Advanced treatment of coking wastewater by coagulation and zero-valent iron processes

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Abstract

Advanced treatment of coking wastewater was investigated experimentally with coagulation and zero-valent iron (ZVI) processes. Particular attention was paid to the effect of dosage and pH on the removal of chemical oxygen demand (COD) in the two processes. The results showed that ZVI was more effective than coagulation for advanced treatment of coking wastewater. The jar tests revealed that maximal COD removal efficiency of 27.5–31.8% could be achieved under the optimal condition of coagulation, i.e. 400 mg/L of $Fe_2(SO_4)_3$ as coagulant at pH 3.0–5.0. On the other hand, the COD removal efficiency could be up to 43.6% under the idealized condition of ZVI upon 10 g/L active carbon and 30 g/L iron being dosed at pH 4.0. The mechanisms for COD removal in ZVI were dominated by coagulation, precipitation and oxidation–reduction. ZVI would also enhance the biodegradability of effluent by increasing BOD_5/COD from 0.07 to 0.53. Moreover, some ester compounds could be produced in the reaction. Although ZVI was found more efficient than coagulation in eliminating low molecular weight (<2000 Da) compounds in the wastewater, there were still a few residual contaminants which could hardly be eliminated by either of the process.

1. Introduction

Coking wastewater is a severe problem all over the world. In China, coal is one of the main energy sources [1]. For example, many coke plants and coal gasification plants have been concentrated in Shanxi Province, the "coal town" in the North China. As consequences, the people there have suffered a great deal from coking wastewater, which is composed of complex inorganic and organic contaminants such as ammonia, cyanide, thiocyanide, phenolic compounds, polynuclear aromatic hydrocarbons (PAHs), polycyclic nitrogen-containing aromatics, oxygen- and sulfur-containing heterocyclics and acyclic compounds [2–4]. Most of these compounds are refractory [5], highly concentrated, toxic, mutative and carcinogenic and may produce long-term environmental and ecological impacts [6,7].

The conventional treatment process of coking wastewater is solvent extraction of phenolic compounds and steam stripping of ammonia, followed by biological treatment, mostly the activated sludge process [8]. Since a certain number of refractory and inhibitory organic compounds in coking wastewater are highly concentrated, the conventional activated sludge process is not effective for COD removal. Recently, a number of new biological reactors and processes have been investigated and extensively applied in coking wastewater treatment [9–11]. These include anoxic–oxic (A–O), anaerobic–anoxic–oxic (A_1–A_2–O) and sequencing batch reactor (SBR), etc., which are found more effective than the conventional activated sludge process in the removal of COD and nitrogen compounds due to their high-efficient anaerobic acidification [12], nitrification and denitrification [13]. Hitherto, the aforementioned processes are not efficient enough to meet the requirements from the National Discharge Standard in China, and more efforts on advanced processes for coking wastewater treatment are still necessary.

Many physico-chemical processes can be applied in the advanced treatment of coking wastewater, such as ozonation, Fenton reagent oxidation, active carbon adsorption, ion exchange, chemical precipitation, membrane separation, coagulation and zero-valent iron (ZVI), etc. In these processes, coagulation and ZVI are relatively cheaper, easier to operate.

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As a result, the two processes are widely used in wastewater treatment [14–18].

Coagulation is an important process in both solid–liquid separation and soluble containments removal from aqueous solution. The usually used coagulants are different kinds of aluminium salts, iron salts and some inorganic/organic polymers. Coagulants and their hydrolysis products play an important role in improving the final contaminant removal efficiency. However, the performances of the chemical coagulants could be quite different under varying conditions, e.g. the dosage of coagulants and pH, etc.

Iron containing materials of low prices are usually adopted in ZVI process. An oxidation–reduction couple with a standard reduction potential of -0.440 V is formed in the reaction [19]. Due to the strong reductive capacity, ZVI can transform the structures and minimize the toxicity of hazardous contaminants, such as atrazine and parathion, carbaryl, benomyl, picloram and dicamba [20–22], nitroaromatic pesticides [23] and molinate [24].

