Journal of Materials, Processing and Design (2022)
Clausius Scientific Press, Canada
DOI: 10.23977/jmpd.2022.060108
ISSN 2516-0923 Vol. 6 Num. 1

Study on Adsorption Mechanism of Naphthalene in Soil by Humic Acid-Based Materials

Weichun Gao*

Shaanxi Province Land Engineering Construction Group Co., Ltd., Xi'an 710075, China
**Corresponding author*

Keywords: naphthalene-contaminated soil, humic acid, biochar, adsorption mechanism

Abstract: Humic acid-loaded biochar (HA-BC) remediation material is a new type of green soil conditioner. The composite material can effectively adsorb and fix naphthalene, an organic pollutant in polluted soil. Through UV-Vis, FT-IR, XPS and other characterization methods, the adsorption mechanism of humic acid-based remediation materials on naphthalene-contaminated soil was explored. The UV-Vis, FT-IR and XPS results showed that naphthalene formed intermolecular hydrogen bonds with the carboxyl groups of oxygen-containing functional groups in the humic acid-biochar material.

1. Introduction

Soil is the material basis for human survival and development. Soil organic pollutants mainly include organic pesticides, petroleum hydrocarbons, plastic products, surfactants, dyes, plasticizers, flame retardants and antibiotics. Among them, pesticides and chemical products are persistent organic pollutants that are more harmful to human health. They have the characteristics of high toxicity and refractory degradation. They not only accumulate in plants, but also accumulate in animals and humans through the food chain, which adversely affects human health and ecological security [1]. Naphthalene, a typical representative of polycyclic aromatic hydrocarbons (PAHs) pollutants, is often studied for remediation.

Soil remediation refers to the process of absorbing, degrading, transferring and transforming pollutants in the soil through physical, chemical, biological, electrochemical and other technologies, so as to greatly reduce the concentration of pollutants, or convert toxic and harmful pollutants into harmless substances [2].

Humic acid is a macromolecular substance that constitutes soil humus, mainly a type of organic matter formed and accumulated by plant remains through the decomposition and transformation of microorganisms and a series of geochemical processes [3]. Humic acid is widely distributed in the soil, which can not only provide nutrients for the plants in the soil, but also improve the soil structure, improve soil fertility, and transform saline-alkali land [4]. In addition, the specific composition of humic acid determines that it plays an important role in soil remediation contaminated by heavy metals and toxic organic pollutants. Therefore, humic acid improves the soil environment, especially in the remediation and treatment of polluted soil, which has broad development prospects.

In this paper, the mechanism of adsorption of naphthalene by humic acid-based remediation materials was studied, and the potential value of humic acid in soil improvement and pollution remediation was also confirmed. Research on the application of remediation in polluted soil has important reference value.

2. Materials and Methods

2.1. Experimental reagents

Sodium humate: taken from industrial lignite, dark brown solid, aqueous solution is tan. The pH value is 10.52, the density is 0.736kg/L, the free value is 55%, and the solubility is >82g; wood vinegar: industrial product, waste liquid from charcoal processing; naphthalene and n-hexane are analytically pure; biochar powder: industrial product, black powder produced by oxygen-limited combustion of wheat straw.

The tested biochar powder (BC) is an industrial biochar powder that has been pulverized, ground, and passed through a 100-mesh sieve. The tested wood vinegar (WV) is the waste liquid produced by the charcoal manufacturing process and left standing for 10 days, filtered, distilled and collected at 130~150℃. This fraction is light yellow clear liquid, acetic acid accounts for 80.40% (mass fraction, the same below), phenol 8.23%, ketones and alcohols 10.38%, other 0.99%, pH value is 2.35, specific gravity is 1.0181, density is 0.996kg/L.

Fourier transform infrared spectrometer (VECTOR-22, Bruker, Germany), ultraviolet spectrophotometer (Gary 60 UV-Vis, Agilent, USA), X-ray photoelectron spectrometer (AXIS Supra, Kratos, UK), gas-mass spectrometer instrument (Type 6890/5975, Agilent, USA).

