吸附硝化抑制剂硝基亚苯在黑土中的吸附特性及机制


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1 Introduction

硝基亚苯是一种早期开发的硝化抑制剂，具有明显的硝化抑制作用效果。*到目前为止，它在农业生产中被广泛研究和应用。在黑土中，硝基亚苯的有效性受到土壤成分、土壤有机质含量、土壤水分内容和土壤微生物的影响。*有机质是土壤中一个重要的成分，对硝基亚苯的有效性通过吸附硝化抑制剂的机理受到显著影响。*前人的研究结果表明，在不同的土壤类型中，硝基亚苯对土壤有机质及土壤微生物的影响不同。例如，Yan等*比较了硝基亚苯在不同土壤类型及不同土壤有机物含量下的吸附效果。与土壤有机质和黏土配位的硝基亚苯在干燥的土壤中被发现有较好的吸附效果。*此外，Kim等*通过研究硝基亚苯对黑土的吸附特性，发现硝基亚苯在黑土中的吸附量比在红土和壤土中的吸附量高。

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The compound nitrapyrin is easily adsorbed by soil organic matter in high-organic matter soils, and this results in its effectiveness reducing significantly. In this study, the adsorption characteristics and mechanisms of nitrapyrin as an adsorptive on humic acid (HA) and fulvic acid (FA) as adsorbents were investigated. The results showed that the kinetics of adsorption of nitrapyrin on both HA and FA followed pseudo-second-order kinetic models ($R^2 \geq 0.925$, $P < 0.05$) and the adsorption process included an initial fast-adsorption stage and a slow-adsorption stage thereafter. The adsorption efficiencies of nitrapyrin on HA + FA were higher than that on HA or FA alone, and that of HA was higher than that of FA. The adsorption isotherms of nitrapyrin on HA and FA could be optimally fitted with the Langmuir equation ($R^2 \geq 0.982$, $P < 0.05$). The maximum adsorption capacities of nitrapyrin on HA, FA and HA + FA were 4896.49, 3173.70 and 4925.56 mg kg$^{-1}$, respectively. Synergistic adsorption of nitrapyrin in coexisting systems of HA and FA was also observed. The adsorption mechanism of nitrapyrin on both HA and FA involved hydrogen bonding and hydrophobic interaction. Therefore, HA and FA in the soil environment can adsorb a large amount of nitrapyrin and reduce its effectiveness, and they have a positive synergistic effect.

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synergistic effect of HA and fulvic acid (FA) in nitrapyrin adsorption and the underlying mechanism are still unclear. Northeast China hosts China’s Golden Corn Belt, which is one of the three major black soil regions in the world. The soil organic matter content is high. The fertilization method “one fertilizer application” used by the local farmers results in a lower utilization rate of nitrogen fertilizer. Under the nitrogen fertilizer reduction policy formulated by the Chinese government, chemical fertilizers contain a certain amount of N. Nitrification inhibitors such as nitrapyrin are an effective tool to improve the utilization rate of nitrogen fertilizers and reduce the use of nitrogen fertilizers. Therefore, it is necessary to study the adsorption of nitrapyrin on soil organic matter with different components and its mechanism at the molecular level. In this study, the classical batch equilibrium method and modern analytical techniques were combined to explore the characteristics and mechanism of nitrapyrin adsorption on HA and FA. This will provide a theoretical basis for elucidating the adsorption mechanism of nitrapyrin in a high soil organic matter environment.

2 Materials and methods

2.1 HA and FA preparation from black soil

The extraction, separation and purification of HA and FA from black soil were carried out according to Wen et al. and Xing et al. The black soil was obtained from Hailun City, Heilongjiang Province (E126°50′55″, N47°26′31″). Corn has been planted there for many years without application of the nitrification inhibitor nitrapyrin. The soil was sampled at a depth of 0–20 cm, and the undecomposed plant residues on the soil surface were removed manually. The underlying physical and chemical properties of the soil are summarized in Table 1.

