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Research on hydrophilicity and hydrophobicity of adsorption of NOM on metal oxide/water interface

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ABSTRACT

Natural organic matter, consisting of 40–60% of humic substances of which the main ingredient is humic acid (HA), is ubiquitous in natural water systems. It poses a potential - threat to a water treatment system. Metal oxides in the form of minerals in water are usually considered as carriers of HA. The main adsorption mechanisms of HA on metal oxides have been electrostatic interaction, ligand exchange, hydrophobic interaction, etc.; however, few researches have done on hydrophobic interaction. Therefore, the goals of this study were to investigate the hydrophobic interaction of HA-Fe_2O_3 complexes and the functional groups of HA under various solution conditions, which can give us a better understanding of the adsorption mechanism. Results showed that the thermal weight loss of HA-Fe_2O_3 complex, which indicated its hydrophilicity and hydrophobicity, changed regularly when the pH value was varying and the ionic strength maintained constant. While the ionic strength was changing and the pH value maintained constant, the weight loss showed a fluctuating trend. FTIR spectra indicated that the HA functional groups, of which the combined effect finally played a significant role in hydrophilicity and hydrophobicity of HA-Fe_2O_3 complex, might be hydrophilic hydroxyl (OH), carbonyl (C=O), and hydrophobic alkane (CH_2). The change trend of HA adsorption amount with solution conditions coincided with that of weight loss of HA-Fe_2O_3 complex, which testified that hydrophobic interaction did affect the adsorption of HA on metal oxides.

Keywords: Adsorption; Functional groups; Fe_2O_3 nanoparticles; Humic acid; Hydrophilicity and hydrophobicity; Solution conditions

1. Introduction

Natural organic matter (NOM) and metal oxides are ubiquitous in nature [1–4]. During water treatment process, the existence of NOM tends to have an adverse impact on coagulation, reduce the filtration efficiency and produce large amounts of disinfection byproducts after chlorination, such as trihalomethans [5,6]. In natural water systems, the aquatic humic substance (HS), whose main ingredient is humic acid (HA), constitutes 40–60% of the NOM [7]. HA is a complex organic polymer, and metal oxides in the form of

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minerals in water are usually considered as carriers of HA. The main adsorption mechanisms of HA on metal oxides are very complicated, including ligand exchange, van der Waals force, electrostatic interaction, hydrophobic interaction, anion exchange and cation bridging [8]. So far, many studies have been done on electrostatic interaction and ligand exchange, but few have been done on hydrophobic interaction which is of great importance for researchers to know more about the adsorption process of NOM on metal oxide/water interface, thus getting a better control of water pollution.

On account of the inherent hydrophobicity of some nonpolar components in NOM, the hydrophobic interaction forms. So NOM is forced to be alienated from water molecules and be adsorbed on metal oxides. Previous studies have noted the significance of hydrophobic interaction in adsorption of NOM on metal oxides. Jardine et al. [9] have observed that in the adsorption process of NOM on soil particles, when the adsorption equilibrium was reached, some hydrophilic components remained in the solution, while hydrophobic components were adsorbed onto mineral surfaces and disappeared from the solution. Ochs et al. [10] have studied the adsorption of a peat-derived HS onto a hydrophobic surface (mercury electrode) and confirmed that hydrophobic interaction prevailed at the mercury surface while coordinative adsorption (ligand exchange) was enhanced by hydrophobic effect and that is the predominant adsorption mechanism at the oxide surface. Hur and Schlautman [11] have found that competitive effect of phosphate on adsorption was closely related to the pH value of the system. When the pH value was higher than its pH_{pzc} (pH value of point of zero charge), competitive effect on adsorption is not obvious so that the adsorption might be resulted from hydrophobic interaction.

The adsorption of HA is closely related to the functional groups present at the surface of metal oxides or in the HA structure and solution conditions such as pH value and ionic strength, etc. [12,13]. The objectives of this study were to investigate, by FTIR spectrum, TGA, TOC analysis, and adsorption density experiment, the hydrophilicity and hydrophobicity changes of HA-Fe_2O_3 complexes and the functional groups of HA under various solution conditions, which play important roles in the adsorption of HA on Fe_2O_3 nanoparticles surfaces.

2. Materials and methods

2.1. Materials

The commercial HA used in this study was purchased from Sigma–Aldrich Company and used with further purification. Properties of the HA supplied by Sigma–Aldrich Company are shown in Table 1. Fe_2O_3 nanoparticles were synthesized using the sol–gel method by School of Materials Science, Wuhan University of Technology with the nanoparticles of average diameter 30 nm, the surface ξ potential 10.25 mV, and the pH_{pzc} 6.4–6.8. Aqueous solutions, suspensions, and samples were prepared with distilled water adsorbed by activated carbon. All other reagents, such as $NaNO_3$, NaOH, and HCl, were analytical reagent grade. Instruments used in this study are shown in Table 2.