There have been few detailed reports about the advanced treatment of coking wastewater by physico-chemical processes, especially by ZVI process. The objective of this study is to investigate the feasibility of coagulation and ZVI processes applied in the advanced treatment of coking wastewater with COD index as the main target parameter. The optimal operation conditions were achieved for both processes in laboratory-scale experiments, respectively. Furthermore, the mechanisms and performances of coagulation and ZVI processes were investigated by ultraviolet (UV) scan, biochemical oxygen demand (BOD_5) determination, gas chromatography/mass spectrum (GCMS) and molecular weight distribution (MWD) studies.

2. Materials and methods

2.1. Raw wastewater and materials

The raw wastewater used in the experiments was collected from the outlet of a coke plant near Beijing City with the treatment processes of extraction of phenolic compounds, steam stripping of ammonia and A_1–A_2–O biological treatment. Even treated by biological process, the wastewater sample was still deep brown in color and badly smelled. Table 1 shows some special chemical parameters of the wastewater sample.

Table 1
Characteristics of raw wastewater

Parameter	Unit	Raw wastewater
pH		7.2 ± 0.3
Temperature (in situ)	°C	30 ± 2
Conductivity	μS/cm	2200 ± 20
COD	mg/L	750 ± 150
BOD_5	mg/L	45 ± 10
TOC[a]	mg/L	195 ± 30
SS[b]	mg/L	100 ± 10

[a] TOC: total organic carbon.
[b] SS: suspended solid.

In the jar tests, an analytical reagent grade $Fe_2(SO_4)_3$ was used as coagulant. $Fe_2(SO_4)_3$ powder was dried at 105 °C for 4 h before the preparation of stock solution concentration of 20 g/L. In the ZVI batch experiments, industrial iron consisted of filings and shavings were largely free from visible rust and retained a metallic glaze (Beijing Institute of Technology). The iron was cut to approximately 1 mm in diameter, 20 mm in length, irregular in shape and with a slightly rough surface. The scrap iron was steeped and washed with NaOH (4.5 M) and HCl (5 M) for 30 min, respectively, and then washed three times with deionized water to remove residual Fe^{2+} and HCl. The clean iron was dried naturally for further use. Active carbon (industrial grade, Guangdong Province, China) was used as macroscopical electrode material. It was about 2 mm in diameter, 10 mm in height and in the shape of a column. In order to eliminate the adsorption effect, the active carbon was saturated with raw wastewater for 24 h before use. NaCl solution (dosage of 200 mg/L) was used as an additional electrolyte in ZVI process.

NaOH (4.5 M) and HCl (5 M) were used for pH adjustment. All the chemical reagents used in the experiments were analytical grade, which were purchased from Beijing Chemical Reagent Corporation. Deionized water (China Agricultural University) was used for preparing stock solution of reagent.

2.2. Experimental procedure

The jar tests were run on an agitation apparatus which had six agitators with same speed simultaneously (Meiyu Environmental Equipment Corporation, Hubei Province, China). The COD value of raw wastewater was diluted to 200–300 mg/L with tap water. One liter of diluted wastewater was added to a beaker and mixed with the agitation apparatus at a high speed (200 rpm) for 5 min followed by a low speed (50 rpm) for 10 min. After 30 min of natural precipitation, the supernatant was taken for analysis. In the jar tests, the dosage of $Fe_2(SO_4)_3$ varied from 0 to 1000 mg/L and the initial pH of wastewater varied from 2.0 to 12.0, from which the optimal dosage and pH conditions in coagulation process could be determined.

In ZVI process, prepared iron, active carbon and NaCl with different dosage were added to a 2 L beaker, respectively. Two liters of diluted wastewater was then added and mixed. In the reaction process, a gas pump was used to mix and supply sufficient oxygen (4.0–7.0 mg/L of dissolved oxygen) to the reaction system. Each batch experiment lasted for 240 min. At different intervals, the supernatant was taken and kept standstill for 60 min before measurement. The dosage of active carbon, iron varied in the range of 0–20 and 5–50 g/L, respectively, and the initial pH was adjusted to 4.0–10.0 in order to achieve the optimal reaction condition.

All the above experiments were conducted at room temperature.

