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Adsorption of lignite humic acid onto magnetite particle surface

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Abstract: Modified humic acid (MHA) binder based on lignite humic substances is a novel sort of promising organic binder for iron ore pellets. Humic acid (HA) is one of the main ingredients of MHA binder. Pure HA was firstly isolated from lignite and then adsorption of HA onto magnetite particle surface was investigated. The final results indicate that the adsorption of HA onto magnetite surface accords with Langmuir model well, and it is evidently influenced by the initial HA concentration and solution pH value. Adsorption depends on chemical interaction at pH values above the PZC (the pH where the Zeta potentials of minerals are zero) of magnetite, while electrostatic attraction and chemical interaction both contribute to the adsorption at pH values below the PZC.

Key words: lignite humic acid; magnetite; adsorption; Zeta potential

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1 Introduction

The key factor for high-quality iron ore pellets is the selection of proper binder [1]. Pellet binders mainly include three types: inorganic binder, organic binder, and a compound of these two fractions. Compared with traditional inorganic binders, for example bentonite, organic binders have been regarded as promising substitutes of inorganic binders for their advantages of lower dosage required, higher strength of green balls, less residue in finished pellets after roasted, etc. Modified humic acid (MHA) binder, a novel type of promising organic binder extracted from lignite, has been proven a suitable binder for iron ore pellets by laboratory studies and patented in China [2]. Previous researches show that, when the dosage of MHA added in pellets reaches 0.25%−0.5% (mass fraction), the quality of finished pellets meets the requirement of blast furnace ironmaking [3]. However, using bentonite as binder, the mass fraction of it is required to be more than 2%, which obviously reduces the total iron grade of pellets. In order that MHA binders can be widely used in the industrial pellet production, it is imperative to understand the adsorption and interaction mechanism of MHA onto iron ore surface.

Humic substances in the MHA binder can be further separated into two fractions: fluvic acid (FA) and humic acid (HA). FA is the fraction of humic substances that is soluble under all pH conditions [4]. HA is defined as the fraction of humic substances that is insoluble at pH values below 2, but becomes soluble at greater pH values [4]. MHA binder is mainly composed of HA and FA, and HA accounts for 80%−90% (mass fraction) of organic ingredients in the MHA binder. In former research, the interaction between FA and iron ore surface has been studied and published [5].

Although the interaction between HA and oxides has been investigated by a number of researchers [6−11] in some fields such as environment and soil science, the adsorption of HA onto a particular iron oxide, the magnetite (Fe_3O_4), which, especially in China, is one of the main raw materials for iron ore pellets, has not been examined deeply and the adsorption mechanism is unclear yet. Even if in a few studies [12] reported, the magnetite as experimental material is usually synthetic agent rather than natural high grade iron ore. Therefore, the conclusion would not be suitable for the real situation of iron ore pellets.

In this work, high grade HA was firstly extracted from lignite. Then, the effect of initial HA concentration and solution pH on the sorption onto natural magnetite as well as the Zeta potential were studied. This work was anticipated to provide direction for the extensive application of novel MHA binder in iron ore pellet production.

2 Experimental

2.1 Materials

Liling lignite, a typical sort of brown coal in Hunan province of China, from which the pure HA used in this

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test was isolated, was dried in air and ground to pass through 2 mm sieve. The industrial analysis results of them, according to China Coal Industry Standard Analysis, are listed in Table 1, indicating that ash content of this lignite reaches up to 51.20%.

Table 1 Proximate analysis results of lignite (mass fraction, %)

Fixed carbon	Ash	Volatile
19.47	51.20	29.33

The sample iron ores (magnetite) were obtained from Australia. Firstly, the magnetite samples were ground and passed through a 30 μm wet sieve. Then, the undersize magnetite granules were dried at 100 °C and used for the tests. Main chemical compositions of magnetite granules were analyzed and presented in Table 2.

Table 2 Main chemical compositions of magnetite granules (mass fraction, %)

Total Fe	FeO	SiO_2	CaO	MgO
68.15	27.54	4.81	0.20	0.30
Al_2O_3	K_2O	Na_2O	S	P
1.25	0.043	0.10	0.024	0.098

It can be obtained from Table 2 that, w(Total Fe)/w(FeO)=2.47(<2.7). This indicates that the iron ore belongs to a typical kind of magnetite [13].

