Study on ecological safety evaluation method for pyrolysis residue of oily sludge

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Abstract. The pollutants in the pyrolysis residue of oily sludge are harmful to the ecosystem, so it is necessary to evaluate its ecological security before it is discharged into the ecosystem. The evaluation methods based on physical and chemical indexes and the evaluation methods based on biological toxicity were summarized and compared in order to provide reference for the safety evaluation of the pyrolysis residue of oily sludge.

1. Introduction
Oily sludge is a kind of hazardous waste generated in the process of petroleum exploitation, gathering and transportation and refining, which contains a variety of harmful substances such as benzene series, polycyclic aromatic hydrocarbons, bacteria and heavy metals [1]. If not properly disposed of or rationally utilized, it will have a serious impact on national survival, social development and human health. In the treatment technology of oily sludge, pyrolysis technology has the advantages of thorough treatment, recovery of oil and gas resources, solidification of heavy metals in sludge, reduction of pollution gas emissions, etc. [2-4]. The three-phase products after pyrolysis treatment contain liquid phase products dominated by water and low freezing point crude oil, gas phase products dominated by small molecular gases such as CH₄, CO₂, CO and H₂, and solid residues (commonly known as residue or carbon residue) remaining in the reactor [5]. In these three kinds of products, residue occupies a large proportion, residue contains residual heavy metals and incomplete recovery of oil resources and salts and other harmful components, if directly discharged, will produce secondary pollution, harm to the ecological environment.

At present, there are few studies on the characteristics of sludge pyrolysis residue, but the characteristics of oily sludge pyrolysis residue and its analysis method are important parameters to identify whether the residue meets the discharge standard, so understanding the characteristics of sludge pyrolysis residue can provide necessary technical support for the resource utilization or direct discharge of residue.
The basic characteristics such as the composition and element analysis of sludge residues, pore structure and morphological characteristics, calorific value and so on play an important role in the toxicity detection in the later stage.

2. Analysis of characteristics of pyrolysis residue of oily sludge

The basic characteristics of the pyrolysis residue of oily sludge play a key role in the study of its toxicity detection method and the reuse after detection. The pyrolysis final temperature, the source of sludge and whether to activate it, the pyrolysis time, nitrogen flow rate and other factors have a great impact on the pyrolysis residue characteristics.

2.1. Composition and elemental analysis of pyrolysis residue of oily sludge

Andres Fullana [6] measured the sludge of sewage treatment plant. At 850 ℃ pyrolysis, the non-metallic elements in the pyrolysis residue mainly included C, H, N and a small amount of S, among which carbon elements were the highest, ranging from 29.2% to 35.3%. Although the kinds of metal elements in the residue are more, but the content is low, mainly Cr, Fe, Ni, Cu, Zn, Sr and Pb, etc., among which the content of Fe is relatively high, up to 4.5%. Li Yan [7] et al. analyzed the elements of nitrogen, carbon, hydrogen and sulfur in the pyrolysis residue with catalyst, and found that the pyrolysis residue had a high carbon content. However, Bandosz [8] found that magnesium was the main metal element in the pyrolysis residue of oily sludge, which was almost twice as much as the iron content in the pyrolysis residue of oily sludge. The above description, although the source of sludge, activation, pyrolysis conditions will affect the type and content of elements in the residue. But the main components of the residue is still carbon, a small amount of iron and magnesium, so the residue has a good adsorption performance.

Abrego [10] analyzed the XRD patterns of residuals with different final pyrolysis temperatures. As shown in Figure 2, the crystal phase components increase due to the higher final pyrolysis temperature, indicating that some inorganic substances and heavy metals finally appear in the form of crystals after pyrolysis. Therefore, the existence form of heavy metals can be considered in the selection of detection methods.

Figure 1. Elemental energy spectrum of pyrolysis residue[9]
2.2. Pore structure and morphological characteristics of pyrolysis residue of oily sludge
Residue is a porous loose structure dominated by large pores and supplemented by micropores, which may be formed by carbon nanotubes during high-temperature pyrolysis [11]. Residue specific surface area and pore volume are mainly affected by final pyrolysis temperature, sludge moisture content, residence time and heating rate.