2.3. Analytical methods

Before analysis, the supernatant sample was filtrated first with filter paper and then with 0.45 μm cellulose acetate membrane. COD, BOD_5, TOC and pH were measured by the potassium
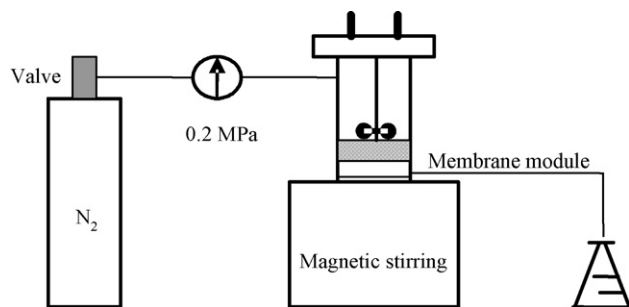
Fig. 1. Membrane separation system for MWD measurement.

dichromate oxidation method (Hach Heating System, Hach Corporation, USA), the respirometric method (OxiTop IS6, Germany), Multi TOC/TN 3000 Analyzer (Analytik Jena AG Corporation, Germany) and pH meter (pH-201, Hanna Corporation, Italy), respectively. UV absorption scan was conducted by UV–vis spectrophotometer (SPECORD 200, Analytik Jena AG Corporation, Germany).

MWD was measured by a set of membrane separation apparatus (KeRui Technology Corporation, Beijing, China). The pressure of 0.2 MPa was provided by highly pure N_2 (99.999%) steadily. The wastewater was first filtrated through the 0.45 μm cellulose acetate membrane and then through the different ultrafiltration membranes with molecular weight cut-off (MWCO) of 2000–30,000 Da (Polyetherssulfone, PES, Institute of Application Physics, Chinese Academy of Sciences). The membranes were steeped and washed with deionized water prior to use. The separation system is shown in Fig. 1.

GCMS was used for organic compounds analysis with liquid-liquid extraction pretreatment using CH_2Cl_2 (chromatogram pure grade, Fisher Corporation, USA). The extraction procedure was conducted at acidic, neutral and alkaline conditions, respectively [25]. Then, 1 μL pretreated sample was analyzed by 6890N/5973 GCMS system (Agilent Corporation, USA). Highly pure He gas (99.999%) was used as carrier gas with a flow rate of 1 mL/min. A DB-35MS capillary column with inner diameter of 0.25 mm and length of 30 m was adopted in the separation system. The temperature for the gasification compartment was maintained at 280 °C. The temperature control program was followed by maintaining at 40 °C for 3 min and then increasing to 280 °C with an increment of 3 °C/min. The electron energy and the electron double voltage were set at 70 eV and 1200 V, respectively, and the molecular weight scan varied from 50 to 800 Da.

3. Results and discussion

3.1. COD removal by coagulation process

3.1.1. Effect of $Fe_2(SO_4)_3$ dosage

The effect of $Fe_2(SO_4)_3$ dosage on COD removal at pH 7.0 is shown in Fig. 2. It is clear that COD was not always reduced by increasing $Fe_2(SO_4)_3$ even more flocs were formed in the wastewater. COD was reduced rapidly during the $Fe_2(SO_4)_3$ dosages of 0–400 mg/L. However, when $Fe_2(SO_4)_3$ dosage
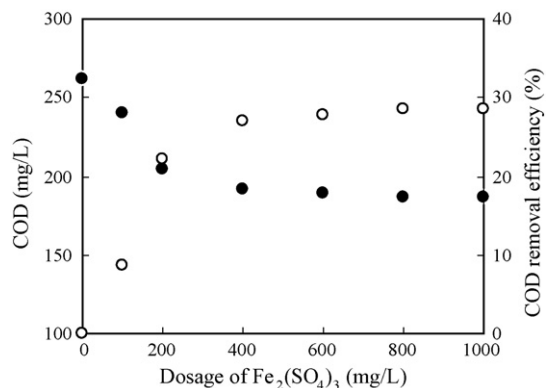

Fig. 2. COD removal at different dosage of coagulant. (●) COD value and (○) COD removal efficiency.

exceeded 400 mg/L, COD was not reduced obviously and remained at 180–200 mg/L. With an addition of 1000 mg/L $Fe_2(SO_4)_3$, COD removal efficiency only reached 28.6%, which was not a great enhancement compared with 26.9% of 400 mg/L $Fe_2(SO_4)_3$. Therefore, 400 mg/L would be a suitable dosage in considering the treatment cost. A few substances in the wastewater, like some special humic substances, could not be effectively removed by coagulation process [26].