2.2 Chemicals and instruments

Ethanol, analytically pure, purchased from the Beijing Chemical Co., Ltd.; acetonitrile, chromatographically pure, obtained from Shandong Yuwang and World New Materials Co., Ltd; nitrapyrin raw medicine (98.0%), purchased from the Wuhan Yuancheng Gonghuang Technology Co., Ltd.; the standard of nitrapyrin (99.0%), purchased from LGC Labort GmbH Bgm, Germany; calcium chloride, analytically pure, obtained from the Huoguo Pharmaceutical Group Co., Ltd. The water used in the experiments was double-distilled water. High-performance liquid chromatography (HPLC, Agilent 1260, SB-C18 stainless steel columns, USA); high-speed refrigeration centrifuge (Z36HK, HERMLE); constant-temperature water bath oscillator (SHA-C, Huapuda Instrument Co., Ltd.); infrared spectroscopy (FTIR-IR, Affinity-1S, Japan); scanning electron microscopy (JSM-7900F, Japan); X-ray energy dispersive spectrometry (C-Max, EDS).

2.3 Adsorption kinetics

1.0000 g of HA, FA or HA + FA (1:1) was added into a 50 mL plugged centrifuge tube. 50 mg L⁻¹ nitrapyrin was added to the soil (the solution comprised 0.01 mol L⁻¹ CaCl₂ and an ethanol/water mixture (v/v = 5:95)), and this was repeated three times in combination with oscillation under dark conditions (constant-temperature water bath oscillator, 200 rpm) at 298 K. The acting time was 5, 10, 30, 60, 120, 240, 360, 480, 720, and 1440 min. The samples were centrifuged at a speed of 10 000 rpm after 5 min. The supernatant was filtered out by a 0.45 µm organic filter membrane and sealed in a brown spectrographic bottle stored in the dark at 3 °C, to determine the content of nitrapyrin by HPLC. For further details on the methods, refer to our previously published research results.

2.4 Adsorption thermodynamics

1.0000 g samples of HA, FA and HA + FA (1:1) were accurately weighed and placed in a 50 mL plugged centrifuge tube. 25 mL of nitrapyrin solution (0.01 mol L⁻¹ CaCl₂ and an ethanol/water solution (v/v = 5:95)) was added. The concentration of the nitrapyrin solution was 0, 5, 10, 15, 25, 50 and 75 mg L⁻¹. The treatments were repeated three times, and the samples were placed in a constant-temperature water bath oscillator. The adsorption experiments were carried out at different reaction temperatures (298, 308, and 318 K) at a 200 rpm oscillation speed. After 24 hours, the samples were centrifuged at a speed of 10 000 rpm. The supernatant was filtered by a 0.45 µm organic filter membrane and sealed in a brown bottle. The supernatant was stored in the dark at 3 °C, and the content of nitrapyrin was determined by HPLC. The remaining solid samples in the centrifuge tube were dried at 50 °C for surface morphology analysis, and element distribution and functional group composition determination. For details of the research methods, refer to our previous published research results.

2.5 HPLC conditions

The HPLC conditions were as follows: the detector, UV-Vis (Agilent 1260, US); the wavelength, 285 µm; the chromatographic column, 1H column (4.6 × 150 mm, 5 µm, Agilent Pursuit); the column temperature, 25 °C; the mobile phase, acetonitrile/water (8/2); the flow rate, 0.8 mL min⁻¹; the injection volume, 20 µL. The concentration gradient of nitrapyrin was 2, 4, 8, 10, 15, 25, 50 and 75 mg L⁻¹.

Table 1 Basic physicochemical properties of the black soil

<table>
<thead>
<tr>
<th>Soil type</th>
<th>pH</th>
<th>Organic matter (g kg⁻¹)</th>
<th>N (g kg⁻¹)</th>
<th>P₂O₅ (g kg⁻¹)</th>
<th>K₂O (g kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black soil</td>
<td>6.55</td>
<td>48.51</td>
<td>13.51</td>
<td>3.23</td>
<td>1.54</td>
</tr>
</tbody>
</table>
2.6 Characterization of HA and FA

The surface morphology of HA/HA-nitrapyrin and FA/FA-nitrapyrin complexes was observed using scanning electron microscopy (JSM-7900F, Japan). The element distribution was determined by using X-ray energy dispersive spectroscopy (C-Max, EDS). The infrared spectra of HA/HA-nitrapyrin and FA/FA-nitrapyrin complexes were recorded using Fourier transform infrared spectroscopy (ftir-IRAffinity-1S, Japan).

2.7 Data processing method

Origin 8.5 software was used to fit the data. An Agilent workstation (Chem Station Edition for LC and LC/MS systems, C0.01.05 (ref. 35)) was used to obtain the chromatogram of nitrapyrin.

