Study on Pollution Characteristics of Shale Refinery Wastewater

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Abstract. This paper studied the pollution characteristics of shale oil refinery wastewater, by using conventional analysis, infrared spectroscopy, ultraviolet spectroscopy, chromatography and mass spectrometry. The results showed that: wastewater contains high concentration of dissolved organic matter, which was poor in biological treatment. The organic structure of wastewater contains groups such as benzene ring, carbonyl group, hydroxyl group, ether group and carboxyl group. The composition of wastewater was very complex, which has phenols and oil compounds, with inorganic pollutants such as iron, calcium, magnesium, and sodium.

1 Introduction

Oil shale is a kind of fine-grained sedimentary rock rich in organic matter, with fine bedding and combustible. By breaking the oil shale and heating it to about 500°C, shale oil can be obtained [1]. After treatment, products such as gasoline, kerosene, diesel and paraffin can also be obtained. In the process of refining oil shale, a large amount of shale oil refining wastewater will be produced. This wastewater has the characteristics of high concentration of pollutants, many toxic and harmful substances, and difficult treatment[2-5]. According to the current research situation at home and abroad, produced one ton of shale oil, 9-13 tons of water are consumed and 2.5 tons of waste water are generated [6]. The shale oil refining wastewater is directly discharged into the environment, which will cause great harm to humans, water bodies, and soil. Affect the harmonious coexistence of man and nature, and cause irreversible harm to the environment [7]. At present, testing with conventional water quality indicators cannot fully reflect the structural characteristics of water quality, nor can it provide a scientific basis for the selection of treatment processes. Therefore, it is necessary to increase detection indicators and increase water quality information to comprehensively evaluate water quality.

This paper analyzed the conventional water quality indicators of shale oil refinery wastewater, using GC-MS, UV-Vis, FT-IR to detect pollutants in the wastewater, and analyzed the pollution characteristics of the wastewater. The purpose is to The treatment of shale oil refinery wastewater provides scientific data [8-10].

2 Materials and methods

2.1 Reagents and instruments

Wastewater source: Experimental wastewater collected from Mining Group Shale Refinery in Fushun.

Reagents: sulfuric acid, sodium hydroxide, sodium chloride and other reagents are of analytical grade. Chloroform is chromatographically pure.

Instruments: iS50 FTIR infrared spectrometer; JB/T 5374-1991 electronic balance; PHS-3C pH meter; OIL 460 infrared spectrophotometer; UV-6000 ultravioletvisible spectrophotometer; 5B-1F (V8) type Smart digester.

2.2 Analysis test method

COD was detected by potassium dichromate method, and ammonia nitrogen was detected by sodium test reagent spectrophotometry. The total nitrogen was measured by ultraviolet spectrophotometry, and the biochemical oxygen demand was measured by the 5-day biochemical culture method. The oil content was detected by infrared spectrophotometry and OIL460 infrared spectrophotometer. The conductivity was measured by a conductivity meter, the total organic carbon was measured by the combustion oxidationnondispersive infrared absorption method, and the total phosphorus was measured by the ammonium molybdate spectrophotometric method. Phosphate and chloride use ion chromatography, pH use PHS-3C type pH meter, iron, calcium, magnesium, sodium use flame atomic absorption spectrophotometry. Hardness uses EDTA titration, alkali-nity uses potentiometric titration.

The gas chromatography-mass spectrometer model was Agilent 7890A 5975C. Chromatographic conditions: HP-5 capillary column (30m×0.25mm×0.25μm); carrier

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gas: high-purity nitrogen (purity 99.999%); column flow: 1.0 mL/min, split flow 2 mL/min; inlet temperature: 280℃; split ratio2:1, injection volume: 1μL, solvent removal time 3min. Program temperature rise: starting temperature 50℃; then 2℃/min to 70℃; then 10℃/min to 250℃; running time 33min. Mass spectrometry conditions: electron impact (EI) ion source, ionization energy 70 eV, ion source temperature 230oC, quadrupole temperature 150oC, transmission line temperature 280oC, solvent delay 5 min, filament current: 100μA, mass scanning range m/z 35-500.

The UV-Vis spectroscopy test uses the Agilent Cary series UV-Vis-NIR spectrophotometer, and uses deionized water as a reference to scan and analyze the wastewater to eliminate system errors. The measurement wavelength range is 200-800nm, and the optical path of the quartz cuvette is 10mm.

The infrared spectrum was analyzed by iS50 FT-IR infrared spectrometer. Potassium bromide was fully ground to powder. As for the tablet press, it was pressed into a transparent sheet. The sample after chloroform extraction was dropped on the sheet for testing. The scanning range was 4000-400cm-1. The number of scans is 32 times.