Yan-jun Hu [12] in exploring such as moisture content for the residue of the influence of pore structure and surface morphology evolution process, found that with the increase of sludge moisture content, pyrolysis residue accumulation of particles BET specific surface area, specific surface area, pore specific surface area and specific surface area of contribution, micro distributed capacity presents increase with the decrease of the first and then decreases, the moisture content of 55% and 75% for the two turning point in the development of pore characteristics change.

Zhao Haipei [13] carried out scanning electron microscope analysis of pyrolysis residue, and the results also showed that the pore distribution of residue was not uniform, and there were no obvious microholes, but mainly pores of micron level, ranging from several microns to dozens of microns. Zhan Yali [14], when exploring the influence of water content on the pore structure and surface morphology evolution of the residue, found that the pore structure of the pyrolysis residue particles of wet sludge was relatively complex, with a wide distribution range of pore size and more developed mesopores. There was a single peak value near the pore size of 3.75nm, and there were few macropores. With the increase of sludge moisture content, the pore size distribution of pyrolysis residue changes greatly, and the number of large pores within the mesoporous range increases significantly. When the sludge moisture content is lower than 55%, with the increase of moisture content, the number of left and right mesoporous residue with a pore size of 3.75nm basically remains unchanged, while the number of 5-10nm decreases, and the number of large pores basically remains unchanged. When the water content is higher than 55%, the pore diameter of the residue is about 3.75nm, and the relative number of pores decreases continuously with the increase of sludge water content. The mesopore of 5-10nm develops greatly, and the pore diameter distribution within the mesopore range tends to be uniform.
2.3. Calorific value of pyrolysis residue of oily sludge

For studying the effect of residual oil content of calorific value, such as Li yan [7] respectively, for without catalyst pyrolysis residue and higher oil recovery rate of pyrolysis residue determination of oil content and calorific value, oily sludge calorific value as high as 14235. 21 kJ/kg, also has a high calorific value of sludge pyrolysis residue 2000 kJ/kg, and the oil content of its calorific value is higher, also add catalyst pyrolysis residue calorific value is lower than that of the added pyrolysis residue not obviously, therefore, the residue can be used for the development of new fuel.

Yang Penghui [1] used Tg-Fourier transform infrared spectrometer to study the pyrolysis of oily sludge and the combustion reaction process of residue and pulverized coal mixture. The results show that the complete treatment and utilization of oily sludge can be achieved by the pyrolysis of sludge and the mixing granulation of pyrolysis residue and pulverized coal as fuel.

3. Study on the toxicity test method of pyrolysis residue of oily sludge

3.1. Heavy metal ion detection

Heavy metals refer to the metal elements with a density of over 4.5g/cm³, a total of 45 kinds [16]. At present, the major pollution heavy metals in China include chromium (Cr), manganese (Mn), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd), mercury (Hg), lead (Pb) and so on. The metal in the residue mainly has Cr, Fe, Ni, Cu, Zn, Sr and Pb, etc., among which Fe content is relatively the highest, up to 4.5%, the existence of heavy metals not only has a certain potential risk to the environment, but also restricts the resource utilization of residue. Domestic and foreign scholars have proposed various heavy metal evaluation methods and applied them to the heavy metal evaluation of soil and dust deposits [17]. There have also been relevant reports on the ecological risk evaluation of heavy metals in sludge, but there are few reports on the heavy metal evaluation of oily sludge residues. As more and more attention is paid to the prevention and control of heavy metal pollution in the environment, the detection of heavy metals in sludge residue is of great significance.

3.1.1. Inductively coupled plasma-atomic emission spectrometry. Inductively coupled plasma-Atomic emission spectrometry (ICP-AES) is a kind of spectral analysis method with inductively coupled plasma moment as excitation source. When the sample to be tested enters the atomizer from the sampler and is brought into the flame moment by carrier gas, the components in the sample to be tested are atomized and ionized, and finally the energy is emitted in the form of light. After the atoms of different elements are excited or ionized, they emit characteristic spectra of different wavelengths when they return to the ground state. According to the characteristic wavelengths and the intensity of the emitted characteristic light, qualitative and quantitative analysis of metal elements can be conducted [18].