2.2 Extraction of HA from lignite

Many methods in other documents [14−17] have been referred to establish this extraction procedure of pure HA, which can be described as follows.

It involved mixing 80 g of lignite with 800 mL 0.1 mol/L $Na_4P_2O_7$ solution in a 1 500 mL round bottom flask with 3 necks. The air in the bottle was replaced with N_2 gas flowing across the two side necks during the whole process. The mixture was heated by water bath at 60 °C and stirred by a plastic agitator for 2 h. The suspension was centrifuged at 3 000 r/min for 30 min, then the supernatant was collected for acidification (pH=1.5 with 6 mol/L HCl). After that, the procedure above was repeated one time. Then, the precipitated HA in the second acidification was de-ashed with 0.1 mol/L HCl/0.3 mol/L HF solution, washed with deionized water to the degree that no Cl^- can be detected by $AgNO_3$ solution, freeze-dried, gently ground to pass through a 100 μm sieve, and stored for subsequent use. All the agents used in this experiment are analytically pure.

2.3 Characterization of HA

The ash content in HA was measured according to China Standard of Industry Analysis of Coal. The total acidity, carboxyl groups and phenol hydroxyl groups in HA were determined by the barium hydroxide and calcium acetate methods [17]. The metal element contents in ash were determined by inductively coupled plasma-atomic emission spectrometry (Model PS-6, Baird Company, USA). The C, H, N and S contents of the HA were determined using a Vario ELIII elemental analyzer (Elementary, Germany) by heating the samples at 800 °C for 4 h. Fourier transform infrared (FTIR) spectra were recorded with a FTIR spectrometer (Nicolet Nexus 670, Thermo, USA). 5 mg of HA was mixed gently with 95 mg of KBr as a background using a pestle and mortar and analyzed. FTIR spectra were recorded from 500 to 4 000 cm^{-1} at 4 000 resolution over 240 averaged scans.

2.4 Adsorption experiments

The solution used in measuring isotherm of adsorption of HA onto magnetite was prepared by adding 1 000 mg magnetite into 80 mL suspension containing 200 mg HA, and the solution was adjusted to pH 10, then the solution was shaken for 72 h before measurement. All the solutions in this work were prepared with deionized water, of which ion strengths were kept at 0.1 mol/L via adding calculated mass of solid NaCl, and solution pH was adjusted by 0.1 mol/L HCl and NaOH. HA concentrations were measured at wavelength of 465 nm with a model 722N visible spectrophotometer. All batch adsorption experiments were conducted twice and the mean values were adopted.

The adsorbed amount of HA by per unit mass of magnetite was estimated as the difference in HA concentrations before and after adsorption:

$$Q=\frac{(C_1-C_2)V}{m} \tag{1}$$

where Q is the amount of HA adsorbed by per unit mass of magnetite, mg/g; C_1 and C_2 are the initial and final concentrations of HA in solution, mg/L, V (L) and m (g) represent the volume of the liquid phase and the mass of magnetite added in the solution, respectively.

2.5 Zeta potential measurements

Zeta potential values of samples were determined with a Coulter Delsa model 44OSX at 25 °C by taking average of three measurements. The concentrations of magnetite solution and HA solution were 1 000 mg/L and 200 mg/L, respectively. The solution of magnetite coated by HA used for determining the Zeta Potential value was prepared through adding 80 mg magnetite into 80 mL HA suspension with concentration of 200 mg/L, then measurement was performed after shaking the solution for 72 h to ensure that adsorption equilibrium had been reached. Solution pH values were adjusted by 0.1 mol/L NaOH and HCl, and checked by an acidometer PHSJ-4A.

3 Results and discussion

3.1 Characterization of HA

The ash content of HA was 5.22% (as listed in Table 3), in which the metal contents are listed in Table 4. The results of element analysis are given in Table 3.