3 Results and discussion

3.1 Routine water quality analysis

Table 1 showed the conventional water quality analysis of shale oil refinery wastewater. It can be seen from Table 1 that the wastewater was brown, has a pungent odor, and has an alkaline pH. The high COD content indicates that the concentration of organic pollutants in the wastewater was high, mainly produced during the dry distillation of oil shale. The high concentration of ammonia nitrogen in wastewater increases the difficulty of wastewater treatment. Containing phenols and other difficult-to-degrade organic substances, which were toxic to microorganisms and have poor biodegradability. The alkalinity was relatively high, and it needs to be neutralized with an acid agent and discharged. The composition was complex and there were many kinds of organic matter. In addition to phenols and oil compounds, the wastewater also contains inorganic pollutants such as iron, calcium, magnesium, and sodium.

Table 1. Conventional water quality of shale oil refinery wastewater

Test items	Content	Test items	Content
COD	6100 mg/L	phenol	200 mg/L
Colour	brown	Volatile phenol	228 mg/L
NH_3-N	4513 mg/L	TOC	1790 mg/L
TN	6500 mg/L	TP	72.28 mg/L
BOD_5	2600 mg/L	PO_4^{3-}	4.38 mg/L
Oil content	150.96 mg/L	pH	9
Conductivity	9320μs	Iron	0.36 mg/L
Cl^-	3.24 mg/L	Calcium	21.8 mg/L
Hardness	101 mg/L	Magnesium	42.3 mg/L
Alkalinity	11836 mg/L	Sodium	56.0 mg/L

3.2 Infrared spectrum analysis

Figure 1 showed the infrared spectrum of soluble organic compounds in shale oil refinery wastewater. Between 3550cm-1 and 3250cm-1 was mainly O-H stretching vibration. The absorption peak in the spectrum was located at 3415cm-1. Its source was the intramolecular or intermolecular hydrogen bond formed by the O-H group in the compound, but due to the pollutant components in the wastewater Complicated, multiple O-H stretching vibration absorption peaks including alcoholic hydroxyl and phenolic hydroxyl were superimposed, resulting in a broad peak shape. In addition, it may also be N-H stretching vibration. From the figure, the absorption peak at 3300cm-1 splits into two absorption peaks of similar height. There were two hydrogen atoms on the N atom with symmetrical and antisymmetric stretching vibrations, which may be primary amines. The asymmetric variable-angle vibration of salt. There were two medium-intensity absorption peaks at wavenumber 1380cm-1, one high and one low. These two absorption peaks may be due to the vibration coupling of two methyl groups and split from the absorption peak at 1380cm-1, indicating that they were tertiary Bending vibration of C-H on butyl. There was COO-symmetric stretching vibration at 1450-1300cm-1, and the wastewater should contain carboxylate, phenol C-O stretching vibration or C-H symmetric bending vibration. The absorption peak at 1680-1620cm-1 was caused by the vibration of the conjugated diene. The absorption peak at 1850-1600 cm-1 indicates the presence of carbon-oxygen double bonds. C-O-C asymmetric stretching vibration or C-O-C ester symmetric stretching vibration, saturated fatty acid anhydride C=O stretching vibration or C-C-C stretching vibration appeared at 800-1300cm-1. The C-N stretching vibration of aliphatic primary amine was located at 1250-1020cm-1. There were absorption peaks at 757cm-1 and 620cm-1, and the C-Cl stretching vibration was at 800-600cm-1 caused by the extractant chloroform. In summary, the organic structure of wastewater contains groups such as benzene ring, carbonyl group, hydroxyl group, ether group and carboxyl group, and the wastewater may contain organic substances such as phenols, carboxylic acids, saturated hydrocarbons, ethers and ketones.

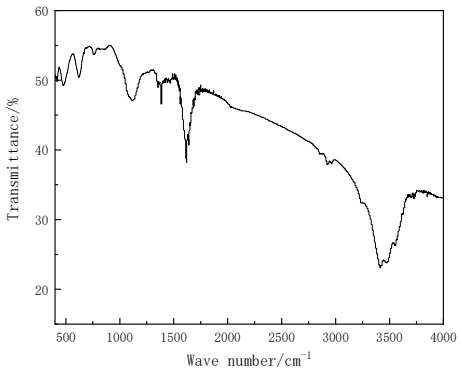

Figure 1. Infrared spectrum of shale oil refinery wastewater

Table 2. Attribution of pollutant absorption peak in shale refinery wastewater

Absorption peak/cm^{-1}	Peak attribution
3415.94	RNH_2 primary amine salt asymmetric variable angle vibration or O-H stretching vibration in phenolic hydroxyl group
1637.52	C=C stretching vibration
1617.26	C=O stretching vibration or C=C-C=C conjugate double bond stretching vibration
1384.56	C-H bending vibration, COO^- symmetric stretching vibration or C-O stretching vibration of phenol on tert-butyl
1120.52	C-O-C asymmetric stretching vibration, C-O-C ester symmetric stretching vibration, saturated fatty acid anhydride C=O stretching vibration or C-C-C stretching vibration
757.75 or 620.37	C-Cl stretching vibration