2.2. Methods

2.2.1. Purification of HA

Further purification of HA which presents a black brown powdery solid state was taken on for high precision. The HA solution was filtered through a 0.45 μm filter membrane and stored in amber borosilicate glass bottles in a refrigerator.

2.2.2. TGA

The coordination bonds, which were formed by the interaction between Fe_2O_3 nanoparticles and various organic functional groups existing in the form of ions in HA, provided steric hindrance. The zeta potential and the surface charge density were then changed by the repulsion, thus making a significant difference in hydrophobicity of the HA-Fe_2O_3 complex. In this study, the changes of hydrophobicity after the adsorption of humic acid under various solution conditions were investigated with TGA method. The weight losses of HA-Fe_2O_3 complexes in different pH values and ionic strengths were quantitatively analyzed with the temperature ranging from 22 to 235℃.

After purification, the commercial humic acid (CHA) was weighed on ten thousandth analytical balance and diluted in activated-carbon-adsorbed distilled water under the alkaline condition (pH value = 10 ± 0.1). The solution should be filtered through a 0.45 μm filter membrane in case of the incomplete dissolution of CHA. DOC (70 mg/L) was

Table 1
Chemical properties of Sigma–Aldrich CHA

Elemental analysis (mass %)			Residue on ignition (mass %)
C	H	N	33
39.72	3.56	0.79	

Table 2
Instruments used

Number	Name	Model and specification	Experimental condition
1	pH meter	CHN868	
2	Liquid ultrasonic dispersion device	AS2060B	
3	Electronic balance	FA2004 N	
4	Multiple low-speed desktop centrifuge	TD6 M	
5	Constant temperature oscillator	FU-HUA ZD-85	25℃ ± 1℃
6	TOC/TN analyzer	HT2100	
7	Filter	0.45 μm	
8	FTIR	NICOLET 6700	
9	Integrated thermal analysis	STA449F$_3$	The test was under a neutral atmosphere of N_2 at the heating rate of 20℃/min, and final temperature was 700℃

then measured by the TOC analyzer, and the solution was stored as the initial solution.

Fe_2O_3 nanoparticles were chosen as the model colloidal particles with particle size of 30 nm and dosage of 750 mg/L. The ionic strength was respectively adjusted to 0, 0.001, 0.005, 0.01, and 0.05 mol/kg with $NaNO_3$. The pH value was adjusted to 7, 10, and 12 (within the margin of error of 0.5) with 0.1 mol/L HNO_3 and 0.1 mol/L NaOH. After adjusting the pH value and ionic strength, 70 mL reaction solution in iodine flask was sonicated in Liquid ultrasonic dispersion device (AS2060B) for 15 min to resuspend the particles and break up aggregates before its use. After cooling down, the samples were oscillated in the constant temperature (25 ± 1℃) oscillator (FU-HUA ZD-85) for 24 h at the rotate speed of 120 r/min in order to reach adsorption equilibrium.

Subsequently, the reaction solutions were centrifuged for 20 min at the speed of 4,000 r/min in 100-mL plastic centrifuge tubes. The supernatants were slightly discarded, and activated-carbon-adsorbed distilled water of 70 mL was added and mixed with the residues. The mixtures were then stirred for 60 times with glass rods and centrifuged again. After having repeated the procedures described above for three times, the final residues were dried to obtain the final HA-Fe_2O_3 complexes which were then analyzed by the TGA.

2.2.3. FTIR analysis

FTIR analysis was employed in this study to quantitatively analyze the types and quantities of functional groups in HA-Fe_2O_3 complexes after adsorption process under different solution conditions in order to find the change rules of the hydrophilicity and hydrophobicity [14,15].

HA solutions of different pH values and ionic strengths were dried to obtain the HA powders. Then, the FTIR spectrum (NICOLET 6700) was taken with 2 mg of the sample mixed with 200 mg of dry KBr, which was pressed into a transparent disk.

2.2.4. Adsorption density experiment

The adsorption experiments were conducted to evaluate the influences of various solution conditions on adsorption behaviors. The adsorption densities of HA on Fe_2O_3 surfaces could be calculated according to the differences of TOC values after the adsorption equilibrium processes with pH value of 7, 10, 12 and ionic strength of 0.001, 0.005, 0.01, and 0.05 mol/kg. The procedures to reach adsorption equilibrium were the same with what were described in TGA process.