2.2. Experimental Materials

2.2.1. Preparation of repair materials

Preparation of humic acid (HA) repair material: sodium humate (NaHA) reacts with refined wood vinegar (WV) to generate humic acid (HA). The experimental results found that when the mass ratio of sodium humate to wood vinegar was 1:3, sodium humate completely precipitated into humic acid.

Sodium humate loaded biochar powder (NaHA-BC) repair material: the biochar powder is ground through a 60-mesh sieve, and the sodium humate material is ground through an 80-mesh sieve. Weigh 10 g of sodium humate and biochar powder with an electronic balance and place them in a glass beaker. After mixing them well, they are naturally air-dried and ground, and passed through an 80-mesh sieve for use.

Preparation of humic acid-loaded biochar powder (HA-BC) repair material: the biochar powder was ground through a 60-mesh sieve, and the humic acid material was ground through an 80-mesh sieve. Weigh 10 g of humic acid and biochar powder with a balance and place them in a glass beaker. After mixing them well, they are naturally air-dried and ground, and then passed through an 80-mesh sieve for use.

The blank group (CK) did not add any repair material, and the remaining condition steps were the same as the experimental group (adding repair material).

2.2.2. Preparation of naphthalene-binding repair materials

Naphthalene combined with sodium humate loaded biochar powder material (Naphthalene+NaHA-BC): use an electronic balance to weigh 0.1g of naphthalene into a 100mL beaker, add 50mL of n-hexane solution to the beaker, stir and mix, and then add 2g of sodium humate, after mixing evenly, place it in a fume hood, air dry it naturally, and then pass it through a 60-mesh sieve for use. Naphthalene combined with humic acid-loaded biochar powder material (Naphthalene+HA-BC): Weigh 0.1g of naphthalene into a 100mL beaker using an electronic balance, add 50mL of n-hexane solution to the beaker, stir and mix well, and then add 2g of humic acid, mix well Then place it in a fume hood, and then pass it through a 60-mesh sieve for use after natural air-drying.

2.3. Characterization methods

Samples were prepared using the potassium bromide tablet method. Fourier transform infrared spectroscopy was used to measure the infrared spectra of sodium humate-biochar powder (NaHA-BC) before and after adsorption of naphthalene, and the infrared spectrum of naphthalene before and after humic acid-biochar powder (HA-BC) adsorption. The spectral data were compared and analyzed by Origin8.5.

The sodium humate solution (NaHA) and humic acid (HA) were diluted by the same factor, and the UV spectra of NaHA and HA were measured with a UV spectrophotometer with a scanning range of 200-400 nm.

Sodium humate-biochar powder (NaHA-BC), sodium humate-biochar powder (NaHA-BC) and naphthalene, humic acid-biochar powder (HA-BC), humic acid-biochar powder (HA-BC) and naphthalene were measured by X-ray photoelectron spectroscopy, respectively. The adsorption mechanism of humic acid-biochar powder (HA-BC) and naphthalene was studied by measuring the binding energy of fixed electrons to analyze the element composition, content ratio and chemical bond samples between elements.

3. Adsorption Mechanism Analysis

3.1. UV analysis of NaHA and HA materials

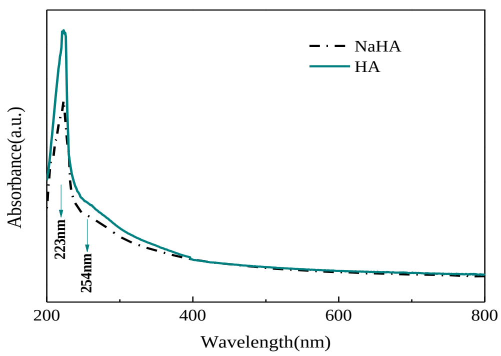


Figure 1: UV spectrum of NaHA and HA materials

As shown in Figure 1, when the humic acid solution (HA) and the humic acid/wood vinegar solution (HA/WV) were diluted with the same multiples, the absorption values of both of them for ultraviolet light increased first and then decreased with the decrease of the wavelength. trend, the peak shape is similar. At 223 nm, the benzene ring reaches the maximum absorption, which is substituted by chromophores such as carboxyl, C=C, C=O, etc., which corresponds to the strong absorption of the π-electron E2 band in the aromatic ring. At 254 nm, the B-band absorption of the aromatic structure appears. Due to the influence of multiple substituents, the fine structure of the benzene ring disappears, and only steps representing the aromatic structure appear. Compared with

HA, the absorbance of HA/WV is enhanced. This is because the addition of wood vinegar increases the content of oxygen-containing groups such as hydroxyl, carboxyl, alkoxy and other oxygen-containing groups, resulting in a color-enhancing effect.

