAAB is about 2.8. When solution pH is below pKa, PAAB exists mainly as cationic form $PAAB^+$; while solution pH is above pKa, the neutral form $PAAB^0$ predominates. All other

*Address correspondence to this author at the Faculty of Earth Sciences, China University of Geosciences, Wuhan, Hubei 430074, China; Tel: 86-27-67884250; E-mail: honghl8311@yahoo.com.cn

chemicals were of analytical grade. Deionized water was used for all the experiments.
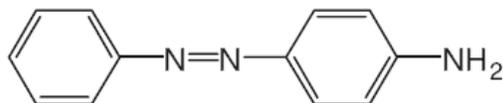

Fig. (1). Molecular structure of p-Aminoazobenzene.

2.2. Batch adsorption

Adsorption of PAAB on kaolinite was performed by adding a certain amount of kaolinite and 50 ml of PAAB solution to a 100 ml centrifuge tube. And then, the centrifuge tubes were continuously shaken a reciprocal shaker at 150 rpm for 24 h. Due to the low solubility of PAAB, it was first dissolved in ethanol, and made a 200 mg/L stock solution that was diluted with deionized water and methanol to desired concentrations. The centrifuge tubes were wrapped with aluminum foils to prevent exposure to light. After equilibration, the mixture was centrifuged at 4200 rpm for 10 min and the supernatant was passed through a 0.45 μm filter. The equilibrium concentration of PAAB in the supernatant was determined *via* UV-vis spectrophotometer. In order to investigate the contribution of different species of PAAB to adsorption, we choose pH=1.4 and 4.0 as the experiment condition, respectively. Although these pH conditions are rare in natural environments, PAAB adsorption conducted under these pH conditions could help elucidate the mechanism of PAAB adsorption on kaolinite. Solution pH was adjusted by adding 0.1 M NaOH and HCl using 100μL syringe.

2.3. Methods of Analysis

The UV-Vis scan (200-900 nm) showed that the wavelengths corresponding to maximum absorbance of PAAB at pH 1.4 and 4.0 were 400 and 312 nm, respectively. In order to ensure the accurate measurement of PAAB concentrations, the PAAB concentration was measured by a UV-vis spectrophotometer at the wavelength of 400 nm at pH 1.4, and 312 nm at pH 4.0, respectively. Calibrations with six initial concentrations ranging from 10 to 50 mg/L at pH 1.4 and 4.0 resulted in a coefficient of determination r^2 >0.99.

Powder XRD analyses were carried out on X'Pert PRO Dy2198 with Cu-Kα radiation at 40 kV and 30 mA. Oriented samples were scanned from 3° to 65° with a scanning speed of 2°/min.

FTIR spectra were obtained on a Nicolet 60 SXB Fourier transform infrared spectrometer using KBr pressing method. The absorbance data were collected by accumulating 256 scans at a resolution 4 cm^{-1} in the range of 4000-400 cm^{-1}.

3. RESULT AND DISCUSSION

3.1. PAAB Adsorption Kinetics

Kinetics of PAAB adsorption onto kaolinite is shown in Fig. (**2**). The data were fitted to both pseudo-second-order and Elovich models. The integrated rate law of the pseudo-second-order kinetics model is:

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \qquad (1)$$

where k (g/mg-h) is the rate constant of adsorption, q_e (mg/g) is the amount of PAAB adsorbed at equilibrium, and q_t (mg/g) is the amount of PAAB adsorbed on the surface of the adsorbent at any time t. The above equation can be converted into a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \qquad (2)$$

where kq_e^2 is the initial rate (mg/g-h). When the kinetic data at pH 1.4 were fitted to Eq. (2), the r^2 was 0.92. The initial rate was 0.85 g/mg-h, the rate constant was 0.77 g/mg-h, and the q_e was 1.05 mg/g. Fitting of the kinetic data at pH 4.0 to Eq. (2) yielded a coefficient of determination r^2 of 0.94. The initial rate was 0.53 g/mg-h, the rate constant was 0.96 g/mg-h, and the q_e was 0.74 mg/g. Compared to azobenzene adsorption on kaolinite, adsorption of PAAB on kaolinite achieved a lower initial rate and equilibrium adsorption capacity, but a much larger rate constant [13]. The Elovich model can be written as:

$$q_t = a \ln(t) + b \qquad (3)$$

where a and b are constants. At pH 1.4, the fitted values for a and b are 0.18 mg/g-h and 0.49 mg/g respectively, with an r^2 0.96. When solution pH increased to 4.0, the two fitted parameters are 0.14 mg/g-h and 0.32 mg/g, respectively, with an r^2 0.97. Compared to the pseudo-second-order kinetic model, the Elovich model describes the PAAB adsorption better.
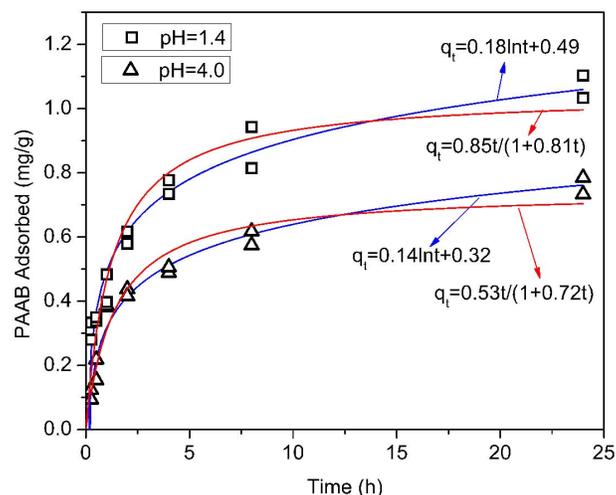

Fig. (2). Kinetics of PAAB adsorption on kaolinite at pH 1.4 and 4.0 fitted to pseudo-second-order (red lines) and Elovich models (blue lines).

3.2. PAAB Adsorption Isotherm

The adsorption of PAAB on kaolinite at pH 1.4 and 4.0 was fitted to the Freundlich and Langmuir isotherms. The Freundlich isotherm is expressed as:

$$C_s = K_F C_L^n \qquad (4)$$

which can be converted into a linear form

$$\log C_s = n \log C_L + \log K_F \qquad (5)$$

where C_s is the amount of PAAB adsorbed on kaolinite at equilibrium (mmol/g), C_L is the equilibrium PAAB

concentration (mg/g), K_F is the Freundlich distribution coefficient, and n is the linear coefficient. The Freundlich isotherm describes the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption. On the contrary, the Langmuir isotherm was assumed with a uniform surface on the adsorbent and all the adsorption sites were equivalent and adsorbed molecules did not interact with each other, resulting in a monolayer adsorption. The Langmuir isotherm has the form of

$$C_s = \frac{K_L S_m C_L}{1 + K_L C_L} \qquad (6)$$

where S_m is the adsorption capacity (mg/g), and K_L is the Langmuir coefficient (L/mg). Eq. (6) can be converted into a linear form

$$\frac{C_L}{C_s} = \frac{1}{K_L S_m} + \frac{C_L}{S_m} \qquad (7)$$

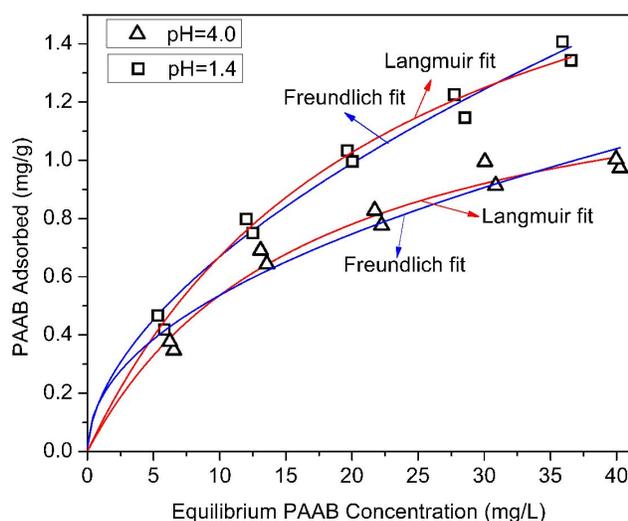So that K_L and S_m can be determined by a linear regression.