The organic groups of HA were analyzed using FTIR spectra (shown in Fig. 1) and analysis for the spectra is presented in Table 5. The FTIR spectra of this HA isolated from lignite is similar to that of HA published in other documents [18−19]. Combined with the measurement of acidic group in Table 3, it is concluded that the extracted HA from lignite is constituted by amounts of aromatic rings and the main functional groups are carboxyl groups and hydroxyl groups.

3.2 Effect of initial HA concentration on adsorption

Figure 2 presents adsorbance of HA as a function of equilibrium concentration. One may realize that the increase of the equilibrium concentration leads to an increase in the adsorbance of HA. This observation is deeply connected with the HA concentration gradient, which means that the values of the equilibrium concentration q increase with the increase of initial HA concentration.

The equilibrium sorption studies can be described by a sorption isotherm. As one of the most commonly used models, Langmuir model suggests that the adsorption occurs by monolayer sorption. The Langmuir equation is

$$q=\frac{Kq_{\max}C}{KC+1} \tag{2}$$

Its linear form is used to fit the adsorption data:

$$\frac{C}{q}=\frac{1}{K\cdot q_{\max}}+\frac{1}{q_{\max}}C \tag{3}$$

In Eq. (3), the linear regression is performed between C/q and C, and $q_{\max}$ and K are obtained from the intercept and slope, respectively. Here, K is a constant, L/mg, $q_{\max}$ represents the capability, mg/g; and C is the equilibrium concentration of HA, mg/L.

The measurement results of adsorption isotherm are plotted in Fig. 2, and the fitting curve according to Langmuir model is shown in Fig. 3. The fitting parameters are given in Table 6. From the fitting results, it can be seen that the adsorption of HA onto magnetite surface is in line with Langmuir model well, indicating that the adsorption belongs to monolayer sorption. The adsorption isotherm $q=2.59C/(47.62+C)$ is obtained. The mono-component Langmuir constant, $q_{\max}$, represents the monolayer saturation at equilibrium or total capacity of magnetite for HA. From Table 6, the maximum loading capacity of magnetite is obtained to be 2.59 mg/L, a little larger than the biggest adsorbance in this batch adsorption experiment, which indicates the adsorption saturation hasn't been reached in this batch adsorption experiment.

3.3 Effect of solution pH on adsorption

It is well known that pH value has a significant effect on adsorption of HA onto minerals [7, 10−11, 19]. It is observed from Fig. 4 that equilibrium adsorbance of HA onto magnetite is reduced rapidly with solution pH value decreasing.

The mechanism of ligand exchange between organic matters, such as HA, and hydroxyl groups on the surface of metal oxides has been proposed [20−21] as follows:

$$\text{Me—OH+H}^+\rightarrow\text{Me—OH}_2^+$$

$$\text{Me—OH}_2^+ + {}^-\text{O—CO—HA}\rightarrow\text{Me—O—CO—HA+H}_2\text{O}$$

When solution pH is lower than the PZC (the pH where Zeta potential of minerals is zero) of magnetite, that is 4.7, the Zeta potential of magnetite is positive due

Table 3 Measurement results of basic properties of HA

Ash content/%	Group content/(mmol·g^{-1})			Element content/%				
	Total acidic group	Phenolic hydroxyl group	Carboxyl group	C	H	O	N	S
5.22	6.11	3.58	2.53	58.49	2.75	35.79	1.32	1.65

Table 4 Metal contents in ash (mass fraction, %)

Fe	Zn	Mn	Mg	Al	Ca	Pb	Cu	Ni
0.183	—	—	0.017 2	0.284	0.036 5	0.003 5	0.017 2	—
Cd	Hg	Ag	K	Na	Ti	S	P	Cr
—	—	0.075 6	0.053 3	0.938 7	0.121	0.524 6	0.097 5	—

"−" means minute amount.