3.1.2. Effect of initial pH of wastewater

The effect of initial pH of wastewater at $Fe_2(SO_4)_3$ dosage of 400 mg/L is shown in Fig. 3. Low pH condition (<3.0) resulted in a poor COD removal efficiency of only 17.5%. When pH was over 5.0, the COD removal efficiency decreased a little. The optimal pH range was 3.0–5.0 with COD removal efficiency of 27.5–31.8%.

Few flocs (complexes of Fe hydroxides and organic compounds) were formed in coagulation process when pH was less than 3.0. With the increase of pH, the formation of flocs increased distinctly but COD removal efficiency did not increase obviously. The reason could be that more Fe^{3+} of positive charge in solution could be available but few flocs were formed when pH was less than 3.0. Since a small portion of these complexes reversed their charges to prevent the complexes from being removed, the organic compounds could not be removed effectively. When pH was over 3.0, different structures of hydroxides
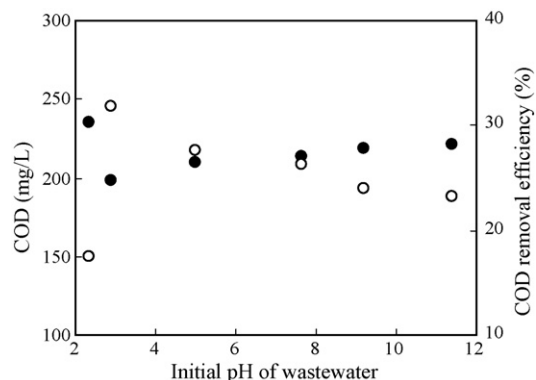

Fig. 3. COD removal at different initial pH of wastewater. (●) COD value and (○) COD removal efficiency.
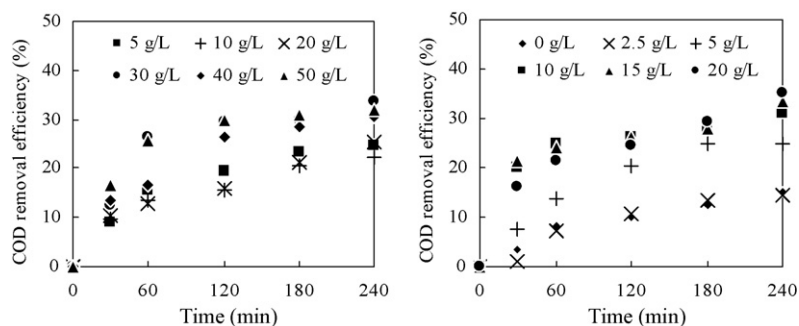
Fig. 4. COD removal at different dosage of iron and active carbon in ZVI process. (Left) Dosage of iron, 10 g/L active carbon, 200 mg/L NaCl, without pH adjustment and (right) dosage of active carbon, 30 g/L iron, 200 mg/L NaCl, without pH adjustment.

with adsorption and enmeshment property were formed widely. The different hydroxides supplied more space and opportunity for complexation [27]. However, the higher pH (>5.0) did not enhance the COD removal efficiency. It was because the hydrolysis rate of Fe^{3+} was enhanced, forming coagulation species with less positive charge. When initial pH was at 3.0–5.0, some special Fe hydroxides would be formed and the complex formation between the hydroxides and the organic compounds enhanced the removal efficiency [28]. On the other hand, the characteristic of some organic compounds in the wastewater would be changed at different pH conditions. Some organic compounds with special groups, such as −OH, −COOH, were deprotonated, resulting in higher negative charge at neutral or alkaline condition. Differently, these compounds had more neutral sites at acidic condition [27], which were easier to be removed by coagulation process.

Due to the discussion above, the removal mechanisms of organic compounds in coagulation process could be charge adsorption–neutralization and complexation followed by precipitation [29]. In this study, the optimal pH range was 3.0–5.0, which was consistent with the studies of Lefebver and Legube [14] and Musikavong et al. [16].