3.3 GC-MS analysis

A total of 89 components were identified in shale oil refinery wastewater by GC-MS. These components mainly include 21 phenols, 9 carboxylic acids, 14 alkanes, 6 ketones, 2 quinolines, and alcohols. 6 kinds of nitriles, 4 kinds of amines, 25 kinds of others. The peak area of phenols was 58.057%; the peak area of carboxylic acids is 11.665%; pyridine accounts for 7.07% of the mass fraction; alkanes account for 6.292% of the mass fraction; ketones account for 3.219% of the mass fraction; alcohols Compounds accounted for 3.569% of the mass fraction; quinoline compounds accounted for 2.312% of the mass fraction; aldehyde compounds accounted for 1.582% of the mass fraction; nitrile compounds accounted for 1.415% of the mass fraction; other types accounted for 5.182% of the mass fraction. Among 22 phenolic substances, phenol and its derivatives account for the largest proportion of 16 kinds, including 2,4-dimethylphenol, p-cresol, o-cresol, etc.; carboxylic acids include: valeric acid, caprylic acid, decanoic acid Acid etc. Pyridines include 2,4,6-trimethylpyridine, 2,3-cyclopentenopyridine, 2,4-lutidine, etc.; Quinolines include: 2-methylquinoline and 5-isoquine The ketones are mostly cyclopentenone compounds, such as 2-methylcyclopentanone, cyclohexanone, etc.; the organic components of alkanes were various, and they were all macromolecular long-chain alkanes, such as: Tetradecane, eicosan and octadecane, etc.

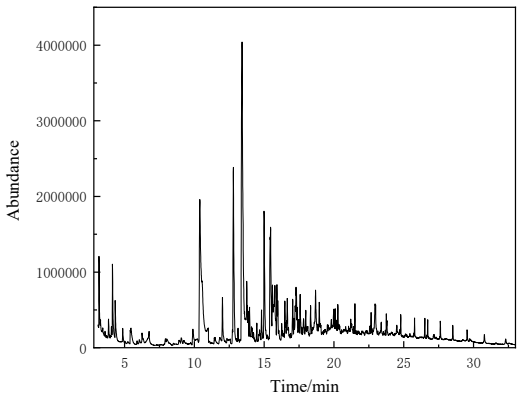

Figure 2. GC-MS total ion spectrum of shale refinery wastewater

3.4 UV-Vis spectrum analysis

The UV-Vis absorption spectrum of shale oil refinery wastewater was shown in Figure 3. A strong absorption peak appears near 200nm, and the absorption spectrum produced by the n→σ* transition was generally around 200nm, which is in the far ultraviolet region. The molecule should contain saturated compounds such as heteroatom O, such as alcohol. A strong absorption peak appears in the near-ultraviolet region (200-400nm), and the absorption spectrum corresponding to the energy required for the n→π* transition was generally in the near-ultraviolet region, indicating that the wastewater contains heteroatomic double bonds, such as C=O. The absorption peak B band of benzene is about 254nm, and the B band of phenol moves to 270nm because of the auxiliary chromophore -OH attached to the benzene ring, so the maximum absorption peak appears at 270nm. There was a strong absorption peak at 200-250 nm. Carboxylic acid compounds and ketone compounds are produced. The π→π* transition occurs in conjugated olefin molecules. The absorption band was characterized by strong absorption intensity. In addition, aromatic compounds The absorption band of π→π* transition also appears on the ultraviolet spectrum of, which was called B band (benzene type band) in spectroscopy. The results of gas chromatography-mass spectrometry showed that most of the substituents on phenol were alkyl groups. Scott estimated that the increase value of the p-position alkyl group was 10nm, and the increase value of the o or m position was 3nm. The red shift occurred and moved toward the long wavelength direction.

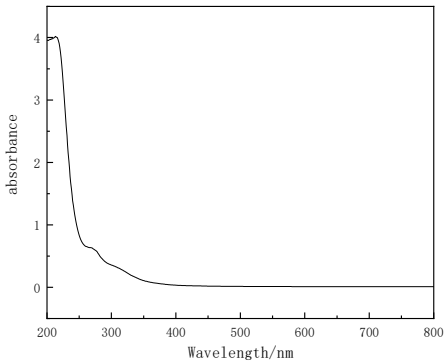

Figure 3. UV-Vis absorption spectrum of shale oil refinery wastewater

4 Conclusion

The results showed that the COD and ammonia nitrogen content of shale oil refinery wastewater was relatively high, which was difficult to treat organic wastewater. There were many kinds of organic matter. The organic matter structure of wastewater contains a large number of groups such as benzene ring, carboxyl group, hydrocarbon group and carbonyl group. Wastewater contains organic matter such as phenols, carboxylic acids, alcohols and ketones. Among them, phenols and their derivatives accounted for the highest proportion, with a relative peak area content of 58.435%, followed by carboxylic acids with 11.665%, pyridines with 7.07%, and alkanes with 6.292%.

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