(1) Adsorption kinetics model

Quasi-first-order dynamics:

\[ \ln(q_e - q_t) = \ln q_e - k_1t \]  

Quasi-second-order dynamics:

\[ \frac{tq_t}{k_2q_t^2 + t/q_e} \]

Elovich equation:

\[ q_t = a + bt \]

“\( q_t \)” is the adsorption amount when time is \( t \) (mg kg\(^{-1}\)). “\( t \)” is the adsorption time (min). “\( a, k^* \)” is a model parameter. “\( q_e \)” is the maximum adsorption capacity (mg kg\(^{-1}\)). “\( A \)” is a constant related to the initial rate of reaction. “\( b \)” is a constant related to the activation energy of adsorption.

(2) Adsorption isothermal equation/adsorption thermodynamic equation

Langmuir:

\[ Q_d = k_1Q_{0d}C_d/(1 + k_1C_d) \]  

Freundlich:

\[ Q_d = k_1C_d^{1/n} \]

\( Q_d \) represents the adsorption amount (mg kg\(^{-1}\)), \( C_d \) is the adsorption equilibrium solution concentration (mg L\(^{-1}\)), \( Q_{0d} \) is the maximum adsorption capacity (mg kg\(^{-1}\)), and \( k \) is a constant.

(3) Gibbs free energy change of adsorption

\[ \Delta G^\circ = -RT \ln k_1 \]  

\[ \Delta H^\circ = R[T_2T_i/(T_2 - T_i)] \ln(k_{2(T_2)}/k_{2(T_i)}) \]  

\[ \Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \]

\( \Delta G^\circ \) is the free energy change (kJ mol\(^{-1}\)), \( \Delta H^\circ \) is the enthalpy change (kJ mol\(^{-1}\)), \( \Delta S^\circ \) is the entropy change (J mol\(^{-1}\) K\(^{-1}\)), \( R \) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \( T \) is the absolute temperature (K), and \( k_1 \) is the equilibrium constant (L mol\(^{-1}\)) of the Langmuir equation.

3 Results and discussion

3.1 Adsorption kinetics of nitrapyrin on HA and FA

The adsorption of pyridine organic compounds (AM, chloropyralid, etc.) on soil organic matter conforms to an initial rapid adsorption and a later slow adsorption.\( ^{25,35-37} \) The adsorption kinetics of nitrapyrin on HA, FA and HA + FA of black soil at 298 K showed that the adsorption process comprised an initial fast adsorption stage and a subsequent slow adsorption stage (Fig. 1). The adsorption equilibrium state was basically reached at 750 min. The adsorption capacity of HA + FA for nitrapyrin was greater than that of HA or FA, and that of HA was greater than that of FA. The nitrapyrin was mainly adsorbed on the outer surface of HA and FA in the fast adsorption stage. This process occurs due to the radial movement of nitrapyrin molecules with the minimum diffusion resistance, and the adsorption rate is fast. In the slow adsorption stage, due to the great resistance of HA with a narrow pore size, the diffusion speed of nitrapyrin through HA and FA was slow, the adsorption rate was slow, and the adsorption equilibrium state was reached gradually.

The adsorption kinetics of nitrapyrin on HA, FA and HA + FA can be fitted by the quasi-first-order kinetic equation, quasi-second-order kinetic equation and Elovich equation, respectively. Previous studies found that the adsorption kinetics of organic compounds on soil or soil organic matter conforms to the quasi-second-order kinetic equation.\( ^{26,37-40} \) The adsorption kinetics of nitrapyrin on HA, FA and HA + FA fit the quasi-second-order kinetic equation best (\( P < 0.05 \)), and the fit equilibrium adsorption capacity was consistent with the experimental results (Table 2). The quasi-second-order kinetic equation fitting effect of nitrapyrin on HA + FA was better than on HA or FA, and that of HA was better than that of FA.

3.2 Thermodynamics of nitrapyrin on HA and FA

The adsorption isotherms of HA, FA and HA + FA at different temperatures (298 K, 308 K and 318 K) are shown in Fig. 2. With the increase of nitrapyrin concentration and temperature, the.
adsorption capacity of HA, FA, and HA + FA for nitrapyrin increased at different rates.

