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# Removal of Aromatic Hydrocarbons Pollutants From Oilfield Wastewater COD By Oxidation-coagulation Process

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**Keywords** oxidation-coagulation; wastewater from oilfield; chemical oxygen demand（COD）; aromatic hydrocarbons pollutants ; water-treatment.

**Abstract** This paper mainly study the mechanism of removing COD of oilfield wastewater by oxidation, coagulation and oxidation-coagulation. The results show that with the increase of oxidant 1# dosage, the total content of the organic matter in wastewater reduces with removal rate of organic matter significantly correlated with the organic molecular structure. The highest removal rate of COD is 53.38% by single oxidation, and the oxidation can remove the pentacyclic organic matter (100%), the bicyclic organic matter (90.6%), tricyclic organic matter (49.48%), and tetracycline organic matter (38.45%) in wastewater. With the increase of coagulant 1# dosage, the total aromatic organic matter content decreased in wastewater with the removal rate of organic matter significantly correlated with the organic molecular structure and solubility (polar). The highest removal rate of wastewater COD is 42.78% by single coagulation, which can remove tricyclic organic matter (82.74%), the pentacyclic compounds (78.64%), tetracycline organic matter (74.93%), and the organic matter (73.35%) in wastewater. The highest removal rate of wastewater COD is 87.82% by oxidation-coagulation, which can remove the pentacyclic organic matter (100%); the tetracyclic matter(93.89%), tricyclic organic matter (91.87%), and bicyclic organic matter (77.69%) in wastewater. The results show that coagulation-oxidation can improve processing efficiency in organic wastewater, the mechanism of which may be interaction of substituted, oxidation, coagulation and stability, adsorption and precipitation, etc.

## Introduction

COD is an important indicator of water pollution control in our country. At present, the COD content in wastewater is reduced mainly by the physical, chemical or biological methods to reduce the environment pollution of water. Coagulation is an economical and convenient water treatment method, which improves the efficiency of wastewater treatment. In most cases It is used with other treatment methods [1,2]. Jing Guolin[3]used the oxidation combined with coagulation method to reduce the COD of Daqing oilfield operation wastewater to 440mg/L from 3788 mg / L with the removing rate 88%. At present, domestic and foreign researches on wastewater COD focus on the determination methods and removal methods, few on the mechanism of the removal of COD. Miao

Zongcheng [4] et al thought that potassium ferrate can strongly remove COD, which mainly relies on the multi phase flocculation function of the $Fe(OH)_3$ with an assistant function of its strong oxidation. By treating organic wastewater with coal cinder as coagulant, Wang Yu [5] found that polycyclic aromatic hydrocarbons in wastewater were removed mainly through single molecule adsorption. Liu Jinquan[6] studied the reaction mechanism of $ClO_2$ oxidizing anthracene which showed that the oxidation reaction was an endothermic process which can occur under conventional water treatment conditions. The study on the COD wastewater treatment by oxidation coagulation process mainly focused on the methods [7-9], with fewer qualitative studies on the removal mechanism. Liu hong[10] has used coupled flocculation and oxidation process to treat acid brilliant scarlet dye wastewater. The results showed that acid brilliant scarlet GR is oxidized into small organic molecules by potassium permanganate, which are adsorbed by the reduction product—newly formed hydrous manganese dioxide, and is enwrapped by poly—silicic—ferric sulfate. Synergistic effect between oxidation and flocculation aggregates the color and COD are removed efficiently. Zhang Huiqin[11] studied degradation and degradation mechanism of printing and dyeing wastewater and slightly polluted raw water with $PPFS/H_2O_2$ coagulation oxidation coupling technology. The results showed that Fenton reaction mechanism dominates in acid medium; the PPFs coagulation sedimentation dominates in alkaline medium. In this paper, the Removal of Aromatic Hydrocarbons Pollutants from wastewater COD by oxidation coagulation process is studied qualitatively and quantitatively, which has great theoretical and practical guiding significance for screening reagent and improving COD removal rate of wastewater.

## Experimental part

### Chemicals

Coagulant 1# and oxidation agent 1# (industrial grade), sulfuric acid (AR), silver sulfate(AR), mercury sulfate(AR), potassium dichromate(AR), sulfate ammonium sulfate(AR), ferrous sulfate(AR), 1,10-phenanthroline(AR), potassium hydrogen phthalate(AR), sodium chloride(AR), n-hexane(AR), Redistilled isooctane (AR) etc.