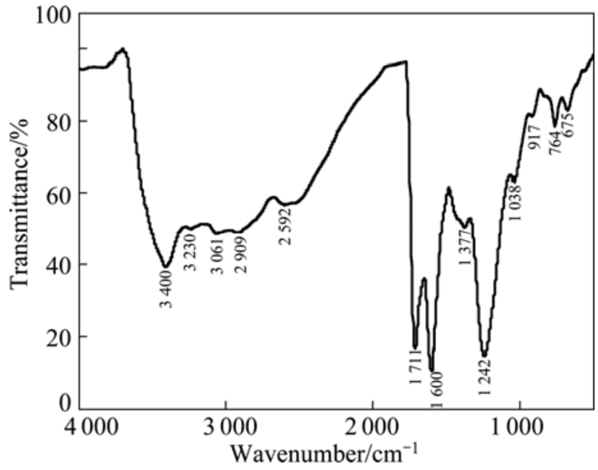

Fig. 1 FTIR spectrum of HA

Table 5 Analysis for FTIR spectra of HA

Wavenumber/cm^{-1}	Attribution
3 400	—OH groups
3 230	—NH$_3$ groups
3 061	Aromatic —C═C— in benzene rings and C—H
2 909	C—H in fatty hydrocarbon
2 592	O—H stretching of COO—H forming hydrogen-bonded groups
917	—OH in carboxyl groups
1 711	C═O in carboxyl groups or ketone groups
1 600	C═C in aromatic rings
1 377	—OH groups and antisymmetric stretching vibration of COOH
1 242	C—O and C—OH in phenol, ether or alcohol
1 038	C—H in trisubstituted aromatic rings
764, 675	C—H in substituted aromatic rings

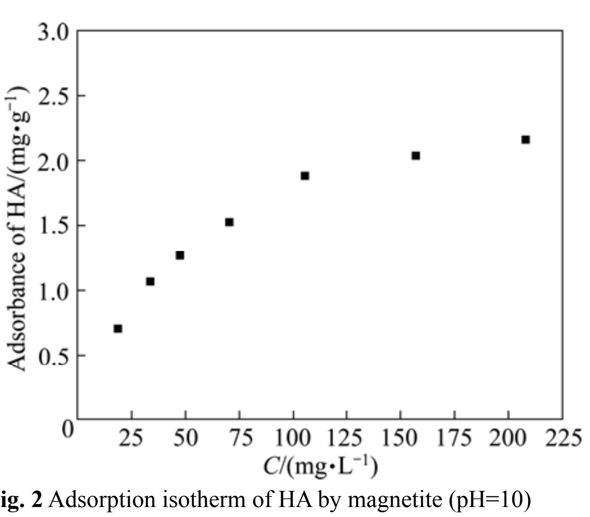

Fig. 2 Adsorption isotherm of HA by magnetite (pH=10)

