Potassium dichromate method of coal gasification the study of the typical organic compounds in water

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Abstract. The national standard method is adopted in this paper the water - digestion spectrophotometry for determination of the chemical oxygen demand (COD), after ultrasonic processing of coal gasification water for CODCr measurement. Using the control variable method, measured in different solution pH, ultrasonic frequency, ultrasonic power, reaction conditions of different initial solution concentration, the change of coal gasification water CODCr value under the action of ultrasonic, the experimental results shows that appear when measurement is allowed to fluctuate, data, in order to explain the phenomenon we adopt the combination of the high performance liquid chromatography and mass spectrometry before and after ultrasonic coal gasification qualitative analysis on composition of organic matter in water. To raw water sample chromatography - mass spectrometry (GC/MS) analysis, combined with the spectra analysis of each peak stands for material, select coal gasification typical organic substances in water, with the method of single digestion, the equivalent CODCr values measured after digestion. Order to produce, coal gasification water contained high concentration organic wastewater, such as the national standard method is adopted to eliminate the organic material, therefore to measure the CODCr value is lower than actual CODCr value of the emergence of the phenomenon, the experiment of the effect of ultrasound [9-13] is promote the complex organic chain rupture, also explains the actual measurement data fluctuation phenomenon in the experiment.

1. Introduction
With the development of economy and the improvement of people's life, and the rapid industrial development, population growth and persistent drought problems, led to a nationwide shortage of clean water, forcing more and more people begin to pay close attention to environmental protection, especially the problem of water environment pollution control and protection [1]. Coal as main energy in our country, the use of coal and its related technology brought about by the related environmental problems have to be reckoned with, especially in high temperature dry distillation process of coal and gas purification, chemical products, such as refining process of waste water[2], containing phenol tar,
cyanide and ammonia, pollutants, phyletic and various, and the pollutant concentration is high, high chromaticity, high toxicity, is a typical refractory organic wastewater[3-5].

At present all sorts of treatment technology is not entirely mineralization of organic matter, coking wastewater after treatment still contains a lot of low concentration of pollutants in wastewater with outer drainage into the environment, most of these pollutants has carcinogenic, teratogenic and mutagenic effects and toxicity, likely the ecological security and human health risk, and on the qualitative and quantitative research of coking wastewater organic matter less [6-8]. As a complex matrix of organic matter enrichment, separation and pretreatment technology development and the popularization of high performance analysis test instrument, make know the components of coking wastewater.

By national standard method the water quality, rapid digestion spectrophotometry for determination of the chemical oxygen demand (COD), as measured in high concentration organic wastewater measurement is allowed to fluctuate, aiming at to explain the phenomenon.

2. Experimental materials and methods

4.5 ~ 5.0 L coal gasification of water in the reactor, the transducer above the highest point 12 ~ 15 mm shall prevail, considering the experimental process to sampling accordingly index measurement, so the initial liquid level as transducer above the highest point of 15 mm. With dry beaker every 30 min take a watery, mild mixing solution before sampling, measuring the COD\textsubscript{Cr}. Coal gasification water from anning city coking plant, the COD\textsubscript{Cr} initial concentration of 3532 mg/L.

With rapid spectrophotometric method of COD\textsubscript{Cr} in ultrasound before and after the change of the concentration of quantitative analysis; Using the combination of the high performance liquid chromatography and mass spectrometry before and after ultrasonic coal gasification qualitative analysis on composition of organic matter in water. To raw water sample chromatography-mass spectrometry (GC/MS) analysis [14-17], combined with the spectrum for each peak stands for materia, the results are shown in table 1.

### Tab.1 Coal gasification suwon wateryGC-MS spectrum diagram

| number | matter           | matter               |
|--------|------------------|----------------------|
| 1      | methylbenzene    | 13 quinoline         |
| 2      | 4roxy-4-metilo-2-pentanone | 14 2-amino-benzonitrile |
| 3      | cyclohexanone    | 15 indole            |
| 4      | Amino-benzene    | 16 Cinnamyl aldehyde |
| 5      | phenol           | 17 1H-indenol        |
| 6      | o-cresol         | 18 2,6-bis-4-methylphenol |
| 7      | p-cresol         | 19 2-isonaphthol     |
| 8      | 2-metilo-indoline | 20 2,5-dimetil-benzimidazole |
| 9      | 2,4-methylphenol | 21 5-hydroxy-isoquinoline  |
| 10     | 3,5-methylphenol | 22 Pyridine          |
| 11     | 3,4-methylphenol | 23 5H-indeno[1,2-b]piridina  |
| 12     | 1-hydroxy-benzocyclobutene |