3.2. FT-IR Analysis of NaHA and HA Materials

Figure 2 is the infrared spectrum of sodium humate, wood vinegar and humic acid. As shown in the figure, 3386cm-1 has a strong absorption peak belonging to the O-H stretching vibration peak, 1572cm-1 is the antisymmetric stretching vibration absorption peak of carboxylate, 1420cm-1 is the symmetrical stretching vibration absorption peak of carboxylate, 1020cm-1 C-O bending vibration peak, it can be seen that humic acid contains many oxygen-containing functional groups. Humic acid (HA) also has the above absorption peaks, and the hydroxyl absorption peak, the antisymmetric stretching and symmetric stretching vibration absorption peaks of carboxylate, and the C-O bending vibration peak absorption peak intensity are higher than those of sodium humate; humic acid is at 1020cm-1C the peak intensity of C-O bending vibration is higher than that of sodium humate, indicating that its carboxyl group content is higher, which can provide more ion exchange sites. The above results proved that the oxygen-containing functional groups (carboxyl groups) were significantly increased after adding wood vinegar to sodium humate, and the structure of humic acid was more conducive to the adsorption of naphthalene.

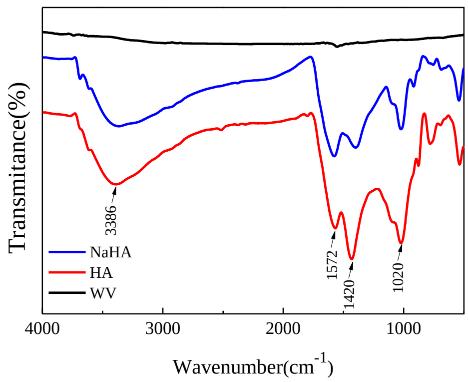


Figure 2: Infrared spectrum of WV, NaHA and HA

3.3. FT-IR analysis of NaHA-BC and HA-BC before and after adsorption of naphthalene

Figure 3(a) is the infrared spectrum of sodium humate-biochar powder (NaHA-BC) before and after adsorption of naphthalene, and Figure 3(b) is the infrared spectrum of humic acid-biochar powder (HA-BC) before and after adsorption of naphthalene. It can be seen from the figure that compared with NaHA-BC, after adding wood vinegar, the antisymmetric stretching and symmetric stretching vibration absorption peaks of carboxylate are enhanced, and the C-O stretching vibration absorption peak is enhanced. NaHA-BC adsorbed naphthalene and HA-BC adsorbed naphthalene after adsorption of hydroxyl absorption peak (3382cm-1), carboxylate antisymmetric stretching vibration absorption peak (1572cm-1), symmetric stretching vibration absorption peak (1420cm-1) and C-O stretching vibration the intensity of the absorption peak (1020cm-1) was weakened, which indicated that the biochar powder-humic acid and the biochar powder-humic acid/wood vinegar were adsorbed by chemical bonds with naphthalene. According to the literature [5-7], it was reported that polycyclic aromatic hydrocarbons are adsorbed on humic acid through chemical bonds such as intermolecular hydrogen bonds formed by hydroxyl and carboxyl groups. The aromatic and hydrophobic surfaces of biochar powder can enhance the adsorption through hydrogen bonding with oxygen-containing groups [8]. Therefore, the addition of wood vinegar not only increases the number of oxygen-containing functional groups (carboxyl groups), but also acts as a Activates the action of humic acid. The humic acid/wood vinegar solution loaded with biochar powder has a stronger adsorption effect on naphthalene and is bound by intermolecular hydrogen bonds.