### Instrument

Agilent Technologies 7890A GC System, separatory funnel, thermostatic bath, COD thermostatic heater etc.

### Experimental method

(1) COD determination: determine COD before and after treating wastewater from an oil field is based on the the national standard GB 119141989 [12], and the original COD is 308.11mg/l.

(2) The extraction of organic compounds in wastewater: aromatic hydrocarbons are extracted from the wastewater before and after the wastewater treatment and the qualitative and quantitative analysis is made. Extraction method: join 100ml-200ml water sample in the separatory funnel , twice adding a total of 50ml hexane or dichloromethane extract organic matter，then is concentrated till the solvent is volatilized completely.

(3) Determination of the organic matter in the wastewater: take a certain amount of dry organic matter to the chromatographic bottle. Prepare sample with 5mg / ml dichloromethane and adding aromatic hydrocarbons standard matter D10- anthracene (0.124mg/ml) 30μl. According to literature [13-18], the species and content of organic compounds in water samples before and after the treatment was determined by GC-MS.

### GC-MS condition

(1) Chromatographic conditions

Agilent HP-5MS chromatographic column 1# (30m×250μm×0.25μm), Agilent 19091S-436UIHP-5MS chromatographic column 2# (60m×250μm×0.25μm); temperature: 50℃ for 1 minute, up to 100℃ at the rate of 20℃/min, up to 315℃ at the rate of 3℃/min, for 28.5min; carrier gas: high pure helium, the total flow rate 34ml/min; shunt ratio of 15:1, shunt flow 14.89ml/min.

(2) Mass spectrometry conditions

The ion source temperature of 230℃, quadrupole temperature of 150℃, EMV mode: gain factor; gain factor: 1; EM voltage: 1765; solvent delay 10min; scanning range m/z50~550.

## Result and Discussion

### Quantitative on organics in wastewater before and after oxidation treatment

4 samples of wastewater 150ml were added into different dosage（%，V/V）of oxidant 1#, then stir for 10min at 100 rpm and settle down quiescently for 45min, then take 100ml supernatant， and extract and analyze it according to the method described above（as of 2.3,2.4）,Take phenanthrene organic compounds in the wastewater, the molecular ion peaks of phenanthrene aromatic hydrocarbons organics in wastewater are shown in figure 1~figure 4 before and after treatment. Phenanthrene aromatic hydrocarbons mainly include phenanthrene (P), 1-methyl phenanthrene(1-MP), 2-methylphenanthrene(2-MP), 3-methyl phenanthrene(3-MP) in wastewater，and their mass charge ratio are 178, 192, 206, 220 respectively. The quantitative results of main components before and after oxidation of aromatic hydrocarbons in wastewater are shown in table 1-table 4.

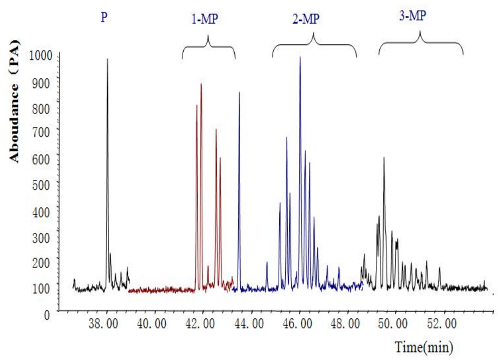


Fig.1 Phenanthrene organic compounds mass mass spectrogram of wastewater

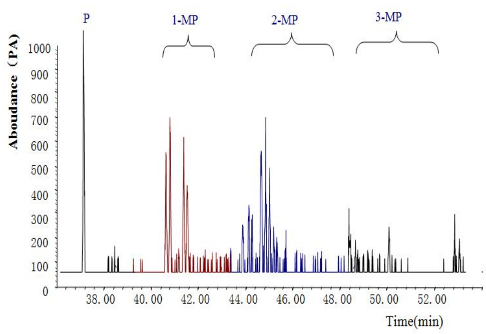


Fig.2 Phenanthrene organic compounds spectrogram after treatment with 1# 1%

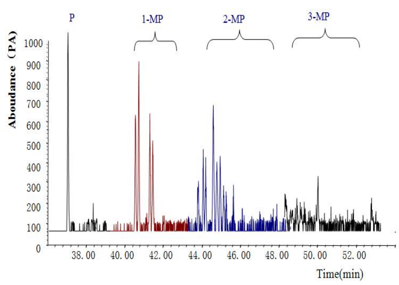


Fig.3 Phenanthrene organic compounds mass spectrogram of wastewater with oxidant 1# 5%