Fig. (3). Adsorption of PAAB on kaolinite at pH 1.4 and 4.0 fitted to Langmuir and Freundlich isotherms.

As shown in Fig. (**3**), Langmuir isotherm fitted the experimental data better than Freundlich isotherm, indicating a surface-limited or charge-limited adsorption rather than a multilayer adsorption. At pH 1.4, the fitted K_L and S_m values were 0.044 L/mg and 2.2 mg/g, respectively, comparable to 0.06 L/mg and 1.43 mg/g at pH 4.0. The fitted K_F and n values were 0.18 and 0.56 L/g, respectively, compared to 0.18 and 0.48 L/g at pH 4.0. The larger adsorption capacity S_m at pH 1.4 than at pH 4.0 indicated that PAAB had higher affinity for kaolinite in more acidic conditions.

As indicated by the higher regression coefficient, Langmuir isotherm was found better describing adsorption of PAAB on kaolinite than Freundlich isotherm. On the contrary, a study of the adsorption of Azo Dye C.I. Acid Red 14 on surface soils indicated that Freundlich isotherm fitted the data better than Langmuir isotherm [9]. However, the adsorption of methylene blue on raw, calcined and NaOH-treated kaolinite could be fitted well by both Freundlich

and Langmuir equations [14]. The adsorption capacity of PAAB on kaolinite in this study is lower than that of azobenzene on kaolinite [13].

3.3. Effect of Temperature on PAAB Adsorption

The temperature effect on PAAB distribution between the solid and the liquid phase is expressed by

$$\log K_d = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{R} \qquad (8)$$

where K_d is the distribution coefficient of PAAB between the solid and liquid phases, ΔH is the change in enthalpy, ΔS is the change in entropy, R is the gas constant (8.31 Jmol^{-1}K^{-1}), and T is the operated temperature (K). When $\log K_d$ is plotted versus 1/T, a straight line is obtained (Fig. **4**). The values of ΔH and ΔS estimated from the slope and intercept are -6.93 kJ/mol and -8.73 J/mol·K at pH 1.4, respectively, compared to -4.72 kJ/mol and -6.15 J/mol·K at pH 4.0. The linear regressions were performed with Origin 8.0. When pH is 1.4, the standard errors of ΔH and ΔS estimated from the fitting results are 0.84 and 1.2, respectively. While pH is 4.0, the standard errors of ΔH and ΔS decrease to 0.39 and 0.56, respectively.