The adsorption isotherms of nitrapyrin on HA, FA and HA + FA were fitted using the Langmuir and Freundlich equations, respectively. Table 3 shows that both the Langmuir and Freundlich equations can be used to fit the adsorption isotherms of nitrapyrin on HA, FA and HA + FA ($R^2 > 0.9300, P < 0.05$). The maximum adsorption capacities of nitrapyrin on HA, FA and HA + FA were 4896.49, 3173.70 and 4925.56 mg kg\(^{-1}\), respectively. The adsorption capacity of nitrapyrin on HA was higher than that on FA, which was consistent with the previous research. However, the adsorption capacity of nitrapyrin on HA + FA was greater than that on HA or FA alone, indicating that there was a positive synergistic effect on the adsorption of nitrapyrin due to the co-existence of HA and FA.

The constant $n > 1$ obtained using the Freundlich equation confirmed that both HA and FA can adsorb nitrapyrin easily, and leads to an L-type isotherm curve. This indicated that nitrapyrin molecules occupy the adsorption sites of HA, FA and HA + FA quickly at the beginning of adsorption, and that surface adsorption was the main type of adsorption. With an increase of reaction temperature, the Langmuir isotherm parameters showed an increasing trend, which indicated that the increase of temperature could promote the adsorption of nitrapyrin by HA, FA and HA + FA. For the adsorption of organic compounds on HA or FA, generally, the Langmuir isotherm parameters increase with an increase of reaction temperature.

![Fig. 2 Adsorption isotherms of nitrapyrin on HA, FA and HA + FA.](image-url)

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Adsorption kinetics model parameters of nitrapyrin on HA, FA and HA + FA</th>
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</thead>
<tbody>
<tr>
<td>Treatment</td>
<td>$q_e$ (mg kg(^{-1}))</td>
</tr>
<tr>
<td>HA</td>
<td>616.84</td>
</tr>
<tr>
<td>FA</td>
<td>467.39</td>
</tr>
<tr>
<td>HA + FA</td>
<td>638.56</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Adsorption isotherm equation parameters of nitrapyrin on HA, FA and HA + FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment</td>
<td>Temperature [K]</td>
</tr>
<tr>
<td>HA</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>308</td>
</tr>
<tr>
<td></td>
<td>318</td>
</tr>
<tr>
<td>FA</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>308</td>
</tr>
<tr>
<td></td>
<td>318</td>
</tr>
<tr>
<td>HA + FA</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>308</td>
</tr>
<tr>
<td></td>
<td>318</td>
</tr>
</tbody>
</table>
the internal pores through the outer boundary of the adsorbent. In addition, the effect of temperature on the adsorption of nitrapyrin on HA was greater than that on FA.

The thermodynamic parameters of adsorption obtained by linear calculation of $\Delta G^\circ - T$ are shown in Table 4. $\Delta G^\circ$ was negative, and the absolute value of $\Delta G^\circ$ increased with an increase of temperature, which indicated that the process of nitrapyrin chemisorption by HA, FA and HA + FA was spontaneous with an increase of temperature. The absolute value of $\Delta G^\circ$ was less than 40 kJ mol$^{-1}$, which indicated that the adsorption of nitrapyrin by FA, HA and FA + FA was mainly physical adsorption. The enthalpy change of adsorption ($\Delta H^\circ$) results indicated that the forces responsible for the adsorption of nitrapyrin on HA, FA and FA + FA were different, but were mainly hydrogen bonding, hydrophobic interaction and dipole interaction. The positive value of $\Delta S^\circ$ indicates that the increase of entropy change of nitrapyrin not adsorbed by HA, FA and FA + FA was greater than that of nitrapyrin adsorbed by HA and FA in the process of nitrapyrin adsorption.

### Table 4. Thermodynamic parameters of nitrapyrin adsorption on HA, FA and HA + FA

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Temperature (K)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>298</td>
<td>-34.77</td>
<td>19.52</td>
<td>292.10</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-37.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-38.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA</td>
<td>298</td>
<td>-36.31</td>
<td>5.01</td>
<td>144.70</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-37.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-39.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HA + FA</td>
<td>298</td>
<td>-32.72</td>
<td>20.35</td>
<td>301.21</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-35.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-36.85</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3 Adsorption mechanism of nitrapyrin on HA and FA