3. Results and discussion

3.1. The influence on the effect of initial pH on COD\textsubscript{Cr} degradation

Raw water initial COD\textsubscript{Cr} 3529.25 mg/L, the pH value of 8.7, the water temperature of 26 ℃, respectively in the raw water with 1 mol/L HCl solution (HCl) and 1 mol/L sodium hydroxide solution (NaOH) adjusting the reaction liquid pH 2.5 and 2.5, in 40 KHz, 300 w, the sound intensity under the condition of 57.09 w/cm\textsuperscript{2} ultrasound alone 180 min, once every 30 min take sample, COD\textsubscript{Cr} after diluted 10 times its absorbance measurement, the COD\textsubscript{Cr} concentration change under different initial
pH value were studied. Due to the raw water pH value neutral alkaline, subsequent experiments not adjusted pH value. Different initial pH value on the effects of the COD\textsubscript{Cr} degradation experiment result is shown in figure 1.

![Figure 1](image1)

**Fig. 1** The influence on the effect of initial pH on COD\textsubscript{Cr} degradation

3.2. The change of COD\textsubscript{Cr} concentration under different ultrasonic power

Raw water initial COD\textsubscript{Cr} 3529.25 mg/L, the pH value of 8.7, the water temperature of 26 °C, under the condition of 40 KHz ultrasonic frequency ultrasound alone 180 min, experiments, respectively, set the size of the power ultrasonic generator to 180 w, 240 w, 300 w, once every 30 min take sample, COD\textsubscript{Cr} after diluted 10 times its absorbance measurement, the COD\textsubscript{Cr} concentration change under different initial pH value were studied. Due to the raw water pH value neutral alkaline, subsequent experiments not adjusted pH value. Under the condition of different ultrasonic power on the effects of the COD\textsubscript{Cr} degradation experiment result is shown in figure 2.

![Figure 2](image2)

**Fig. 2** The change of COD\textsubscript{Cr} concentration under different ultrasonic power
3.3. The change of CODCr concentration under different ultrasonic frequency

Raw water initial CODCr 3529.25mg/L, the pH value of 8.7, the water temperature of 26 ℃, under the condition of ultrasonic power is 300 w, ultrasound alone 180 min, the experiment set the frequency of ultrasonic generator size respectively for 20 KHz, 28 KHz, 40 KHz, once every 30 min take sample, CODCr after diluted 10 times its absorbance measurement, the CODCr concentration change under different initial pH value were studied. Due to the raw water pH value neutral alkaline, subsequent experiments not adjusted pH value. Under the condition of different ultrasonic frequency influence on CODCr degradation effect, the experimental results are shown in figure 3.3.

![Fig.3](image)

Fig.3 The change of CODCr concentration under different ultrasonic frequency

3.4. The change of CODCr concentration under different initial concentrations

In order to ensure the water samples were used as raw water samples, sample pretreatment and dilution. In ultrasonic power is 300w, ultrasonic frequency of 40 KHz, under the condition of single ultrasound, 180 min, once every 30 min take sample, CODCr after diluted 10 times its absorbance measurement, the CODCr concentration change under different initial pH value were studied. Due to the raw water pH value neutral alkaline, subsequent experiments not adjusted pH value. A research on the ultrasonic function under different initial concentration of CODCr degradation effect, the experimental results are shown in figure 4.
Fig. 4 The change of CODCr concentration under different initial concentrations

In the above four figure show that the different initial concentration and different ultrasonic power, ultrasonic frequency, ultrasonic degradation process of CODCr under the conditions of different initial pH, the CODCr degradation regularity is not obvious, with no obvious trend of rise and fall. Experiments with rapid spectrophotometry (HJ/T399-2007) the principle is: the reagent adding known quantity of potassium dichromate solution, in strong acid medium, with silver sulfate as the catalyst, after high temperature resolution, by spectrophotometer method determination of CODCr value. But there are also some disadvantages: under the condition of acid potassium dichromate, some aromatic hydrocarbon organic matters, such as pyridine compounds [14-17] difficult to oxidation, the oxidation efficiency is low, and even cannot be oxidized. Therefore, will exist in the CODCr measurement to measure the CODCr value does not response the real CODCr value