3 Results and discussion

3.1. Effect of pH value

With the temperature ranging from 22 to 235℃, the effect of pH value on weight loss of HA-Fe_2O_3 complex at certain ionic strengths is shown in Fig. 1. The weight losses of adsorption complexes are mainly attributed to the losses of water on their surface. The decomposition of HA with low molecular weight and volatile substances within the complexes is so slight that can be ignored [16]. It is clear that the weight loss decreased firstly and then increased with the pH value

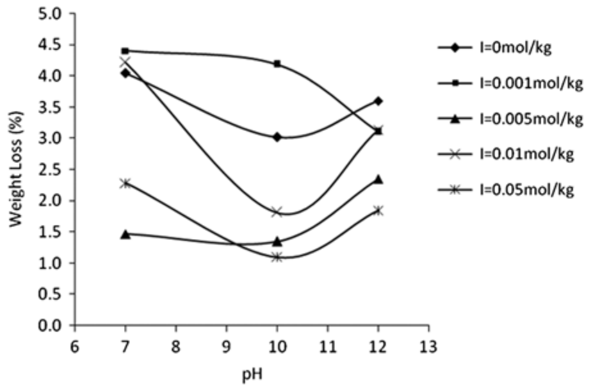

Fig. 1. Effect of pH value on weight loss of HA-Fe_2O_3 complex at certain ionic strengths.

increasing from 7 to 12 at the ionic strength of 0, 0.001, 0.005, 0.01, and 0.05 mol/kg. It is deduced that the hydrophobicity enhanced while the hydrophilicity reduced as the pH value increased from 7 to 10, causing more water lost at low pH value, that is 7, while less water lost at high pH value, thus the weight loss decreased. However, the weight loss increased as pH value increased from 10 to 12, indicating that the hydrophobicity reduced while the hydrophilicity enhanced. It is noted that, at the ionic strength of 0.001 mol/kg, the weight loss showed a continuous decline with the growing up of pH value from 7 to 12, which might also be attributed to the enhancement of hydrophobicity and reduction of hydrophilicity.

Figs. 2 and 3 show the FTIR spectra of HA powders at the pH value of 7 and 10 with the ionic strength maintained constant at 0.05 mol/kg. It can reflect the types and quantities of functional groups [17–19].

It is obvious from Figs. 2 and 3 that as the pH value increased from 7 to 10 at the ionic strength of 0.05 mol/kg, the heights of stretching vibration absorption peak of hydroxyl (OH) at 3,455 cm^{-1} and carbonyl (C=O) at 1,636 cm^{-1} decreased, while the height of wagging vibration absorption peak of alkane (CH_2) at 1,385 cm^{-1} increased.

According to TGA in Fig. 1, the hydrophilicity of HA-Fe_2O_3 at pH value = 7 was stronger than that of pH value = 10 with the ionic strength of 0.05 mol/kg. Functional groups of HA with different hydrophilicity and hydrophobicity, which are supposed to impact predominantly on the hydrophilicity and hydrophobicity of HA-Fe_2O_3, might be hydrophilic OH, C=O,

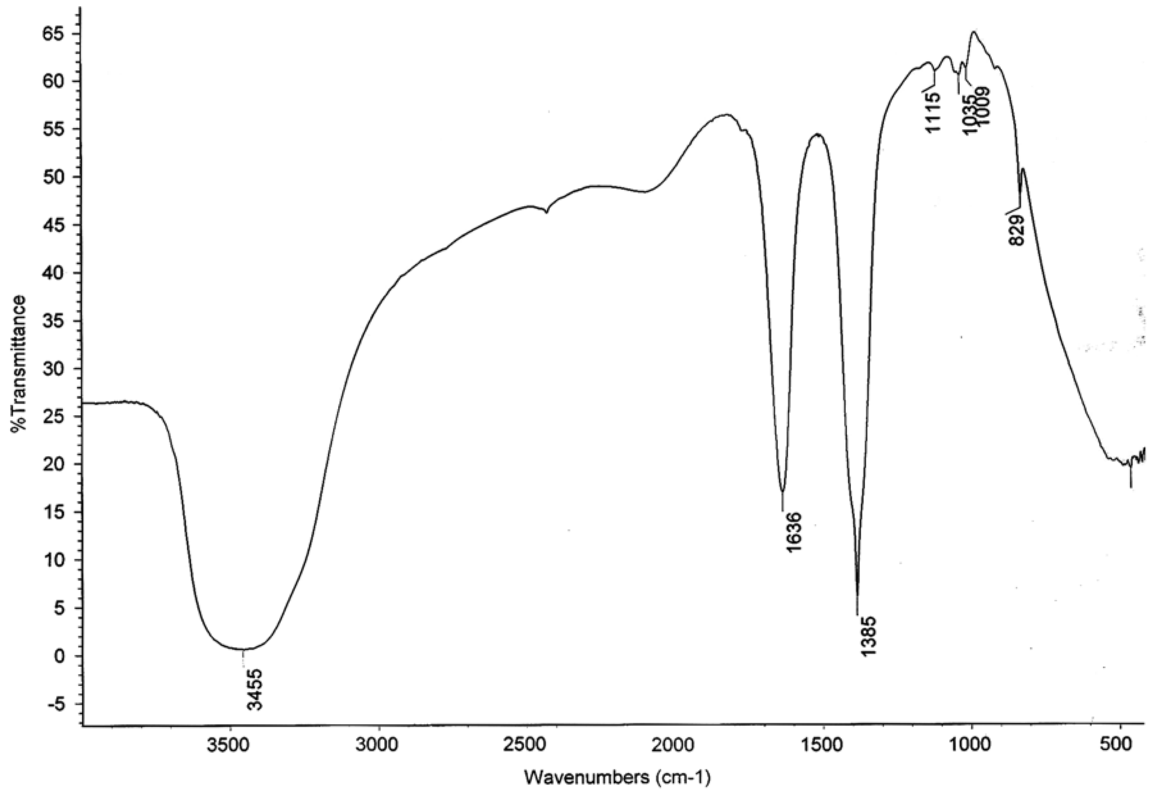

Fig. 2. FTIR spectrum at pH value = 7, I = 0.05 mol/kg.