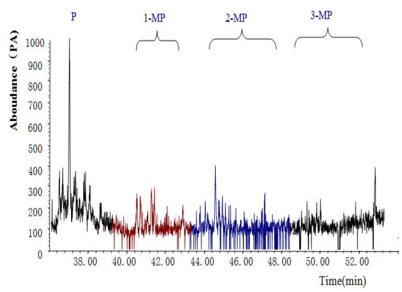


Fig.4 Phenanthrene organic compounds mass spectrogram after treatment with oxidant 1# 7%

Table 1 Comparison of dicyclic aromatic hydrocarbons content in wastewater before and after oxidation treatment

| Organics classification | Composition and content | Content in waste water/μg/L | Oxidant 1# dosage/%（V/V） | | | Maximum removal rate / % |
|---|---|---|---|---|---|---|
| | | | 1 | 5 | 7 | |
| Dicyclic aromatic hydrocarbon | Naphthalene and itsderivatives/μg/L | 2912.84 | 1921.15 | 853.99 | 807.63 | 72.27 |
| | Biphenyl and its derivatives/μg/L | 441.13 | 434.35 | 237.82 | 219.82 | 50.17 |
| | Dibenzothiophene and its derivatives/μg/L | 19753.12 | 823.2 | 647.68 | 558.80 | 97.17 |
| | Dibenzofuran and its derivatives/μg/L | 646.32 | 457.1 | 248.86 | 208.23 | 67.78 |
| | Fluorene and its derivatives/μg/L | 819.89 | 795.9 | 743.82 | 515.04 | 37.18 |
| Total organics content/μg/L | | 24573.3 | 4431.7 | 2732.17 | 2309.52 | 90.60 |
| COD/mg/L | | 308.11 | 198.39 | 167.54 | 143.63 | 53.38 |

Table 1 shows that with the increasing of oxidant 1# dosage, the total content of bicyclic aromatic hydrocarbons decreased, and with the oxidant 1# dosage 7% (V/V), total bicyclic aromatic hydrocarbons removal rate reach 90.6%. The removal rate of COD is 53.38% with the highest the removal rate 97.17% of dibenzothiophene and its derivatives. The removal rate of fluorene and its derivatives is the lowest 37.18%; The reason is the C atom in the benzene ring in the structure of fluorene and its derivatives and dibenzothiophene and its derivatives are formed as delta bond by SP2 hybrid orbitals. Electronegativities of S atoms in dibenzothiophene is stronger than C atoms, which weakens conjugation between the none shared electrons and the ring double bond. The electron density on sulfur atoms increases, increasing the oxidation activity [19,20], so sulfur atoms in dibenzothiophene are easily electrophilic attacked by free radicals in oxidant 1# to be oxidized and removed.

Table 2 Comparison of triaromatics hydrocarbons content in wastewater before and after oxidation treatment

| Organics classification | Composition and content | Content in waste water/μg/L | Oxidant 1# dosage/%（V/V） | | | Maximum removal rate / % |
|---|---|---|---|---|---|---|
| | | | 1 | 5 | 7 | |
| Triaromatics hydrocarbons | phenanthrene and its derivatives/μg/L | 8149.81 | 7259 | 6475.65 | 4034.73 | 50.49 |
| | anthracene/μg/L | 158.10 | 0 | 0 | 0 | 100 |
| | fluoranthene/μg/L | 464.77 | 452.9 | 435.85 | 364.21 | 21.64 |
| | benzofluorene/μg/L | 234.36 | 220.5 | 191.13 | 151.82 | 35.22 |
| Total organics content/μg/L | | 9007.04 | 7932.4 | 7102.63 | 4550.76 | 49.48 |
| COD/mg/L | | 308.11 | 198.39 | 167.54 | 143.63 | 53.38 |

From table 2, we can see that with the increase of the dosage of oxidant 1#, the total content of triaromatics hydrocarbons decrease, the dosage of oxidant 1# is 7% (V/V), the total removal rate is 49.48%, and the removal rate of COD is 53.38%. The anthracene removal rate reaches 100%, but the removal rate of fluoranthene is the lowest, only 21.64%; The reason may be the phenyl ring of polycyclic aromatic hydrocarbons in straight line arrangement was more active than the twists and turns arrangement of polycyclic aromatic hydrocarbons in the reaction activity [9,21]. All C and H atoms of anthracene molecules are arranged in a straight line in the same plane, which leads to active chemical properties, while atoms of fluoranthene molecules are arranged in a corner shape cross combinations into different planes, which leads to the structural stability, and isn't as active as anthracene, so removal rate of fluoranthene is low.