3.2. COD removal by ZVI process

3.2.1. Effect of dosage of iron and active carbon

The change of COD removal efficiency with different dosage of iron and active carbon at pH 7.0 is shown in Fig. 4. The COD removal efficiency increased with increasing dosage of iron in a two-stage pattern. With the lower dosage of iron at 5, 10 and 20 g/L, COD removal efficiency were 24.5, 22.1 and 25.3%, respectively, after 240 min reaction time. Once the dosage of iron exceeded 20 g/L, COD removal increased distinctly. Similarly, there were no obvious changes at the dosage of 30, 40 and 50 g/L. After 240 min, COD removal efficiency remained at about 32.0%. It could be concluded there was a transition in ZVI process between the iron dosage of 20 and 30 g/L. Since an excess amount of iron would affect the mass transfer efficiency, 30 g/L would be an appropriate dosage. In all batch experiments, flocs in the sample taken from the reaction system increased obviously with longer reaction time. The flocs, which were produced due to the iron corrosion, were brown. With the mixing and oxidation by aeration, more Fe^{3+} hydroxides were formed in the system, which could act as effective coagulant. Coagula-

tion, flocculation and precipitation should be part of the reaction mechanisms in ZVI process.

Fig. 4 also shows the COD change at different dosage of active carbon. Since the waste iron contained Fe and C, they would be considered as many microcosmic electrodes in the reaction system. It was found that COD could be reduced when active carbon was not added. With the addition of active carbon, the reaction of macroscopical electrodes increased the COD removal efficiency. In Fig. 4, it is clear that there was a rising trend of COD removal efficiency with the addition of active carbon. However, as in the addition of iron, there was no obvious enhancement with further increase of the active carbon. When the active carbon dosage was at 10, 15 and 20 g/L, the COD removal efficiencies were 30.9, 33.3 and 35.1%, respectively. Taking both the treatment effect and cost into consideration, 30 g/L of iron and 10 g/L of active carbon would be the optimal dosage condition.

3.2.2. Effect of initial pH of wastewater

The effect of initial pH in ZVI process is shown in Fig. 5. It revealed that ZVI was more effective at acidic condition. With initial pH decreased, COD removal efficiency increased evidently. After 240 min reaction time, COD was reduced to 114.2 mg/L and the removal efficiency was 43.6% at pH 4.0, which was much better than 23.1% at pH 10.0.

In the discussion of coagulation process in Section 3.1.2, higher COD removal efficiency was achieved at acidic condition.
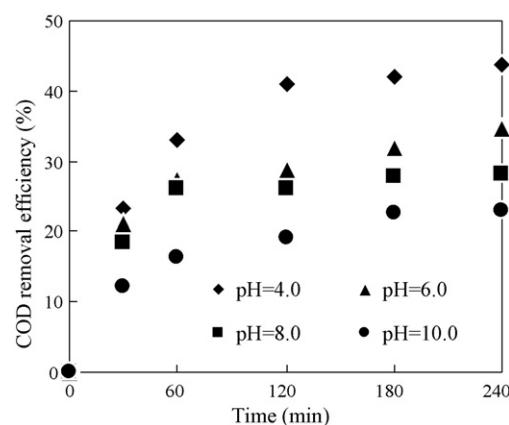

Fig. 5. COD removal at different initial pH of raw wastewater in ZVI process, addition of 10 g/L active carbon, 30 g/L iron and 200 mg/L NaCl.

Similarly higher efficiency could be expected in ZVI process at acidic condition partially because of the functions of the accompanied coagulation process. On the other hand, ZVI was different from coagulation because of its oxidation–reduction ability. Based on the Nernst equation below (Eqs. (1) and (2)), the electrical potential energy between anode and cathode could be enhanced when pH got lower in the reaction system, which resulted in an improvement of ZVI. Cao et al. [17] also found that pH strongly affected the degradation rate in dye wastewater treatment by ZVI. They found that the degradation rate increased rapidly with the increase of acidity. However, an extremely low pH condition would increase operation difficulty and treatment cost. Moreover, it would result in color problem when discharge due to the strong corrosion of iron. In ZVI process, the optimal pH range would be 4.0–6.0.