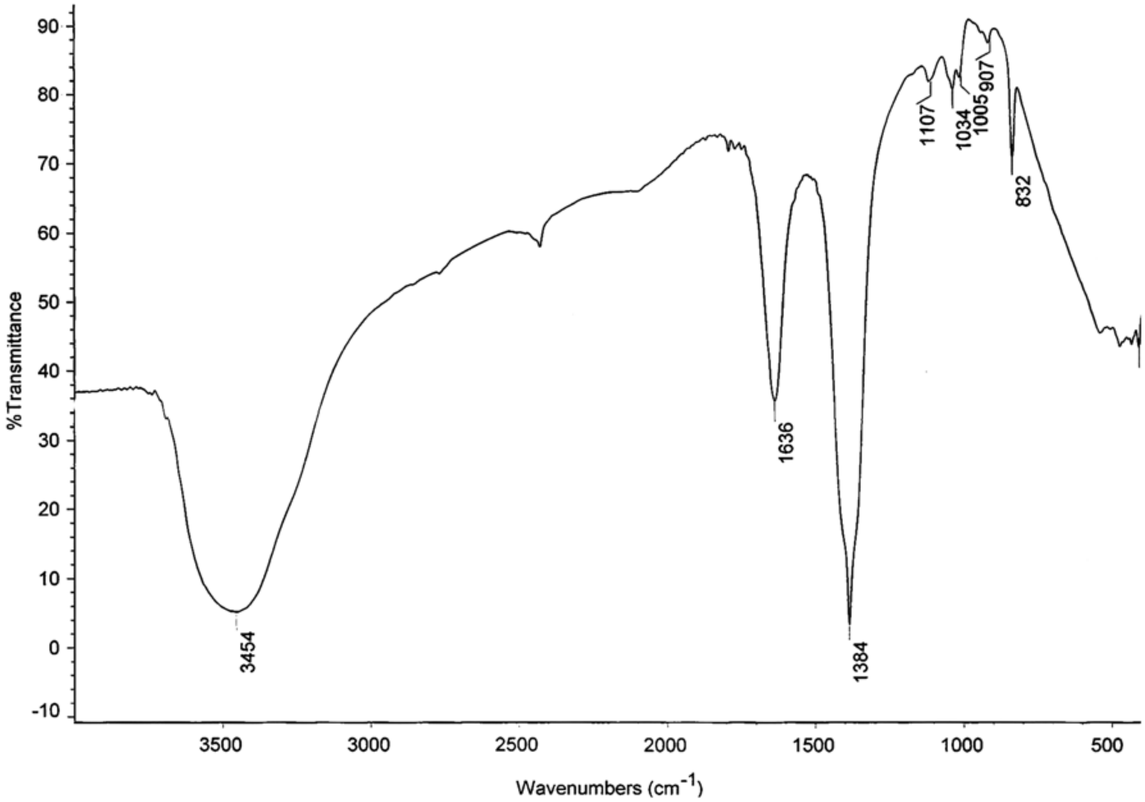

Fig. 3. FTIR spectrum at pH value = 10, I = 0.05 mol/kg.

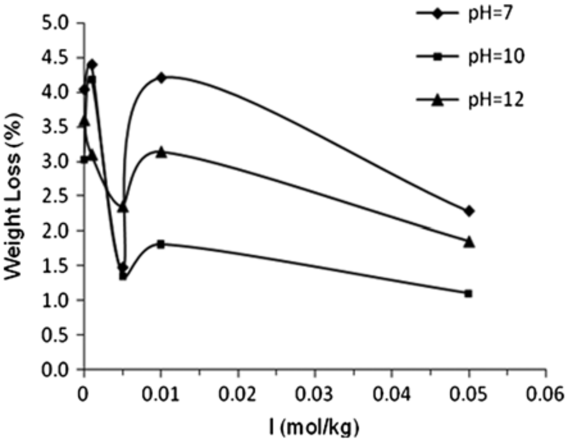

Fig. 4. Effect of ionic strength on weight loss of HA-Fe_2O_3 complex at certain pH value.

and hydrophobic CH_2. The heights of absorption peak of OH (3,455 cm^{-1}) and C=O (1,636 cm^{-1}) decreased, indicating that the quantities of hydrophilic functional groups decreased, thus resulting in the weakening of hydrophilicity. Meanwhile, the height of absorption peak of CH_2 (1,385 cm^{-1}) increased, which means the quantities of hydrophobic functional groups increased, thus causing the enhancement of hydrophobicity. It was the combined impact of functional groups that finally reduced the hydrophilicity of HA-Fe_2O_3. It is also assumed that the quantities of functional groups are affected by solution conditions.