Table 3 Comparison of tetra aromatics hydrocarbons content in wastewater before and after oxidation treatment

| Organics classification | Composition and content | Content in wastewater /μg/L | Oxidant 1# dosage/%（V/V） | | | Maximum removal rate / % |
|---|---|---|---|---|---|---|
| | | | 1 | 5 | 7 | |
| Tetracyclic aromatics hydrocarbons | Chrysene and its derivatives/μg/L | 1806.97 | 1646.75 | 1638.75 | 1048.71 | 41.96 |
| | benzanthracene/μg/L | 106.32 | 105.92 | 105.34 | 63.01 | 40.74 |
| | Benzo flouranthene/μg/L | 175.05 | 135.45 | 0 | 0 | 100 |
| | Pyrene and its derivatives/μg/L | 3479.21 | 2705.07 | 2618.78 | 2315.07 | 33.46 |
| Total organics content/μg/L | | 5567.55 | 4593.19 | 4362.87 | 3426.79 | 38.45 |
| COD/mg/L | | 308.11 | 198.39 | 167.54 | 143.63 | 53.38 |

From table 3, we can see that with the increase of the oxidant 1# dosage, the total content of tetra aromatics hydrocarbons decreases. With the dosage of oxidant 1# increasing from 1% to 7%, the removal rate of total amount of tetra aromatics hydrocarbons is not high, only 38.45%, and the removal rate of COD is 53.38%. The benzofluoranthene removal rate reaches 100%. The possible reason for that is the large relatively stable pi electron conjugated system of chrysene, benzoanthracene while pyrene and benzofluoranthene structure has a five-membered ring, which isn't stable and easily react.

Table 4 Comparison of pentacyclic aromatic hydrocarbonscontent in wastewater before and after oxidation treatment

| Organic matter classification | Organic matter classification | Content in wastewater /μg/L | Oxidant 1# dosage/%（V/V） | | | Maximum removal rate / % |
|---|---|---|---|---|---|---|
| | | | 1 | 5 | 7 | |
| Pentacyclic aromatichydrocarbons | Benzopyrene/μg/L | 293.97 | 284.55 | 0 | 0 | 100 |
| | Perylene and its derivatives /μg/L | 109.42 | 0 | 0 | 0 | 100 |
| Total organic matter content/μg/L | | 403.39 | 284.55 | 0 | 0 | 100 |
| COD/mg/L | | 308.11 | 198.39 | 167.54 | 143.63 | 53.38 |

Table 4 shows that with the increase of oxidant 1# dosage, the total content of pentacyclic aromatic hydrocarbons decreases. When the oxidant 1# dosage is 5% (V/V), the removal rate of pentacyclic aromatic hydrocarbons total content reaches 100%. The reason is that the perylene molecules are coplanar and the structure of perylene is easily modified to react because of its chemical activity while 1, 6, 12 carbon bit of benzopyrene has a lot of negative charges which are more easily oxidized and is conducive to be electrophilic attacked by free radicals.

Table 1~ Table 4 data shows that with the oxidant dosage of 7% 1# (V/V), the difficulty of the removal of different organic matter is as follows: tetracyclic aromatic hydrocarbons(38.45%) ＞ tricyclic aromatic hydrocarbons (49.48%) ＞ ring aromatic hydrocarbons (90.6%) ＞ five aromatic hydrocarbons ((100%), and the highest COD removal rate is 53.38%，This suggests that the residual COD may be produced mainly residues of the tetracyclic aromatics hydrocarbons and a small number of Triaromatics hydrocarbons & dicyclic aromatic hydrocarbon in wastewater.

From Figure 1 ~ Figure 4， we can see that raw water contained more organic molecular ion peak abundance but some of the molecular ion peak abundances reduce or disappear, and also new molecular ion peaks are produced by being treated with different amounts of oxidant 1#, which indicates that the organic matter in water is partially degraded or completely removed under the action of oxidant1 #.

From Figure 1 ~ Figure 4， the mass chromatogram of molecular ion peak of phenanthrene organics containing in raw water have higher abundance， after treatment with different dosage of oxidant1#， in addition to P, the compounds of 1-MP, 2-MP, 3-MP mass chromatography molecular ion peak abundance decreased, but also the molecular ion peak of new generated, and this show that the organic in water are partially degraded or completely removed under the function of free radical, nascent state O produced by the oxidant 1#.