3.5. Equivalent to phenol was dispelled, measured CODCr value

Fig. 5 Equivalent to phenol was dispelled, measured CODCr value
3.6. Equivalent to quinoline was dispelled, measured CODCr value

In potassium dichromate digestions of pyridine with different concentration gradient, eventually couldn't measure the equivalent CODCr value. To use potassium dichromate digestion of 50 mg/L pyridine solution product analysis, because the product concentration is too high, so adopt the method of deionized water diluted 104 times were measured, using spectrophotometer wavelength scanning method in 190-600 nm in the scan after digestion solution, the determination results as shown:

![Fig.6 Equivalent to quinoline was dispelled, measured CODCr value](image)

By as shown in figure: the 50 mg/L pyridine solution after digestion solution using the wavelength scanning spectrophotometer, measuring the product. Because the concentration of certain substances after digestion is exorbitant, absorbance measurement range of the instrument is limited, need to dilute the solution after digestion. Appeared a peak at 200 nm, shows the peak as the peak of total nitrogen, depending on the absorbance to reflect the content of how much; Appeared a peak at 350 nm, the peak peak value of the display of flavonoids, according to difference of absorbance to reflect how much content.

![Fig.7 50 mg/L pyridine by potassium dichromate solution after digestion with spectrophotometer spectrum scan](image)
3.7. Uses the method of ultrasonic degradation of 50 mg/L pyridine solution measure equivalent CODCr value of the solution

Uses the method of ultrasonic degradation of 50 mg/L pyridine solution, experimental condition is: the ultrasonic power is 300 w, ultrasonic frequency for 28 KHz, in the process of the reaction is not adjusting test of pH, temperature and other conditions, over time, and reaction results shown:

![Graph showing COD (mg/L) versus time (min)](image)

**Fig.8** The method of ultrasonic degradation of 50 mg/L pyridine solution

Equivalent CODCr value

The results show that under the action of ultrasonic, over time, pyridine in the reaction of ring fracture, the generated intermediate can be potassium dichromate digestion. Therefore, in the actual containing pyridine class refractory organic wastewater, such as using potassium dichromate method is difficult to determine the inside of the organic matter to times by potassium dichromate, also it will be difficult to ensure the accuracy of the data of the measurement of CODCr, there will be a CODCr data measured values than the phenomenon of low CODCr value in actual production.

4. Conclusions

Ultrasonic degradation of coal gasification by above knowable, reuse water raw water measuring CODCr value, the volatility, considering the reasons as follows:

1)The determination of CODCr by potassium dichromate digestion spectrophotometry to measure, because of the complexity of coal gasification of water inside the type of organic matter, and the organic matter degradation characteristics, some organic matter cannot be digested with potassium dichromate, ultrasonic wave, hydroxyl radicals can make some complex organic compounds produced by the open loop or bounce the oxidation and then transformed into other oxidizable substances digestion.

2)CODCr measurement is still behind some fluctuation, because the material is difficult to degradation degree under the effect of ultrasonic, some material is easy to ultrasonic degradation, some are difficult to ultrasonic degradation, so there will be a variety of fluctuation.

3)Phenol, quinoline, the two substances to digest by potassium dichromate.

4)The heterocyclic pyridine organic matter cannot be eliminated by potassium dichromate.

5)Also explains why along with the advancement of ultrasonic processing time of coking wastewater, the determination of CODCr value volatility, started to use potassium dichromate in determination of CODCr value, the inside of the pyridine (and other organisms) equivalent of the
COD$_{Cr}$ value has not been measured, with time, the effect of ultrasonic wave can be converted into other substances that pyridine, can be eliminated by potassium dichromate, and can measure equivalent COD$_{Cr}$ value.

6) In an actual containing pyridine class refractory organic wastewater, such as using potassium dichromate method is difficult to determine the inside of the organic matter to times by potassium dichromate, also it will be difficult to ensure the accuracy of the data of the measurement of COD$_{Cr}$, there will be a COD$_{Cr}$ data measured values than the phenomenon of low COD$_{Cr}$ value in actual production.

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