$$\text{Anode reaction}: Fe - 2e \rightarrow Fe^{2+},$$

$$E = -0.440 + 0.03 \log \alpha_{Fe^{2+}} \tag{1}$$

$$\text{Cathode reaction}: 2H^+ + 2e \rightarrow H_2,$$

$$E = -0.059pH - 0.03 \log \alpha_{p_{H_2}} \tag{2}$$

3.3. Comparison between coagulation and ZVI processes

3.3.1. UV scan

UV scan results before and after treatment by coagulation and ZVI processes is shown in Fig. 6. It was found that the contaminants which had strong absorption peaks between 230 and 400 nm were well removed by both processes. In Fig. 6, it is clear that there was a similar trend in absorption peaks between coagulation and ZVI processes. However, the residual absorption peaks showed some contaminants in the raw wastewater could not be removed by the two processes. Due to the limitation of UV scan method and complex ingredients in the wastewater, it was difficult to distinguish these contaminants only by their special absorption peaks. The residual contaminants had high absorbency at 200–230 nm. However, the

intensities of these peaks of the effluent by ZVI were lower than those by coagulation process. Therefore, it could be concluded that ZVI was more effective in advanced treatment of coking wastewater.

Fig. 6 also indicates that coagulation and ZVI had similar mechanisms during the treatment for the similar UV scan result at 200–230 nm. It was proved that coagulation was the main mechanism for the removal of contaminants in ZVI process. Furthermore, Kang et al. [30] found that coagulation was the main mechanism for COD removal of textile wastewater in an oxidation and coagulation process. Similar results were also reported earlier about dye wastewater treatment with ozone/coagulation process [31]. On the other way, ZVI would be an improved coagulation process since the contaminants removal was enhanced by oxidation–reduction reaction in the system.

3.3.2. BOD5 analysis

The calculation results of BOD_5 measurement before and after treatment by coagulation and ZVI processes are shown in Fig. 7. The BOD_5 values of the effluent by the two processes were 23.0 and 75.0 mg/L, respectively, which were both higher than that of the raw wastewater. For ZVI process, the BOD_5 value was five times high compared to the raw wastewater. The BOD_5/COD increased from 0.07 to 0.53 by ZVI process, which was much higher than that in the coagulation process. The results indicated the improvement of biodegradability by both processes, especially the remarkable enhancement by ZVI. The different mechanisms of the two processes contributed to the different biodegradability of their effluent. In coagulation process, some refractory compounds in the wastewater were only removed by physical reactions, such as adsorption–neutralization, complexation and precipitation. In ZVI process, there were electrical oxidation and reduction reactions which could transform the structures and characteristics of some refractory compounds. It was similar to the reduction of $-NO_2$ to $-NH_2$ [32,33] and the dehalogenation of volatile chlorinated hydrocarbons [34].
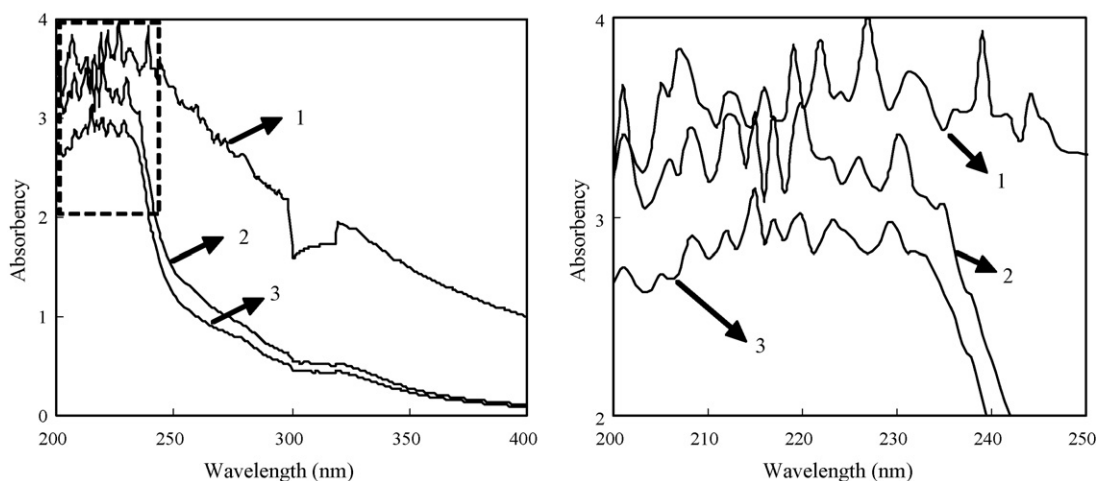