Zhu Congling [19] determined 9 heavy metal elements in soil by inductively coupled plasma emission spectrometry through the heating plate digestion system of nitric acid-hydrofluoric acid-perchloric acid, including Cd(cadmium), Mn(manganese), Ni(nickel), Pb(lead) Zn(zinc), Mo(molybdenum), Ba(barium), V(vanadium) and Co(cobalt). The results showed that the RSD% of 9 heavy metal elements ranged from 0.5% to 6.2%. Wang Xiaoyan [20] treated the soil samples with microwave digestion method, and measured various elements of the soil samples simultaneously with inductively coupled plasma emission spectrometry, and compared them with national standards. The results showed that Cr: 21.00 mg·kg⁻¹, Mn: 340.12 mg·kg⁻¹, Cu: 21.88 mg·kg⁻¹, Zn: 151.25 mg·kg⁻¹. The contents of Cr and Cu meet the national first-level standards, the contents of Zn meet the national second-level standards, and Mn is not regarded as a pollutant. Inductively coupled plasma atomic emission spectrometry, high sensitivity, short time consuming, the results are accurate, and not only has the advantages of multielement simultaneous determination of atomic emission spectrometry, and has a wide linear range, the main and second, to simultaneous determination of trace element composition is suitable for direct analysis of solid, liquid and gaseous samples, with many elements, many lines at the same time.
3.1.2. Laser induced breakdown spectroscopy. Laser induced breakdown spectroscopy is the use of high energy pulse laser make it gathered on the samples, the samples of instant vaporization, plasma excited state, with the plasma emission out with element characteristic wavelength characteristic spectral lines, composition of the sample were analyzed, and the use of spectral line of the wavelength and intensity to analyze the elements of the composition and content. Lin Zhaoxiang [21] used laser-induced breakdown spectroscopy to detect arsenic in industrial wastewater, analyzed the characteristic spectral lines of As element, and determined the calibration curve of arsenic element. Lu Cuiping[22] used laser-induced breakdown spectroscopy to detect the content of chromium in national standard soil samples, and obtained the relationship curve between chromium concentration and spectral line strength.

Laser induced breakdown spectroscopy is a relatively new atomic emission spectroscopy analysis method. It plays a key role in the elemental analysis of a wide range of samples. It is a multi-element analysis method and is considered a powerful sensor technology for laboratory and field systems. Compared with traditional analytical techniques, LIBS has many advantages: it can be analyzed quickly and requires little sample preparation; Not destructive in nature, easy to operate; It is also applicable to the composition analysis of liquid phase [23], gas phase [24] and other samples. By using portable and remote-controlled laser-induced breakdown spectroscopy instruments, its technology allows for elemental analysis both in situ and remotely.

The most commonly used techniques for elemental analysis and the study of the composition of different materials are atomic or mass spectrometers. They include: atomic absorption spectrometry, inductively coupled atomic emission spectrometry, X-ray fluorescence spectrometry and energy dispersive X-ray spectrometry. Although most of these analytical techniques are highly sensitive and accurate, they produce large amounts of toxic waste. In addition, they require reagents, sample dissolution, and very complex sample preparation. Compared with these methods, LIBS method is simple, safe and has a wide range of applications without sample preparation. At present, conventional detection of sludge residues is mainly focused on the detection of physical and chemical indicators, and less consideration is given to the comprehensive toxicity of pollutants, but the comprehensive toxicity detection can truly reflect the comprehensive toxic effect of pollutants on the ecosystem. Therefore, in addition to the detection and analysis of conventional physical and chemical indexes, the comprehensive biotoxicity effects of pollutants should also be paid attention to.

3.2. Residual oil toxicity detection

The biotoxicity test method can well analyze the toxicology of the residual oil. The biotoxicity test method plays an important role in the soil quality evaluation. This test method can directly reflect the comprehensive toxicity characteristics of all co-existing pollutants in the samples to be tested, and can well detect the soil pollution caused by the residual oil. The biotoxicity test method studies the influence of toxic and harmful pollutants on the health status of the samples by taking the individuals or cells of model organisms as the subjects, so as to reflect the pollution degree of pollutants. The following is a review of biotoxicity testing methods from the luminescent bacteria method, algal growth toxicity inhibition method, and fish toxicity experiment method, so as to detect the toxicity of residual oils.

