

Studies on the Adsorption of p-Aminoazobenzene onto Kaolinite

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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 $\text{C}_{12}\text{H}_{11}\text{N}_3$ and structure is presented in Fig. (1). The dissociation constant (pK_a) of PAAB is about 2.8. When solution pH is below pK_a , PAAB exists mainly as cationic form PAAB^+ ; while solution pH is above pK_a , the neutral form PAAB^0 predominates. All other

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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.

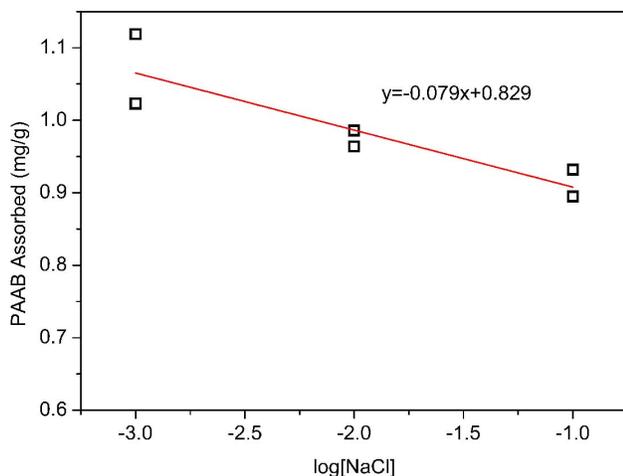


Fig. (5). Influence of ionic strength on PAAB adsorption.

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.

ACKNOWLEDGEMENTS

The study is supported by the Key Project of Chinese Ministry of Education (10706) and the Technology Creative Project of Excellent Middle & Young Team of Hubei Province (T201204).

CONFLICT OF INTEREST

Declared none.

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Received: February 22, 2012

Revised: March 22, 2012

Accepted: April 2, 2012

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