Fig. 6. UV scan results before and after treatment by coagulation and ZVI processes: (1) raw wastewater, (2) effluent by coagulation, (3) effluent by ZVI; without adjustment of initial pH, 400 mg/L $Fe_2(SO_4)_3$ for coagulation, 10 g/L active carbon, 30 g/L iron and 200 mg/L NaCl for ZVI.
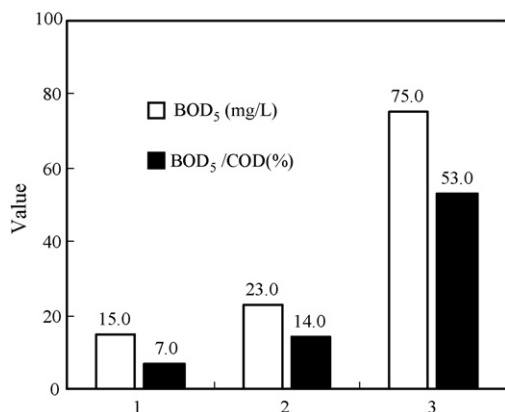
Fig. 7. BOD$_5$ analysis before and after treatment by coagulation and ZVI processes: (1) raw wastewater, (2) effluent by coagulation, (3) effluent by ZVI; without adjustment of initial pH, 400 mg/L Fe$_2$(SO$_4$)$_3$ for coagulation, 10 g/L active carbon, 30 g/L iron and 200 mg/L NaCl for ZVI.

3.3.3. GCMS analysis

The GCMS analysis result is shown in Table 2. It was found that there were quite a few refractory organic compounds in the raw wastewater even it was treated by A$_1$–A$_2$–O biological process. These organic compounds were hardly degraded by microorganisms, which had been proved by the result of BOD$_5$ measurement in the above section. The dominant compounds in the refractory contaminants were phenolic and heterocyclic compounds, such as 2,5-dimethylphenol, 3,5-dimethylphenol, 2,4,6-trimethyphenol and 2-methylquinoline, as shown in Table 2. After the treatment by coagulation process, most of these refractory compounds were removed and only 2-methylquinoline was detected in the effluent. Differently, all the refractory compounds in the raw wastewater could not be detected and some new ester compounds were produced by ZVI process. Compared with the refractory organic compounds in the raw wastewater, the ester compounds were much easier to be utilized by microorganisms, which resulted in the improved BOD$_5$ and the increased BOD$_5$/COD.

Some other studies could also prove the enhancement of biodegradability by ZVI treatment. Nam and Tratnyek [18] studied the reduction of recalcitrant azo dyes by ZVI and the products

were aromatics amines which improved the biodegradability. Oh et al. [35] found ZVI could enhance the biodegradability of hexahydro-1,3,5-trinitro-1,3,5-triazine and the major product was formaldehyde which could be readily biodegraded. In this study, it was proved that there should be not only coagulation and precipitation, but also oxidation–reduction reaction in ZVI process, which transformed some refractory compounds into easily degradable ones such as ester compounds, and improved the biodegradability of effluent remarkably. It could be concluded that the main mechanisms for COD removal in ZVI process were coagulation, precipitation and oxidation–reduction.