3.2. *Effect of ionic strength*

Fig. 4 illustrates the effect of ionic strength on weight loss of HA-Fe_2O_3 complex at certain pH value. It is shown that when pH value was fixed, the weight loss of the HA-Fe_2O_3 kept changing with the increasing of the ionic strength from 0 to 0.05 mol/kg, and the curves showed fluctuating trends which meant the hydrophilicity and hydrophobicity changed alternately.

The FTIR spectra of HA powders at various pH values and ionic strengths are shown in Figs. 2, 3 and, 5–8.

According to TGA in Fig. 4, the hydrophilicity of HA-Fe_2O_3 at ionic strength of 0.001 mol/kg was stronger than that of 0.05 mol/kg with the pH value of 7, which, as was stated above, could be attributed to the

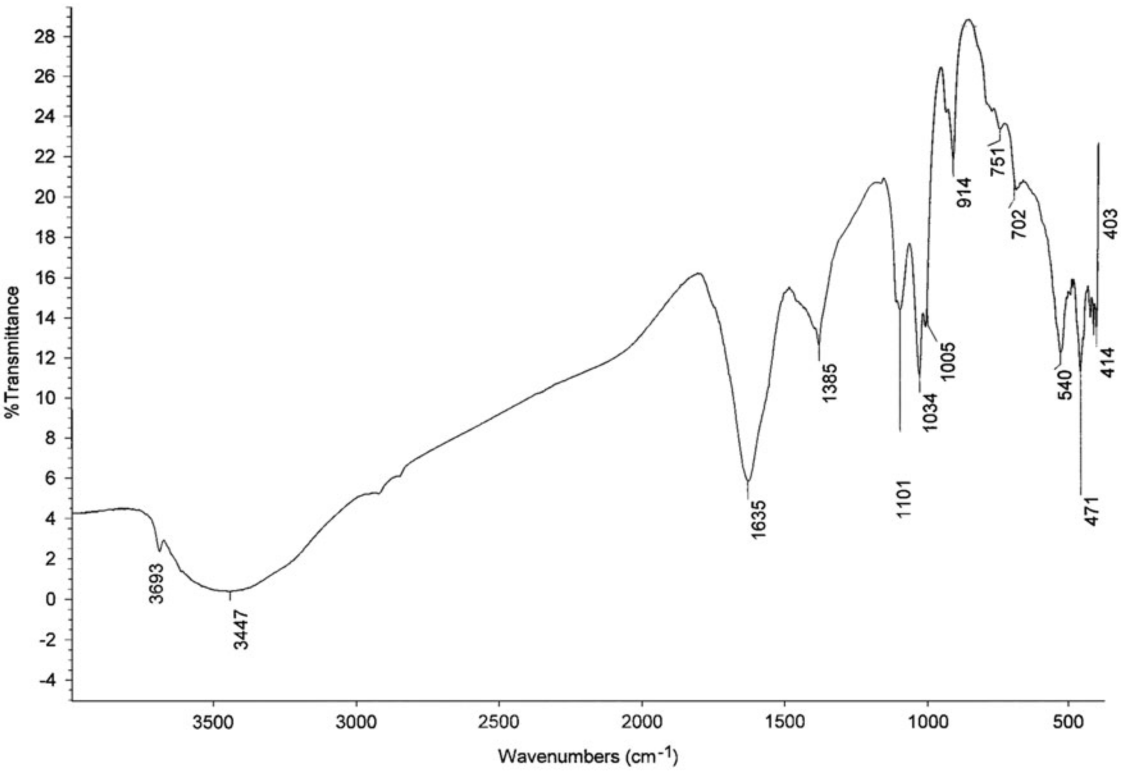

Fig. 5. FTIR spectrum at pH value = 7, I = 0.001 mol/kg.

functional groups with different hydrophilicity and hydrophobicity. From Figs. 2 and 5, as the ionic strength increased at pH value of 7, the stretching vibration absorption peak of hydrophilic OH (3,693 cm^{-1}) disappeared, indicating that the quantities of hydrophilic functional groups decreased and were too little to be measured. Meanwhile, the absorption peak of hydrophilic OH at 3,447 cm^{-1} moved to 3,455 cm^{-1}. The increasing heights of hydrophilic OH (3,455 cm^{-1}) and C=O (1,636 cm^{-1}) showed the rising of hydrophilic functional groups. While the height of absorption peak of hydrophobic CH_2 (1,385 cm^{-1}) also showed an increase, on the contrary, illustrating the growth of hydrophobic functional groups. Consequently, the combined effect of different functional groups resulted in the weakening of hydrophilicity and enhancement of hydrophobicity of HA-Fe_2O_3.