**Quantitative on the organic matter in wastewater before and after coagulation treatment**

4 samples of wastewater 150ml are added to different dosage （%，V/V）of coagulant 1#, then stir for 10min at 100 rpm and settle down quiescently for 45min, then take 100ml supernatant， and extract and analyze it according to the method described above（as of 2.3,2.4）. Take phenanthrene organic compounds in the wastewater, the molecular ion peaks of phenanthrene aromatic hydrocarbons organics (P、1-MP、2-MP、3-MP) in wastewater are shown in figure 5~figure 7 after treatment， and their mass charge ratio are 178, 192, 206, 220 respectively. The quantitative results of main components before and after coagulation treatment of aromatic hydrocarbons in wastewater are shown in table 5-table8.

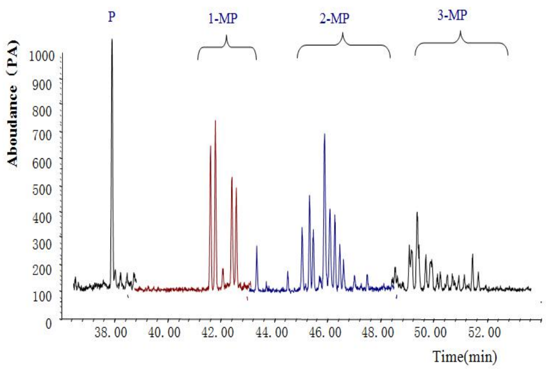


Fig.5 Phenanthrene organic compounds mass spectrogram of wastewater with coagulant 1# 1%

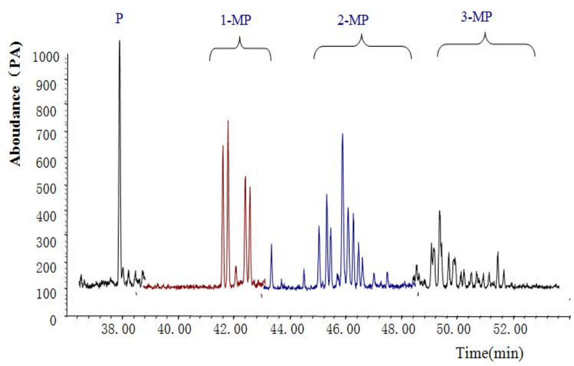


Fig.6 Phenanthrene organic compounds mass spectrogram after treatment with coagulant 1# 3%

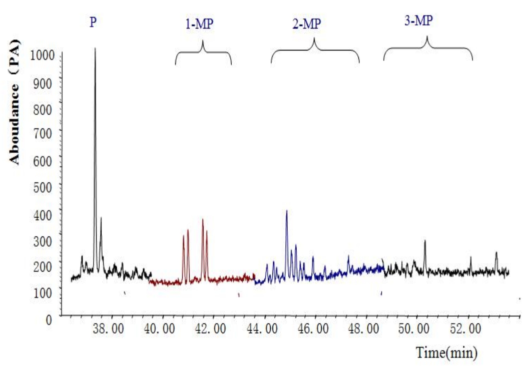


Fig.7 Phenanthrene organic compounds mass spectrogram of wastewater with coagulant 1# 5%

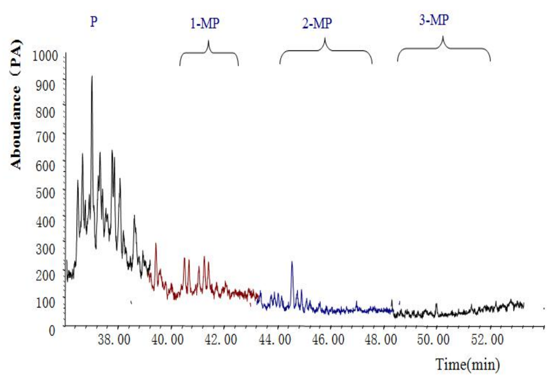


Fig.8 Phenanthrene organic compounds mass spectrogram after treatment with coagulant 1# 5% & oxidant 1#5%