$$\Delta G = \Delta H - T \Delta S \qquad (9)$$

The change in free energy ΔG after PAAB adsorption at pH 1.4 and 4.0 calculated based on equation (9) is −4.33 kJ/mol and -2.89 kJ/mol(at 25 °C), respectively. The negative ΔG value indicated the adsorption of PAAB on kaolinite was a spontaneous process. The ΔG value from this study is less negative compared to those for methylene blue adsorption on kaolinite. The negative ΔH value suggested that PAAB adsorption was an exothermal process and therefore decrease in temperature should facilitate the adsorption of PAAB onto kaolinite. The ΔH could be used to make a distinction between physical and chemical adsorption with a borderline at -40 kJ/mol. The ΔH value of -6.93 and -4.72 kJ/mol suggested that the physical adsorption was the main interaction mechanism. The electrostatic attraction and van der Waals' force played an important role in the adsorption of PAAB on kaolinite.
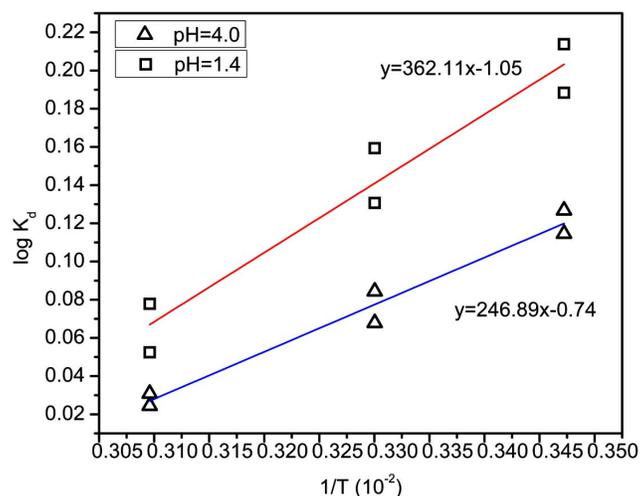

Fig. (4). Linear relation between $\log K_d$ and 1/T.

3.4. Effect of Ionic Strength on PAAB Adsorption

In general, there is a certain concentration of inorganic salt in natural environment. Thus, it is essential to investigate the effect of inorganic cations on the adsorption of PAAB on kaolinite. As illustrated in Fig. (**5**), a decrease in PAAB adsorption is accompanied by an increase in ionic strength. In acidic condition, PAAB molecules exist in a cationic form due to the protonation of the amine group, and the adsorption of PAAB on kaolinite was mainly *via* cation exchange. With the increasing Na^+ concentration, the increasing competition between Na^+ and the cationic form PAAB for adsorption sites results in lower adsorption of PAAB.
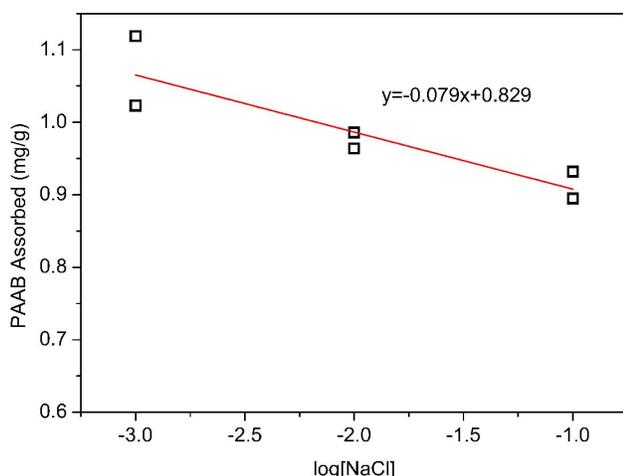

Fig. (5). Influence of ionic strength on PAAB adsorption.

3.5. XRD Analysis

The XRD analysis indicated that no change in the d_{001}-spacing of kaolinite was observed after equilibrium with PAAB for 24 h, suggesting that the adsorption takes place mainly on the external surface of kaolinite (Fig. **6**). Comparatively, the adsorption benzaminde, nitroaniline and cyclic imides on kaolinite resulted in the expansion of interlayer space [15-17].
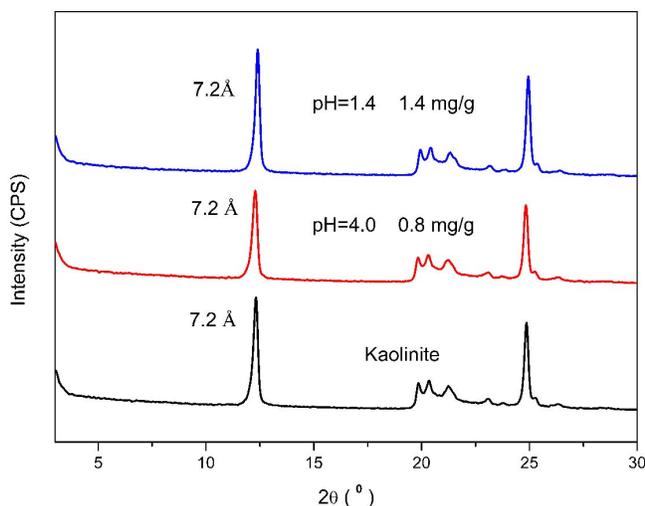

Fig. (6). XRD patterns of kaolinite and PAAB-loaded kaolinite.