From Fig. 4, when the pH value was fixed at 10, the hydrophilicity of HA-Fe_2O_3 at ionic strength of 0.001 mol/kg was stronger than that of 0.05 mol/kg. Figs. 3 and 6 show that as the ionic strength increased, the absorption peak of OH (3,693 cm^{-1}) disappeared, the height of absorption peak of OH (3,440 cm^{-1}) and C=O (1,636 cm^{-1}) decreased, and that of CH_2 (1,385 cm^{-1}) increased. Similarly, the combined effect of different functional groups resulted in the weakening of hydrophilicity and enhancement of hydrophobicity of HA-Fe_2O_3.

It can be clearly observed that the hydrophilicity of HA-Fe_2O_3 at ionic strength of 0.005 mol/kg was stronger than that of 0.05 mol/kg when the pH value was 12, which was also ascribed to the combined effect of different functional groups. From Figs. 7 and 8, as the ionic strength increased, the absorption peak of OH (3,693 cm^{-1}) disappeared, the height of absorption peak of OH (3,440 cm^{-1}), C=O (1,636 cm^{-1}), and CH_2 (1,385 cm^{-1}) decreased, thus leading to the final weakening of hydrophilicity and enhancement of hydrophobicity of HA-Fe_2O_3.

It is inferred that in Fig. 4, the fluctuating trends of the curves which meant the hydrophilicity and hydrophobicity of HA-Fe_2O_3 changed alternately with the iconic strength increasing from 0 to 0.05 mol/kg are, in the same way, due to the changing quantities of functional groups under different solution conditions.

3.3. Effects of solution conditions on adsorption density

As the hydrophobic effect is closely related to adsorption behaviors of NOM on metal oxide/water

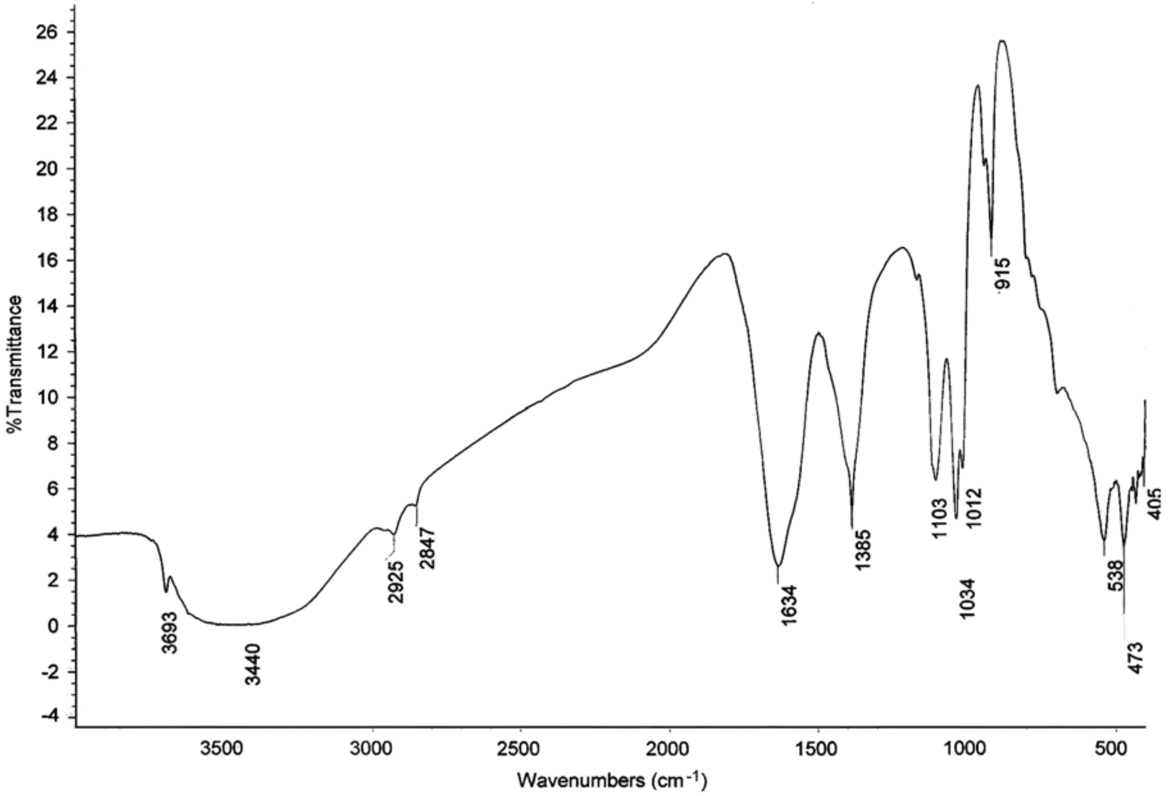

Fig. 6. FTIR spectrum at pH value = 10, *I* = 0.001 mol/kg.