3.3.4. MWD measurement

The MWD change after the treatment by coagulation and ZVI processes is shown in Fig. 8. It is clear that the raw wastewater and the treated effluent were mainly made up of low molecular weight (0–2000 Da) compounds. It was found that the molecular weight range of the compounds removed by coagulation and ZVI processes were different. It was more effective for coagulation in eliminating contaminants at 2000–4000 and 10,000–30,000 Da. But in the range of 0–2000 and 4000–10,000 Da, ZVI was much more effective in TOC reduction especially at 0–2000 Da,
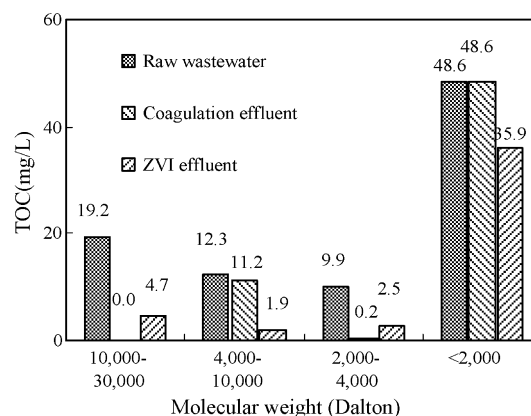

Fig. 8. MWD measurement before and after treatment by coagulation and ZVI processes; without adjustment of initial pH, 400 mg/L Fe$_2$(SO$_4$)$_3$ for coagulation, 10 g/L active carbon, 30 g/L iron and 200 mg/L NaCl for ZVI.

Table 2
Qualitative analysis of main organic compounds in effluent after coagulation and ZVI

Organic compound	Raw wastewater	Coagulation	ZVI
2,5-Dimethylphenol	√[a]	–[b]	–
3,5-Dimethylphenol	√	–	–
2,4,6-Trimethyphenol	√	–	–
2-Methylquinoline	√	√	–
1(2H)-Isoquinolinone	√	–	–
Acridine	√	–	–
Carbazole	√	–	–
9-Acridinecarbonitrile	√	–	–
Fluoranthene	√	–	–
Pyrene	√	–	–
1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	–	–	√
1,2-Benzenedicarboxylic acid, butyl-1,2-ethylhexyl ester	–	–	√

[a] "√": detected.
[b] "–": not detected.

where coagulation had no effect on the TOC removal but ZVI could remove about 30.0% of TOC. After the treatment by coagulation and ZVI processes, the percentages of residual compounds at 0–2000 Da were 80.1 and 79.7%, respectively. From above results, it was concluded that ZVI was more efficient in removing the low molecular weight (0–2000 Da) compounds. There were quite a few other organic compounds in the effluent, which had different molecular weight ranges and could not be detected by GCMS but contributed to part of COD.

Tambo and Kamei [26] reported that there were many humic substances which could not be degraded by biological process and most of them could not be removed by coagulation effectively as well. These humic substances had molecular weight less than 1500 Da, like fulvic acid substances. In Fig. 8, the effluent by the two processes was both mainly made up of substances of less than 2000 Da. It was proved that some residual organic pollutants of the effluent by the two processes were from the untreated coking wastewater, similar to these low molecular weight and hydrophilic humic substances.

4. Conclusions

Both coagulation and ZVI processes were investigated for advanced treatment of coking wastewater. In coagulation process, the optimal dosage and pH were 400 mg/L of $Fe_2(SO_4)_3$ and 3.0–5.0, respectively. In ZVI process, the optimal operation condition was addition of 10 g/L of active carbon and 30 g/L of iron at pH 4.0–6.0 after 240 min reaction time. The increase of acidity could enhance the COD removal efficiency evidently. ZVI was more feasible for advanced treatment of coking wastewater than coagulation, taking the treatment effect and cost into consideration.

The main mechanisms for COD removal in coagulation process could be charge adsorption–neutralization and complexation followed by precipitation. For the removal of organic pollutants in ZVI process, however, the oxidation–reduction mechanism must be considered in addition to the coagulation and precipitation mechanism. The oxidation–reduction ability of ZVI could transform the structures and characteristics of some refractory compounds. ZVI enhanced the biodegradability of effluent obviously by increasing BOD_5/COD from 0.07 to 0.53. There were some refractory organic compounds in the raw wastewater such as 2-methylquinoline. Both coagulation and ZVI processes could eliminate most of these compounds. Some ester compounds were produced by ZVI which increased the biodegradability of the effluent. ZVI was more efficient in eliminating low molecular weight (0–2000 Da) compounds than coagulation, but there were still some residual contaminants could not be removed by these two processes.

Acknowledgements

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