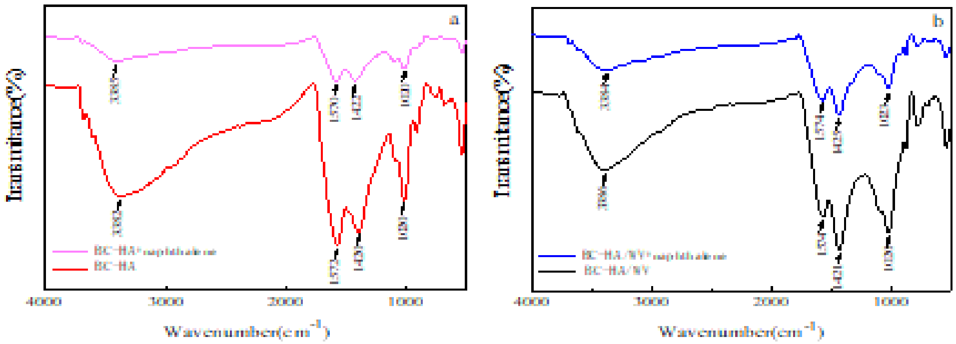
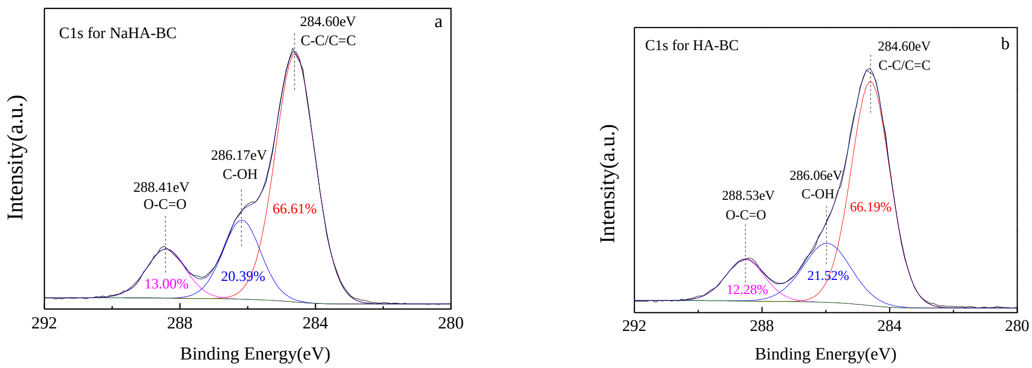


Figure 3: (a) Infrared spectra of NaHA-BC before and after naphthalene; (b) Infrared spectra of HA-BC before and after naphthalene

3.4. XPS analysis of NaHA-BC and HA-BC before and after adsorption of naphthalene

Figure 4(a), (b), (c), (d) are the C1s spectra of NaHA-BC, HA-BC, NaHA-BC combined with naphthalene, and HA-BC combined with naphthalene, respectively. The signal peaks correspond to carbon-carbon double bonds C=C or single bonds C-C, hydroxyl groups C-OH and carboxyl groups O-C=O on aromatic rings/aliphatic carbons, respectively [9]. In the C1s spectrum, the C-C/C=C content of NaHA-BC combined with naphthalene increased from 66.61% to 77.66%, the C-OH content decreased from 20.39% to 12.67%, and the O-C=O content decreased from 13.00% to 12.67%. 9.67%; the C-C/C=C content of HA-BC combined with naphthalene increased from 66.19% to 74.59%, the C-OH content decreased from 21.52% to 14.19%, and the O-C=O content decreased from 12.28% to 11.22%. The results show that the carboxyl groups of the oxygen-containing functional groups in NaHA-BC and HA-BC form intermolecular hydrogen bonds with naphthalene, resulting in a significant reduction in oxygen content, which is consistent with the performance of infrared spectroscopy., which further proved that naphthalene binds with sodium humate-biochar (NaHA-BC) and humic acid-biochar powder (HA-BC) in the form of intermolecular hydrogen bonds.