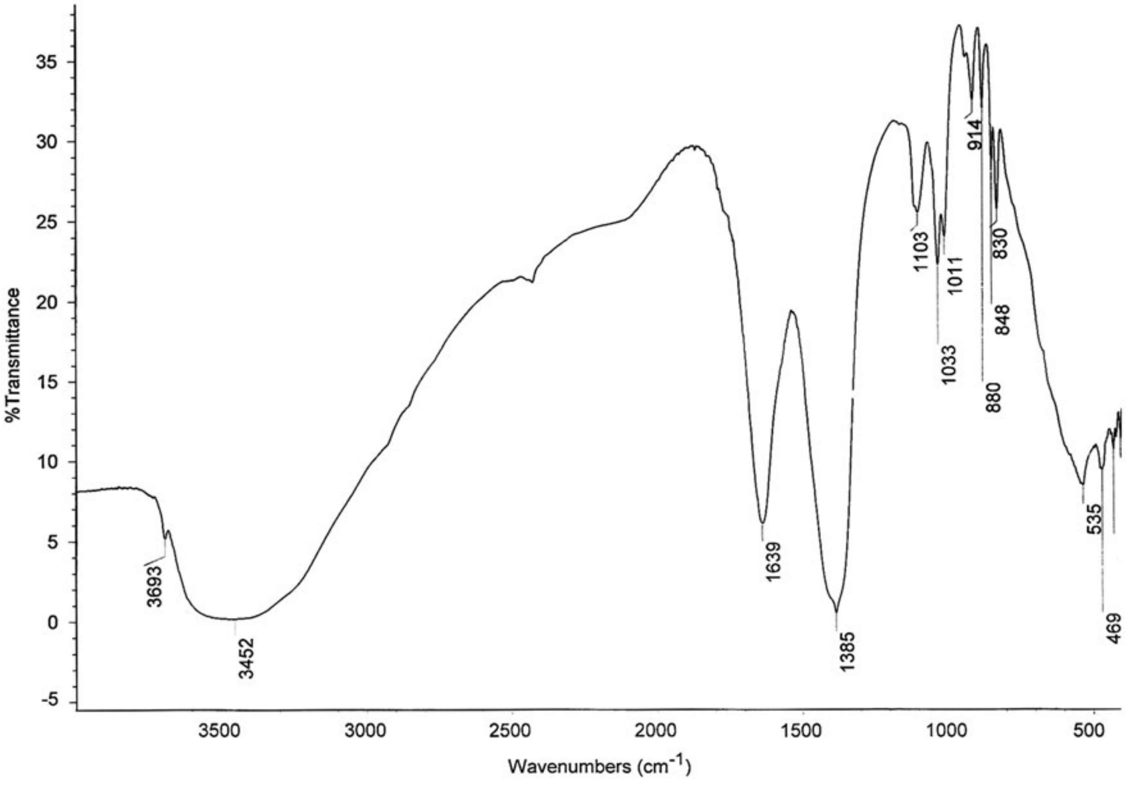

Fig. 7. FTIR spectrum at pH value = 12, *I* = 0.005 mol/kg.