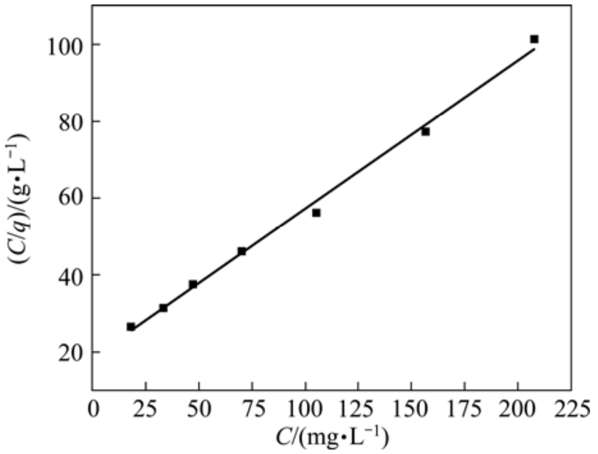

Fig. 3 Langmuir fitting of adsorption isotherm of HA by magnetite

Table 6 Fitting parameters for Langmuir model

$q_{\max}$/(mg·g^{-1})	K/(mg·L^{-1})	R^2
2.59	0.021	0.9946

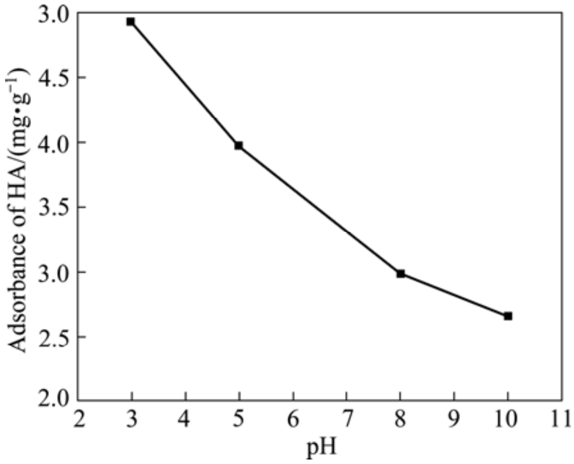

Fig. 4 Relationship between equilibrium adsorbance of HA and solution pH (Initial HA concentration: 100 mg/L)

to protonation, then ligand exchange occurs among parts of carboxyl groups, phenolic hydroxyl groups and magnetite surface. And the other parts of functional groups unionized could be adsorbed onto mineral surface via hydrogen bond even hydrophobic interaction [11, 19]. However, at higher solution pH values, more OH^- competes with negative ions of HA for adsorption sites on the surface. Hydrogen bond effect is weakened at the site that more positive charges on mineral surface are neutralized. At the same time, hydrophobic effect is also weakened for HA produces more negative ions because of ionization. All these factors mentioned above result in the reduction of adsorption amount of HA. Besides, the electrostatic repulsion at high pH values (referring to Fig. 5) also leads to the decrease of the adsorption of HA.

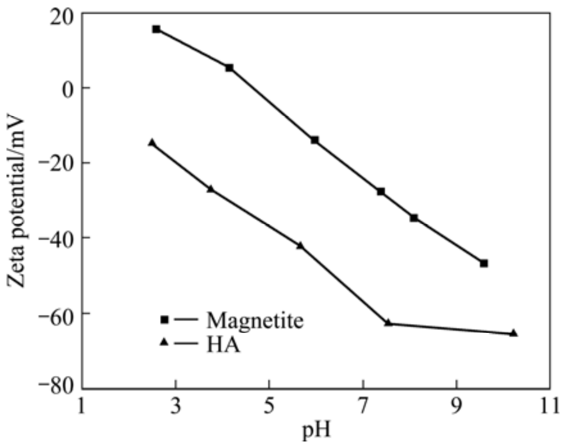

Fig. 5 Zeta potential values of magnetite and HA as function of solution pH values (Initial HA concentration: 100 mg/L)

3.4 Zeta potential value study

Zeta potential, often, can be used to estimate the likely effect of various adsorbates on the properties of minerals. The Zeta potential versus pH curves respectively matching the suspension of HA and natural magnetite granules are shown in Fig. 5. Zeta potential values in the investigated pH range are negative and decrease with increasing pH values. This result is consistent with the other researcher's conclusion [10], and this phenomenon can be explained from the structure of HA [22−23]. There are varieties of organic groups in the structure of HA, such as carboxyl, phenolic hydroxyl and hydroxyl groups, most of which negatively charge through ionization in the solution. The ionization is intensified when pH value is increased, then the Zeta potential is declined correspondingly.

PZC of the magnetite measured in this experiment is 4.7. If pH≤4.7, the magnetite surface possesses positive charges; while pH>4.7, it charges negatively. Because the HA in the solution always has negative charges in the measured pH range (bellow the PZC of magnetite), electrostatic attraction exists between the positive charges on magnetite surface and negative charges of HA. However, in relatively higher pH ranges, the interaction between HA and magnetite surface turns into electrostatic repulsion at the site that they both charge negatively. Moreover, the higher the pH value is, the greater the repulsion force is. Electrostatic interaction and ligand exchange proposed for adsorption of organic matters onto mineral surfaces [20, 24] could also be employed to explain the HA adsorption onto magnetite. Under the conditions of pH=8 and pH=10 (Fig. 4), the observation that the adsorption of HA onto magnetite surface occurs tells us significant information: When pH is higher than PZC of magnetite, the adsorption of HA onto magnetite depends on chemical effects such as ligand exchanges or hydrogen bond effect rather than electrostatic attraction; when pH is bellow the PZC of magnetite, both electrostatic attraction and the chemical effects contribute to the adsorption. It may also be responsible for the fact observed by many researchers that the adsorption of HA onto some other minerals is stronger at lower pH value than that at higher one [7, 10−11, 19].