3.2.1. Study on the toxicity of luminescent bacteria. Luminous bacteria can emit visible light by themselves and are widely distributed. Most species are distributed in the ocean, while a few species are distributed on land. The four genera known as luminescent bacteria are Vibrio, Luminescent bacilli, Shivella, and Photobacterium, all of which belong to the -prion group and are gram-negative bacteria [25]. Such bacteria can emit fluorescence at a wavelength of 450-490nm for biochemical reaction by their own cells [26]. If their own body carries out normal metabolism and is not disturbed by the outside world, their luminous intensity can be maintained stable for a long time. But if toxic substances will make contact with luminescent bacteria cell state (including the cell wall, cell membrane, electron transfer system, enzyme, and the structure of the cytoplasm) change, which will lead to the glowing is abate, the stronger the toxicity of toxic substances, inhibit the metabolism will be stronger, luminous inhibition will be more obvious, so you can samples toxicity through determination of luminous intensity
changes. In addition, luminescent bacteria all react significantly to different types of toxic substances, which can be used to effectively detect the toxicity of environmental pollutants [27].

Xinjing [28] established a method for the rapid determination of biotoxicity of petroleum contaminated soil using luminescent bacilli through orthogonal experiments and single-factor experiments. Under the premise of prescribed pre-treatment conditions, the method required 14 hours less than the treatment method of American Association of Materials and Experiments. Qin Jijie [29] determined the luminescence inhibition of 8 nitrobenzene compounds and their mixtures to luminescence bacteria, using Qinghai Vibrio as indicator organisms. The results showed that the toxicity of luminescence bacteria was in the order of o-nitroaniline, p-nitroaniline, p-nitrophenol, p-nitrotoluene, o-nitrophenol, m-nitrophenol, M-nitroaniline and nitrobenzene.

Above all, compared with other biological toxicity test method, the sensitive degree of photobacteria method to toxic substances, higher reliability and even fish acute toxicity method for the determination of 96 h training in [30], in addition, the method of instrument automation degree is higher, so the operation more simple, usually in 30 minutes can result, measurement speed is very fast, which can reduce the difficulty.

3.2.2. Inhibition of algal growth toxicity. Algae is the primary producer of aquatic ecosystem [31]. Algae has great potential in toxicity testing. Some algae are even more sensitive to toxic substances than fish, so they are often selected by researchers for toxicity testing. Chlorella has nitrogen phosphating potential, so it can grow in a variety of nitrogen and phosphorus media.

Majid [32] studied the simultaneous use of common chlodomonas and iron oxide nanoparticles (NPs) to purify aquaculture wastewater in the designed bioreactor, and the results showed that it was feasible to apply common chlodomonas and nanoparticles to the purification of aquaculture wastewater at the same time. Lu [33] studied the acute toxicity of titanium dioxide to Alga oblique phyllostachytes as the subject, so as to evaluate the safety of nano-titanium dioxide. The results showed that the acute toxicity of nano-titanium dioxide to Alga oblique phyllostachytes was 0.140 mg·L⁻¹, and the toxicity level was high. Cui Jiansheng [34] selected chlorella nucleoli and microcystis aeruginosa as experimental algae to conduct biological toxicity evaluation, so as to evaluate the comprehensive toxicity of haze. The results showed that chlorellae was sensitive, and the fluorescence parameters decreased significantly. In particular, the parameter NPQ decreased by 46.3% and 40.2%, respectively, under the influence of haze absorption solution for two days with heavy pollution. Therefore, it was feasible to select the NPQ parameter of Chlorellae with protein nucleus as an indicator of haze biotoxicity.

The biological detection of water pollution refers to that aquatic organisms are taken as test objects and will have biological reactions under the influence of pollutants, so as to judge the pollution status of water [35]. Therefore, it can be used to detect the toxicity of residue leachs. Algae are widely distributed and represent important aquatic ecological groups. Moreover, the biotoxicity test of algae is relatively simple, which can be used not only for the detection of soil residual oil, but also for the detection of heavy metal ions. However, its sensitivity in the test process is lower than that of bacteria.