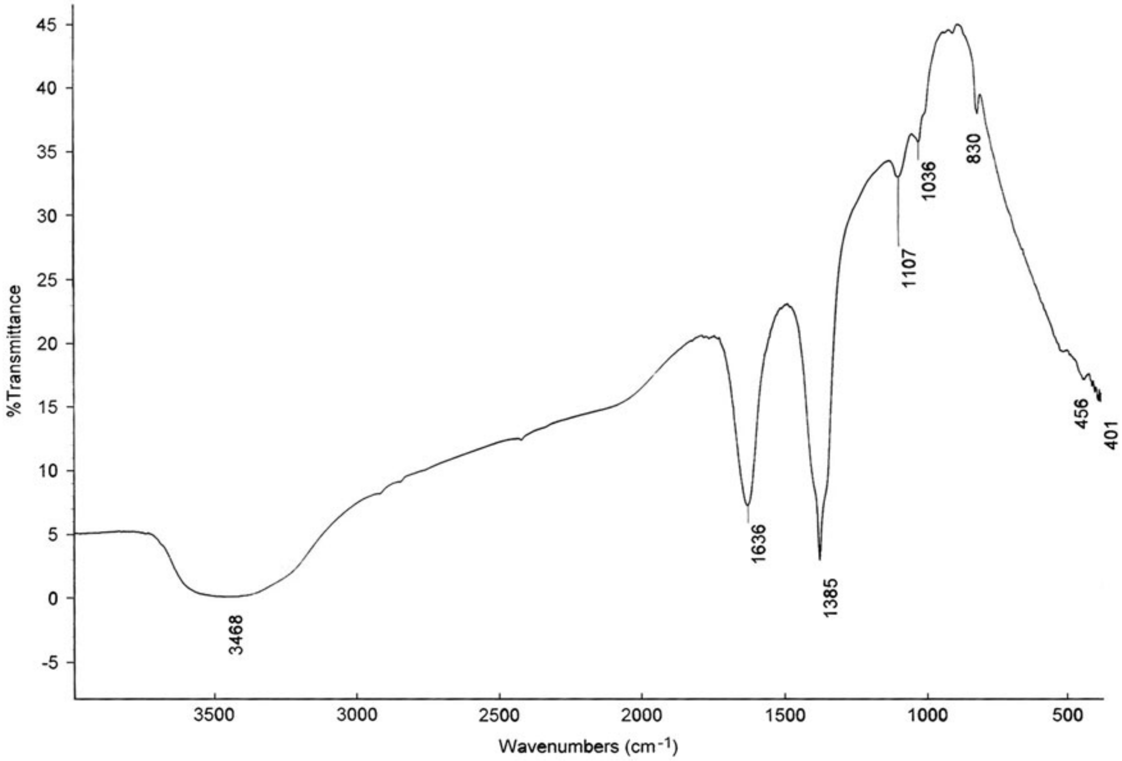

Fig. 8. FTIR spectrum at pH value = 12, I = 0.05 mol/kg.

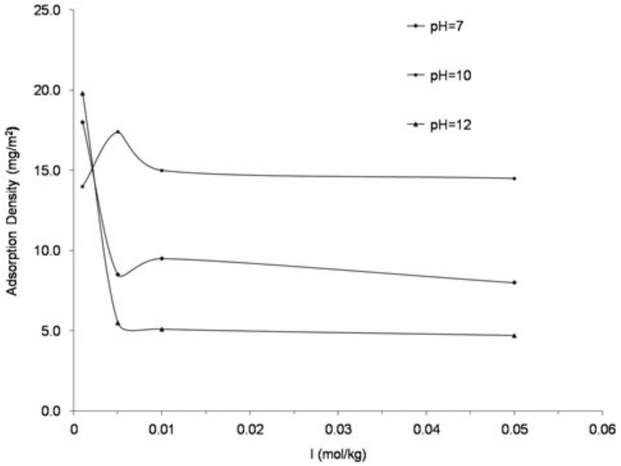

Fig. 9. Changes of amount of HA adsorption with solution conditions.

interface, solution conditions which play important roles in hydrophobic effect are supposed to have impacts on adsorption behaviors as well [20]. In this study, the different adsorption behaviors were also investigated by adsorption density experiment with the change of solution conditions. The result is shown in Fig. 9.

As is shown in Fig. 9, the adsorption density increased with the pH value increasing from 7 to 10 at the ionic strength of 0.001, 0.005, 0.01, and 0.05 mol/kg, which coincided with the increase of hydrophobicity and decrease of hydrophilicity of HA-Fe_2O_3 according to Figs. 1 and 4. In other words, the increase of hydrophobicity and decrease of hydrophilicity were beneficial to the adsorption process. Conversely, the adsorption density decreased as pH value increased from 10 to 12 which meant that the increase of hydrophilicity and decrease of hydrophobicity were of no good to the adsorption process. Therefore, the changing regularity of adsorption density was closely related to the hydrophilicity and hydrophobicity of HA-Fe_2O_3 complex, which indicated that the change of solution conditions would have a significant impact on adsorption behaviors.

4. Conclusions

The solution conditions play an important role in hydrophobic effect during the adsorption of HA on Fe_2O_3 nanoparticles surfaces. Results showed that when the ionic strength was kept at 0, 0.005, 0.01, and 0.05 mol/kg, the thermal weight loss of the complex, which indicated its hydrophilicity and hydrophobicity, decreased at first and then increased as the pH value increased from 7 to 12. The hydrophilicity reduced and hydrophobicity enhanced as the pH value increased from 7 to 10, while the hydrophilicity enhanced and hydrophobicity reduced as the pH value increased from 10 to 12. When the ionic strength was kept at 0.001 mol/kg, the thermal weight loss of the complex decreased as the pH value increased from 7 to 12, which provided the evidence that the hydrophilicity reduced and hydrophobicity enhanced.

When the pH value was kept constant and the ionic strength changed, the thermal weight loss of the complex kept changing with the increase of the ionic strength, the curves showed fluctuating trends, and the hydrophilicity and hydrophobicity changed alternately.

The FTIR spectra results indicated that the HA functional groups, of which the combined effect played a significant role in hydrophilicity and hydrophobicity of HA-Fe_2O_3 complex, might be hydrophilic hydroxyl (OH), carbonyl (C=O), and hydrophobic alkane (CH_2).

The change trend of HA adsorption amount with solution conditions coincided with that of weight loss of HA-Fe_2O_3 complex, which testified that hydrophobic interaction did affect the adsorption of HA on metal oxides.

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