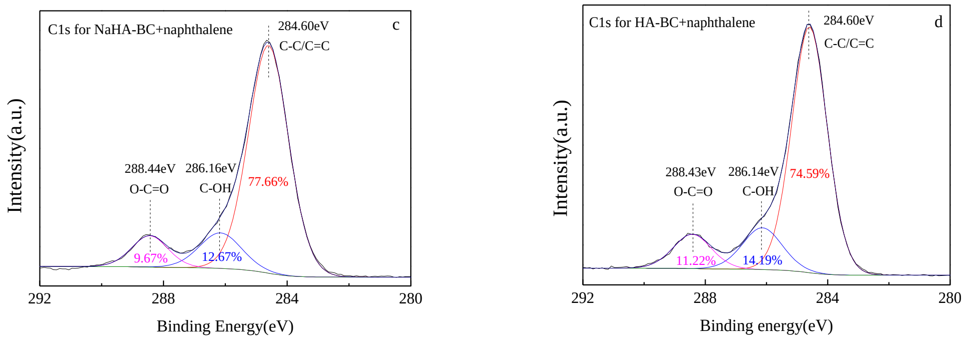


Figure 4: (a) C1s high-resolution spectrum of NaHA-BC; (b) C1s high-resolution spectrum of HA-BC; (c) C1s high-resolution spectrum of NaHA-BC combined with naphthalene; (d) HA-BC High-resolution spectrum of C1s after binding to naphthalene

4. Conclusion

A novel humic acid-loaded biochar (HA-BC) remediation material was studied, which has a good effect on adsorption and immobilization of naphthalene in organically polluted soil. The adsorption mechanism of humic acid-based remediation materials on naphthalene-contaminated soil was revealed by UV-Vis, FT-IR, XPS and other characterization methods. The UV-Vis, FT-IR and XPS analysis indicated that intermolecular hydrogen bonds were formed between naphthalene and the carboxyl groups of oxygen-containing functional groups in the humic acid-biochar material. The addition of wood vinegar increases the number of oxygen-containing groups and enhances the formation of intermolecular hydrogen bonds between humic acid-loaded biochar and naphthalene. Wood vinegar, as a cheap activator, is used to enhance humic acid to repair polycyclic aromatic hydrocarbon pollution Soil provides theoretical basis and practical basis.

Acknowledgements

This work was granted by Shaanxi Provincial Land Engineering Construction Group Project (Grant No. DJNY2022-49).

References

[1] Yang Zhenzhen, Geng Bing, Tian Yunlong, Li Hongna. Research progress on electrochemical remediation technology of soil organic pollutants[J]. Soil Journal, 2021, 58(5): 1110-1122.

[2] Song Jie. Research on the status quo of soil pollution and its control measures [J]. Environment and Development, 2019(11): 23-24.

[3] Huang Yanfeng, Zheng Jiliang, Yang Jinchang, Zhao Dongye, Su Xintai. Research progress of humic acid in heavy metal-contaminated soil remediation[J]. Humic Acid, 2021, (03): 54-60.

[4] Huang Zhanbin, Hao Wenjing, Feng Zeshen, Kong Lingjian, Ma Qian, Zhao Peng.Application status and research prospect of humic acid in soil improvement and pollution remediation [J]. Soil and Water Conservation Bulletin, 2022, 42(02): 354-361+376.

[5] Li Yuanyuan, Li Xia, Hu Linchao, et al. Structural characterization of fulic acid components in paddy soil and adsorption characteristics of PAHS pyrene [J]. Journal of Agro-Environmental Science, 2009, 28 (2): 269-274 (in Chinese)

[6] Cho H, Smith B A, Wnuk J D, et al. Influence of surface oxides on the adsorption of naphthalene onto multiwalled carbon nanotubes [J]. Environmental Science & Technology, 2008, 42(8): 2899-2905

[7] Vasilkonov E S, Zavgorodnyaya Y A, Demin V V, et al. Interaction of naphthalene and naphthol with soil organic matrix [J]. Moscow University Soil Science Bulletin, 2008, 63(1): 17-22

[8] Fang Q, Chen B, Lin Y, et al. Aromatic and Hydrophobic Surfaces of Wood-derived Biochar Enhance Perchlorate Adsorption via Hydrogen Bonding to Oxygen-containing Organic Groups[J]. Environmental Science & Technology, 2014, 48(1): 279-288
[9] Descostes M, Mercier F, Thromat N, et al. Use of XPS in the determination of chemical environment and oxidation state of iron and sulfur samples: Constitution of a data basis in binding energies for Fe and S reference compounds and applications to the evidence of surface species of an oxidized pyrite in a carbonate medium[J]. Applied Surface Science, 2000, 165(4): 288-302.