(1) SEM analysis

The SEM images of HA, HA–nitrapyrin, FA and FA–nitrapyrin are shown in Fig. 3. HA has a fluffy, rough and porous surface structure (a). After adsorption of nitrapyrin, the surface structure of HA changed, a granular agglomerated structure formed, and some sediment appeared on the surface (b). It is possible that nitrapyrin may undergo chemisorption on the HA surface and the appearance of surface agglomeration was probably due to the reaction between the chemical groups on the HA surface and nitrapyrin, and the formation of new substances attached to the surface of HA. Fig. 3(c) and (d) show the SEM scanning results before and after nitrapyrin adsorption on FA. Before adsorption, FA had an irregular granular structure with a fluffy, rough and porous surface (c); after adsorption of nitrapyrin, the FA surface structure exhibited agglomeration, the particles became tightly bound, and the rough porous surface structure became smooth and compact (d). This indicated that nitrapyrin underwent physical adsorption on the FA surface and the appearance of surface agglomeration should be related to a decrease of the number of negative charges on the surface of FA after adsorption of nitrapyrin, thus reducing the repulsive force between molecules.

(2) EDS analysis

According to the elemental results, the unabsorbed HA contains more carbon and oxygen related functional groups, with the contents of 19.56% and 35.26%, respectively (Table 5). After adsorption, the mass and atomic percentage of carbon and oxygen decreased obviously (Table 5), which resulted from the adsorption reaction of the functional groups containing carbon and oxygen with nitrapyrin. The mass and atomic percentage of sodium and aluminum increased, indicating that the two metal elements were closely combined with the organic components of HA and were difficult to exchange into the solution. The mass and atomic percentage of chlorine increased significantly (Table 5), which also confirmed that

Fig. 3 SEM images of (a) HA, (b) HA–nitrapyrin, (c) FA and (d) FA–nitrapyrin.
nitrapyrin was adsorbed on HA because nitrapyrin contains a lot of chlorine.

The contents of carbon and oxygen in the unabsorbed FA were 52.14% and 28.24%, respectively (Table 5), indicating that FA contained more carbon and oxygen related functional groups. After adsorption, the mass and atomic percentage of carbon and oxygen in FA decreased (Table 5), indicating that the functional groups containing carbon and oxygen participated in the adsorption reaction with nitrapyrin. The mass and atomic percentage of chlorine in FA increased evidently (Table 5), which indicated that nitrapyrin was greatly absorbed because of the large amount of chlorine in nitrapyrin attached to FA.

(3) FTIR analysis

Fig. 4(a) shows the infrared spectra of HA and the HA–nitrapyrin complex, with the band at 3400 cm⁻¹ representing the –OH bond and N–H stretching vibration, the band at 2920 cm⁻¹ representing asymmetric aliphatic C–H stretching vibration, the band at 2850 cm⁻¹ belonging to –CH₂- symmetric stretching vibration, the band at 1720 cm⁻¹ representing carboxyl C=O stretching vibration, the band at 1620 cm⁻¹ representing carboxyl C=O stretching vibration, the band at 1257 cm⁻¹ representing C–O stretching vibration and O–H deformation vibration related to the carboxylic acid functional group, and the bands at 914 cm⁻¹ and 757 cm⁻¹ representing external bending vibrations of carboxylic acid O–H and aromatic hydrocarbon C–H groups, respectively. Further, the band at 617 cm⁻¹ represents an external bending vibration formed by alcohol hydroxyl groups.⁴⁵,⁴⁶ Two new absorption bands at 2360 cm⁻¹ and 625 cm⁻¹ were found in the spectra of HA–nitrapyrin, which were attributed to the bonding of quaternary ammonium salts and the extension of C–C bonding, respectively. The increase of absorption intensity observed near 2100 cm⁻¹ is a direct effect of nitrapyrin, which produces a strong absorption band in this region. Fig. 4(b) shows the spectra of FA and the FA–nitrapyrin complex, with aliphatic –CH₂- asymmetric and symmetrical resonance absorption peaks at 2920 cm⁻¹ and 2860 cm⁻¹, C–C vibration absorption of the aromatic ring skeleton at 1650 cm⁻¹ and stretching vibrations at 1510 cm⁻¹.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Element</th>
<th>Before adsorption</th>
<th>After adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt (%)</td>
<td>wt sigma (%)</td>
<td>Atomic percentage wt (%)</td>
</tr>
<tr>
<td>HA</td>
<td>C</td>
<td>19.56</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>35.26</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>1.15</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>5.90</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>34.72</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>0.23</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.77</td>
<td>0.05</td>
</tr>
<tr>
<td>FA</td>
<td>C</td>
<td>52.14</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>28.24</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>4.99</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.86</td>
<td>0.05</td>
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Fig. 4 FTIR spectra of (a) HA and HA–nitrapyrin, and (b) FA and FA–nitrapyrin.
vibration of –C–O polysaccharide at 1000 cm\(^{-1}\). The special features of the FA–nitrapyrin spectrum included the disappearance of the shoulder at 1725 cm\(^{-1}\) and a remodeling of the band near 1400 cm\(^{-1}\), indicating that the –COOH and –OH groups of FA participate in the adsorption of nitrapyrin. The absorption intensity increased at 1650 cm\(^{-1}\), which should be due to the interaction between the C–O group of FA and the pyridine ring of nitrapyrin. The FA–nitrapyrin complex had multiple absorption bands at 2320 cm\(^{-1}\), which was attributed to the NH stretching effect of the pyridinium salt.