Table 5 Comparison of wastewater in bicyclic aromatic hydrocarbons content before and after coagulation treatment

| Organics classification | Component and content | Content in waste water/μg/L | Coagulant 1# dosage/% （V/V） | | | Maximum removal rate / % |
|---|---|---|---|---|---|---|
| | | | 1 | 3 | 5 | |
| Dicyclic aromatic hydrocarbon | Naphthalene and itsderivatives/μg/L | 2912.84 | 1475.80 | 1452.55 | 921.89 | 68.35 |
| | Biphenyl and its derivatives/μg/L | 441.13 | 254.80 | 188.15 | 149.84 | 66.03 |
| | Dibenzothiophene and its derivatives/μg/L | 19753.12 | 5238.26 | 5107.84 | 5038.02 | 74.50 |
| | Dibenzofuran and its derivatives/μg/L | 646.32 | 388.61 | 255.37 | 230.36 | 64.36 |
| | Fluorene and its derivatives/μg/L | 819.89 | 799.62 | 350.32 | 209.88 | 74.40 |
| Total organics content/μg/L | | 24573.3 | 8110.97 | 7354.23 | 6549.99 | 73.35 |
| COD/mg/L | | 308.11 | 240.16 | 204.13 | 176.30 | 42.78 |

Table 5 shows that with the increase of coagulant 1# dosage, total content of bicyclic aromatic hydrocarbons declines. When the coagulant 1# dosage is 5% (V/V), total bicyclic aromatic hydrocarbons removal rate reaches 73.35% and the removal rate of COD is 42.78%. Dibenzothiophene and its derivatives have the most residual amount, but the removal rate is also the highest. The effect is not as good as that of oxidation treatment. The possible reason is that S atoms in the molecule of dibenzothiophene and its derivatives leads to the large molecular electron cloud density, which is conducive to the adsorption and desorption of the coagulant which is removed by the adsorption settlement of the flocculation.

Table 6 Comparison of triaromatics hydrocarbons content in wastewater before and after coagulation treatment

| Organics classification | Component and content | Content in waste water/μg/L | Coagulant 1# dosage/% （V/V） | | | Maximum removal rate / % |
|---|---|---|---|---|---|---|
| | | | 1 | 3 | 5 | |
| Triaromatics hydrocarbons | Phenanthrene and its derivatives/μg/L | 8149.81 | 1772.81 | 1532.69 | 1261.54 | 84.52 |
| | Anthracene/μg/L | 158.10 | 152.07 | 62.94 | 55.32 | 65.01 |
| | Fluoranthene/μg/L | 464.77 | 250.04 | 212.76 | 189.01 | 59.33 |
| | Benzofluorene/μg/L | 234.36 | 71.57 | 58.78 | 48.95 | 79.11 |
| Total organics content/μg/L | | 9007.04 | 2246.49 | 1867.17 | 1554.82 | 82.74 |
| COD/mg/L | | 308.11 | 240.16 | 204.13 | 176.30 | 42.78 |

From table 6, we can see that with the increase of coagulant 1# dosage, the total content of tricyclic aromatic hydrocarbons decreases. When the dosage of coagulant 1# is 5% (V / V), the total tricyclic aromatic hydrocarbon removal rate reaches 82.74% and removal rate of COD was 42.78%; Among them, the removal rate of the phenanthrene and its derivatives is the highest and reaches

84.52%, which is better than the oxidation treatment effect.

Table 7 Comparison of tetraaromatics hydrocarbons content in wastewater before and after coagulation treatment

| Organics classification | Component and content | Content in waste water/μg/L | Coagulant 1# dosage/%（V/V） | | | Maximum removal rate / % |
|---|---|---|---|---|---|---|
| | | | 1 | 3 | 5 | |
| Tetra aromatics hydrocarbons | Chrysene and its derivatives/μg/L | 1806.97 | 173.72 | 154.60 | 144.19 | 92.02 |
| | Benzanthracene /μg/L | 106.32 | 29.16 | 28.59 | 22.34 | 78.99 |
| | Benzo flouranthene/μg/L | 175.05 | 66.76 | 51.10 | 42.80 | 75.55 |
| | Pyrene and its derivatives/μg/L | 3479.21 | 1501.73 | 1227.63 | 1186.24 | 65.90 |
| Total organics content/μg/L | | 5567.55 | 1771.37 | 1461.92 | 1395.57 | 74.93 |
| COD/mg/L | | 308.11 | 240.16 | 204.13 | 176.30 | 42.78 |

Table 7 shows that with the increase of coagulant 1# dosage, the total content of tetracyclic aromatic hydrocarbon decreases. When the dosage of coagulant 1# is 5% (V/V), the total tetracyclic aromatic hydrocarbon removal rate reaches 74.93% and removal rate of COD is 42.78%; Among them, the removal rate of chrysene and its derivatives is the highest and reaches 92.02% ， which is better than the oxidation treatment effect.