3.6. FTIR Analysis

The FTIR spectra of PAAB, mixture of PAAB and kaolinite and PAAB-loaded kaolinite are shown in Fig. (**7**). As indicated in Fig. (**7**), the characteristic spectrum of PAAB did not appear in the spectra of mixture of PAAB and kaolinite, which may be attributed to the fact that the amount of PAAB in mixture is too small. The absorption bands at 3694 and 3623 cm^{-1} are ascribed to the stretching vibration of the surface hydroxyl. The peaks at 1105 and 1026 cm^{-1} are due to stretching vibration from Si-O, while the peak at 918 cm^{-1} is assigned to the deformation vibration of Al-O-H [18]. Compared with the spectra of mixture of PAAB and kaolinite, new bands at 1515 cm^{-1} were observed in the spectra of the PAAB-loaded kaolinite, which originated from the PAAB adsorbed on the surface of kaolinite [19, 20]. As shown in Fig. (**7**), the main band position for Si-O, Al-O-H and PAAB show no apparent shift, indicating that the adsorption of PAAB on kaolinite surface was attributed to the electrostatic attraction and van der Waals' force between the surface and PAAB molecules.
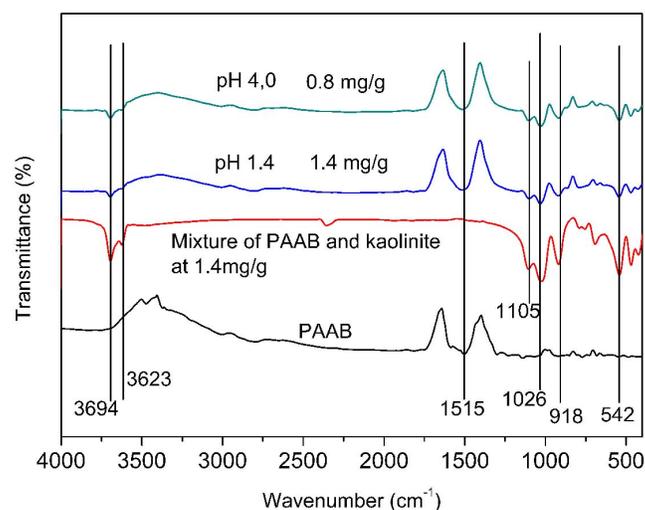

Fig. (7). FTIR spectra of mixture of PAAB and kaolinite and PAAB-loaded kaolinite.

CONCLUSION

The adsorption of PAAB on kaolinite was systematically studied under different conditions. The adsorption of PAAB was found to increase with decreasing pH and ionic strength. The change in free energy ΔG after PAAB adsorption at pH 1.4 and 4.0 is -4.33 and -2.89 kJ/mol, respectively. The negative ΔG value indicated that the adsorption of PAAB on kaolinite is a spontaneous and favorable process. The enthalpy change (ΔH) at pH 1.4 is -6.93 kJ/mol, compared to -8.73 kJ/mol at pH 4.0, suggesting that the interaction between the adsorbent and the adsorbate molecules was physical rather than chemical. X-ray diffraction and FTIR spectroscopy exhibit no significant change in XRD pattern and FTIR spectra, indicating the adsorption of PAAB on kaolinite was mainly attributed to the electrostatic attraction and van der Waals' force between the surface of kaolinite and the PAAB molecules.

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CONFLICT OF INTEREST

Declared none.

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