(4) Adsorption mechanism

HA and FA are the main components of soil organic matter, and they contain various organic functional groups such as carboxyl and hydroxyl groups and so on (Liu et al., 2017). The

Fig. 5  Plausible interaction mechanism between HA, FA and nitrapyrin.
presence of these functional groups can lead to complex interactions of HA and FA with nitrapyrin. The adsorption isotherm study showed that the maximum adsorption capacity of nitrapyrin on HA was greater than that on FA, which was probably due to the fact that the number of oxygen-containing functional groups in HA was greater than that in FA (Table 2). The adsorption capacity for nitrapyrin in HA + FA was greater than that of HA or FA alone, which should be related to a positive synergistic effect on the adsorption of nitrapyrin due to the co-existence of HA and FA. Fig. 3 shows that the surface structure of HA and FA changed significantly before and after adsorption, indicating that there was strong interaction between some functional groups of HA and FA and nitrapyrin. The infrared spectra (Fig. 4) show that O–H (3390 cm$^{-1}$) and C–O (1118 cm$^{-1}$) are the main components of HA–nitrapyrin and FA–nitrapyrin. This indicated that the mechanism of adsorption included hydrogen bond interaction between aromatic carboxyl groups or hydroxyl groups on HA and FA, nitrogen with lone pair electrons on nitrapyrin and oxygen in hydrolyzed carboxyl groups (Fig. 5). The pyridine ring of nitrapyrin contacts with the benzene ring face-to-face, which results in effective adsorption of nitrapyrin on HA and FA through hydrophobic interaction (Fig. 5). Therefore, hydrogen bonding and hydrophobic interaction should be the most important adsorption pathways of nitrapyrin on HA and FA, and the change of adsorption enthalpy also showed that hydrogen bonding and hydrophobic interaction were the main adsorption forces. Meanwhile, the absolute values of free energy of nitrapyrin adsorbed on HA, FA and HA + FA ranged from 34.77 to 39.57 kJ mol$^{-1}$, indicating that the dipole moment, electrostatic interaction and ion exchange interaction were secondary factors affecting the adsorption of nitrapyrin on HA, FA and HA + FA.

4 Conclusion

The kinetics of adsorption of nitrapyrin on both HA and FA followed pseudo-second-order kinetic models ($R^2 \geq 0.925$, $P < 0.05$) and the adsorption process included an initial fast-adsorption stage and a slow-adsorption stage thereafter. The adsorption efficiencies of HA + FA for nitrapyrin were higher than that of HA or FA alone, and that of HA was higher than that of FA. The adsorption isotherms of nitrapyrin on HA and FA could be optimally fitted with the Langmuir equation ($R^2 \geq 0.982$, $P < 0.05$). The maximum adsorption capacities of nitrapyrin on HA + FA were the largest. The adsorption of nitrapyrin on co-existing systems of HA and FA involves a positive synergistic effect. The adsorption of nitrapyrin on HA and FA occurred through hydrogen bonding and hydrophobic interaction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The present study was supported by grants from the National Key Research and Development Program of China (2016YFD0200403) and the Scientific Technology Development Research Plan Project of Jilin Province in China (20180201035NY).

References

13 G. Barth, S. V. Tucker and U. Schmidhalter, Influence of soil parameters on the effect of 3,4-dimethylpyrazole-phosphate