Table 8 Comparison of pentacyclic aromatic hydrocarbonscontent in wastewater before and after coagulation treatment

| Organics classification | Component and content | Content in waste water/μg/L | Coagulant 1# dosage/%（V/V） | | | Maximum removal rate / % |
|---|---|---|---|---|---|---|
| | | | 1 | 3 | 5 | |
| Pentacyclic aromatichy drocarbons | Benzopyrene /μg/L | 293.97 | 101.71 | 89.62 | 63.95 | 78.25 |
| | Perylene and its derivatives/μg/L | 109.42 | 45.94 | 33.17 | 22.23 | 79.68 |
| Total organics content/μg/L | | 403.39 | 147.65 | 122.79 | 86.18 | 78.64 |
| COD/mg/L | | 308.11 | 240.16 | 204.13 | 176.3 | 42.78 |

From table 8 we can see that with the increase of coagulant 1# dosage, the total content of pentacyclic aromatic hydrocarbons decreases. When the dosage of coagulant 1# is 5%, total pentacyclic aromatic hydrocarbons removal rate reaches 78.64% and the removal rate of COD is 42.78%. Two kinds of organic matter removal rate all reach up to 78%. The reason is the more benzene ring in aromatic compound is, the smaller the water solubility number [22-26]is and the lower the organic polar is, which more easily removed organic matter in wastewater with floc through the desorption and adsorption of coagulant 1#, so as to reduce the COD content.

Figure 5~Figure 7， with the increase of coagulant 1# dosage, with the exception of P, the compounds of 1-MP, 2-MP, 3-MP mass chromatography molecular ion peak abundance decrease in wastewater with no new generation of molecular ion peak, which indicates that the Phenanthrene organics in water are partially removed with no degradation under the function of the coagulant 1#. To sum up, removal efficiency of organic compounds in the wastewater with coagulation is decided mainly by destabilization, flocculation, aggregation and flocculation, and is related to the solubility (polarity) of organic matter.

**Quantitative on the organics in wastewater before and after the treatment of oxidation-coagulation**

150ml wastewater is added 1%（V/V）dosage of coagulant 1# and 5%（V/V）dosage of oxidant 1#, then stir for 10min at 100 rpm and settled quiescently for 45min, then take 100ml supernatant. and extract and analyze it according to the method described above （ as of 2.3,2.4 ） . Take phenanthrene organic compounds in the wastewater. the molecular ion peaks of phenanthrene aromatic hydrocarbons organics (P、1-MP、2-MP、3-MP) in wastewater after treatment are shown in figure 8， and their mass charge ratio are 178, 192, 206, 220 respectively. The quantitative results of main aromatic hydrocarbons organics in wastewater before and after oxidation-coagulation treatment are shown in table 9-table12.

Table 9 Comparison of dicyclic aromatic hydrocarbons content in wastewater before and after oxidation-coagulation treatment

| Dicyclic aromatic hydrocarbons | Naphthalene and its derivatives | Biphenyl and its derivatives | Dibenzothioph -ene and its derivatives | Dibenzofur an and its derivatives | Fluorene and its derivatives | Total orga -nics cont- ent/μg/L | COD/ mg/L |
|---|---|---|---|---|---|---|---|
| Content in raw water/μg/L | 2912.84 | 441.13 | 19753.12 | 646.32 | 819.89 | 24573.3 | 308.11 |
| Organics content after treatment /μg/L | 323.28 | 41.29 | 5072.25 | 18.25 | 26.33 | 5481.4 | 37.54 |
| Removal rate / % | 88.90 | 90.64 | 74.32 | 97.18 | 96.79 | 77.69 | 87.82 |

Table 10 Comparison of triaromatics hydrocarbons content in wastewater before and after oxidation-coagulation treatment

| Triaromatics hydrocarbons | Phenanthrene and its derivatives | Anthracene | Fluoranthene | Benzofluorene | Total organics content/μg/L | COD/ mg/L |
|---|---|---|---|---|---|---|
| Content in raw water/μg/L | 8149.81 | 158.1 | 464.77 | 234.36 | 9007.04 | 308.11 |
| Organics content after treatment /μg/L | 546.09 | 0 | 186.45 | 0 | 732.54 | 37.54 |
| Removal rate / % | 93.30 | 100 | 59.88 | 100 | 91.87 | 87.82 |