3.2.3. Experimental study on fish toxicity. Fish play the role of consumers in the ecosystem. Changes in water environment will also cause changes in fish behavior, physiological and biochemical characteristics, population composition and distribution, etc. Biological fish toxicity experiments, including acute fish toxicity experiments and experiments using fish as carriers to analyze their physiological and biochemical indicators, can grasp the pollution situation of the water body to be measured by observing the symptoms of fish poisoning and recording the behavioral, physiological and biochemical characteristics of fish [36].

Li Qingxue [37] took zebrafish as experimental organisms to study the toxic effect of target pollutants on zebrafish, and calculated the semi-lethal concentration of target pollutants on zebrafish. The results showed that zebrafish can respond even if the concentration of water source pollutants is very low. So the zebrafish toxicity test method can be used for water source biological warning. Taking zebrafish as the indicator, Wang Yingcai [38] systematically studied the change rules of zebrafish movement.
behavior under Cu$^{2+}$ stress, and found that zebrafish swimming speed, population distribution characteristics, distribution area and swimming attitude would all significantly change.

In the test of fish toxicity, the selection of fish species is also very important. Generally, fish species that are sensitive to pollutants, rich in sources and easy to feed are selected, and have a certain representative biological background. Zebrafish was selected as indicator because as a universal model species, zebrafish has rich research background, which is convenient for comparison of experimental results. Zebrafish has been cultivated in a standardized way in China. The National Zebrafish Center is located in the Institute of Hydrobiology of the Chinese Academy of Sciences in Wuhan, which makes it easier to obtain experimental materials. Moreover, the gene sequence of zebrafish has a high degree of coincidence with that of human, so the experimental results have a great reference significance for human research.

4. Application of pyrolysis residue of oily sludge
Although the pyrolysis residue of oily sludge is listed in the National Hazardous Waste List, oils and metallic inorganic minerals in oily sludge have important reuse value [39]. In addition, the pyrolysis residue is composed of carbon and inorganic elements, and its adsorption properties, such as specific surface area and pore structure, indicate that the pyrolysis residue of oily sludge has a very good adsorption performance. Yang Huifen [40] took the pyrolysis residue with a porous structure similar to activated carbon as raw material to remove low concentration heavy metals from the synthetic flotation wastewater. The results show that the pyrolysis residue can effectively remove Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ from the flotation liquid, and increase the pH value of the water at the same time, the removal rates of Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ reach 99.3%, 98.9% and 99.4% respectively, indicating that the pyrolysis residue has a certain effect on the removal of low concentration heavy metals. Pamreishang Kasara [41] made high-quality products from two materials with relatively low gradation, waste plastics and pyrolysis residue of oily sludge, which could be further refined in the refinery and then reprocessed, and found that it might be used as transport fuel and further refined into other chemical raw materials. Liu Longmao [42] used pyrolysis residue to catalyze sludge pyrolysis, and the liquid yield, oil yield and gas yield were significantly increased, while the solid yield was decreased, indicating that the presence of residue promoted the pyrolysis of sludge.

5. Conclusion
The characteristic analysis and effective treatment of oily sludge residues have become the key factors restricting the harmless and recycling of residues. For detection of heavy metals in the residue with inductively coupled plasma emission spectrometry and laser induced breakdown spectroscopy, inductively coupled plasma atomic emission spectrometry was mainly laboratory commonly used methods of element analysis, by contrast, the laser induced breakdown spectroscopy method is simple, safe, do not need sample preparation applicability is wide and is suitable for laboratory and field system.

The toxicity of residual oil in the residue was analyzed by biological toxicity detection method, including luminescent bacteria method, algal growth toxicity inhibition method, and fish toxicity experiment method. Each biological toxicity test method has its applicable scope, high sensitivity, fast test speed and high reliability of luminescent bacteria. Algal organisms are often used in heavy metal ion detection, but their sensitivity is lower than that of bacteria. The gene sequence of zebrafish has a high degree of coincidence with that of human, and the experimental results have a great reference significance for human research.

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