Figure 6 shows the relationship between the Zeta potential of magnetite coated by HA and solution pH value; Fig. 7 illustrates the effects of initial HA concentration on the Zeta potential of magnetite. Compared with Fig. 5, the Zeta potential value of magnetite is changed from positive to negative after it is coated by HA, and the Zeta potential decreases with the pH value increasing. This result should be related with the macromolecule structure of HA and its amounts of organic groups [17, 22]. Quantities of groups, for instance carboxyl and phenolic hydroxyl groups, in aromatic rings or branches, exclude water layer and insert the inner layer of double electric layer of magnetite through ligand exchange, hydrogen bond, or electrostatic attraction to form adsorption. While the other parts of HA and considerable amounts of groups, most of which present negative electric property, still stretch in the

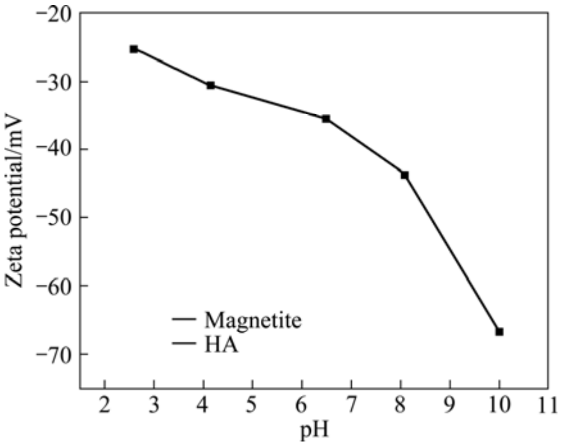

Fig. 6 Zeta potential of magnetite coated by HA as function of solution pH value (Initial HA concentration: 100 mg/L)

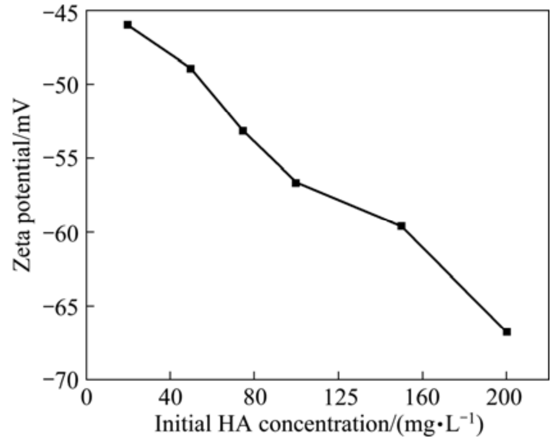

Fig. 7 Zeta potential of magnetite coated by HA as function of solution initial HA concentration (pH=10)

solution. So, the Zeta potential value of magnetite presents negative and reduces seriously after it is coated by HA. Furthermore, ionization of these groups is strengthened with pH value ascending. As a result, the Zeta potential of magnetite is cut down. On the other hand, when HA concentration is increased, more HA molecules are adsorbed by magnetite; therefore, the Zeta potential value of magnetite coated by HA is reduced, as shown in Fig. 7.

4 Conclusions

1) The adsorption behavior of humic acid onto magnetite accords to Langmuir model well, with which the adsorption equation $q=2.59C/(47.62+C)$ is obtained. The absorbance of HA onto magnetite surface decreases with solution pH increasing and increases with the initial HA concentration increasing in proper HA concentration range.

2) The Zeta potential of magnetite decreases after it is adsorbed by HA. At a certain HA concentration, the Zeta potential diminishes as solution pH increases; at a certain pH, the Zeta potential of magnetite decreases as HA concentration increases within proper range.

3) When the solution pH value is higher than 4.7, that is the PZC of magnetite, the occurrence of adsorption of HA onto magnetite depends on chemical interaction. When the pH value is below 4.7, electrostatic attraction and chemical interaction both contribute to the adsorption.

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