Table 11 Comparison of tetra aromatics hydrocarbons content in wastewater before and after oxidation-coagulation treatment

| Tetra aromatics hydrocarbons | Chrysene and its derivatives | Benzanthracene | Benzo flouranthene | Pyrene and its derivatives | Total organics content/μg/L | COD/ mg/L |
|---|---|---|---|---|---|---|
| Content in raw water/μg/L | 1806.97 | 106.32 | 175.05 | 3479.21 | 5567.55 | 308.11 |
| Organics content after treatment /μg/L | 47.44 | 18.21 | 0 | 274.63 | 340.28 | 37.54 |
| Removal rate / % | 97.37 | 82.87 | 100 | 92.11 | 93.89 | 87.82 |

Table 12 Comparison of pentacyclic aromatic hydrocarbons content in wastewater before and after oxidation-coagulation treatment

| Pentacyclic aromatichydrocarbons | Benzopyrene | Perylene and its derivatives | Total organics content/μg/L | COD/ mg/L |
|---|---|---|---|---|
| Content in raw water/μg/L | 293.97 | 109.42 | 403.39 | 308.11 |
| Organics content after treatment /μg/L | 0 | 0 | 0 | 37.54 |
| Removal rate / % | 100 | 100 | 100 | 87.82 |

From the table 9- table 12, we can see that after oxidation-coagulation treatment, the removal rate of the total dicyclic aromatic hydrocarbons reaches 77.69%, the removal rate of dibenzofuran and its derivatives is the highest, and up to 97.18%. The removal rate of total tricyclic aromatic hydrocarbons reaches 91.87%, anthracene and benzofluorene could be completely removed. The removal rate of total tetra aromatics hydrocarbons is 93.89%, the removal rate of chrysene and its derivatives is the highest, and up to 97.37%. The removal rate of the total pentacyclic aromatic hydrocarbons is 100%, and the removal rate of COD reaches up to 87.82%.

Figure 8 shows that compared with the raw water, because of oxidation-coagulation, the mass spectrogram molecular ion peak number and abundance of phenanthrene aromatic hydrocarbons organics (P、1-MP、2-MP、3-MP) change significantly, which shows that the oxidation treating organic wastewater with coagulation, the synergistic effect of coagulation-oxidation can improve processing efficiency. The mechanism may be the combining function of oxidation, substitution, coagulation and desorption, adsorption and precipitation etc.

## Conclusion

(1) From high to low , the content of aromatic hydrocarbons in wastewater is: dicyclic aromatichydrocarbons,triaromatics hydrocarbons,tetra aromatics hydrocarbons,pentacyclic aro-matic hydrocarbons. The main content of organic from high to low is dibenzothiophene andits derivatives,phenanthrene and its derivatives,pyrene and its derivatives ,naphthalene and its derivatives,chrysene and its derivatives,fluorene and its derivatives.

(2) From high to low, the COD removal efficiency of three kinds of method is as follows：

oxidation-coagulation method， oxidation and coagulation, COD removal efficiency is 87.82%, 53.38%, 42.78%，respectively.

（3）When the dosage of oxidant 1# is 7% (V/V), the dicyclic aromatic hydrocarbons removal rate is 90.6%, the triaromatics hydrocarbons removal rate is 49.48%,the tetra aromatics hydrocarbons removal rate is 38.45%,the pentacyclic aromatics hydrocarbons removal rate is 100%。

(4) When the dosage of coagulant 1# is 5% (V/V), the dicyclic aromatic hydrocarbons removal rate is 73.35%, the triaromatics hydrocarbons removal rate is 82.74%,the tetra aromatics hydrocarbons removal rate is 74.93%,the pentacyclic aromatics hydrocarbons removal rate is 78.64%。

（5）5% (V/V) oxidant 1# and 5% (V/V) coagulant 1# are added to treat waste water simultaneously, the dicyclic aromatic hydrocarbons removal rate is 77.69%, the triaromatics hydrocarbons removal rate is 91.87%,the tetra aromatics hydrocarbons removal rate is93.89%,the pentacyclic aromatics hydrocarbons removal rate is100%。

(6) Oxidant for removing COD in wastewater is mainly through oxidative decomposition, so that organic matter in water partly is degraded or completely removed, and the oxidation is closely related to the molecular structure of organic matter. Coagulant removing organic matter is mainly flocculation, and the adsorption of flocs sedimentation and related to organic matter solubility (polar).

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