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JOURNAL OF ENVIRONMENTAL SCIENCES

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Advanced treatment of biologically pretreated coal gasification wastewater by a novel heterogeneous Fenton oxidation process

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ARTICLE INFO

Article history:
Received 19 October 2014
Revised 5 December 2014
Accepted 6 December 2014
Available online 14 April 2015

Keywords:
Biologically pretreated coal gasification wastewater
Heterogeneous Fenton oxidation
Catalyst
Biodegradability
Mechanism

ABSTRACT

Sewage sludge from a biological wastewater treatment plant was converted into sewage sludge based activated carbon (SBAC) with $ZnCl_2$ as activation agent, which was used as a support for ferric oxides to form a catalyst (FeOx/SBAC) by a simple impregnation method. The new material was then used to improve the performance of Fenton oxidation of real biologically pretreated coal gasification wastewater (CGW). The results indicated that the prepared FeOx/SBAC significantly enhanced the pollutant removal performance in the Fenton process, so that the treated wastewater was more biodegradable and less toxic. The best performance was obtained over a wide pH range from 2 to 7, temperature 30°C, 15 mg/L of H_2O_2 and 1 g/L of catalyst, and the treated effluent concentrations of COD, total phenols, BOD_5 and TOC all met the discharge limits in China. Meanwhile, on the basis of significant inhibition by a radical scavenger in the heterogeneous Fenton process as well as the evolution of FT-IR spectra of pollutant-saturated FeOx/BAC with and without H_2O_2, it was deduced that the catalytic activity was responsible for generating hydroxyl radicals, and a possible reaction pathway and interface mechanism were proposed. Moreover, FeOx/SBAC showed superior stability over five successive oxidation runs. Thus, heterogeneous Fenton oxidation of biologically pretreated CGW by FeOx/SBAC, with the advantages of being economical, efficient and sustainable, holds promise for engineering application.

Introduction

The coal gasification industry in China has been rapidly developed in order to supplement the natural gas shortage, and has played a key role in new clean and renewable market in recent years. However, coal gasification wastewater (CGW) contains considerable amounts of complex, toxic and refractory pollutants in spite of physicochemical pretreatment (Wang et al., 2011), which would cause significant deterioration of the environment. Most biological treatments have shown limited success and fall short of meeting the strict requirements of the National Discharge Standard of China (Wang and Han, 2012). Biologically pretreated CGW still contains a large number of toxic and refractory compounds as well as their derivatives, such as phenolic compounds, polycyclic aromatic hydrocarbons, nitrogenous heterocyclic compounds, long-chain hydrocarbons, and ammonia, with lower biodegradability than the raw wastewater (Zhuang et al., 2014a). According to the latest national policy, zero liquid discharge has been set as a requirement to resolve the conflicts between environmental

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http://dx.doi.org/10.1016/j.jes.2014.12.015
1001-0742/

protection and CGW discharge in China. The wastewater control task had become a bottleneck for the development of the coal gasification industry. Thus, the search for an efficient and cost-effective process for advanced treatment of biologically pretreated CGW is very urgent.

The Fenton process has recently been intensively investigated for mineralizing refractory pollutants in industrial wastewater, due to its use of inexpensive chemicals, ease of operation and high oxidation performance (Chakinala et al., 2008). However, this type of chemical oxidation treatment usually presents certain limitations (An et al., 2013), such as a narrow working pH range (2–4) and the accumulation of iron-containing sludge, which makes the process complicated and uneconomical, and even generates secondary pollution (Ventura et al., 2002; Murray and Parsons, 2004). The heterogeneous Fenton process is a promising alternative that avoids these drawbacks and permits the reuse of catalysts, and has attracted more and more attention. Catalysts are usually prepared in this process by immobilizing iron ions or oxides on supports, which can confer excellent catalyst performance and practicability. Various supports such as mesoporous activated carbon (Karthikeyan et al., 2011), nanoporous activated carbon (Karthikeyan and Sekaran, 2014), activated carbon fibers (Wang et al., 2014a), zeolites (Fukuchi et al., 2014), resin (Shu et al., 2010), and hydrogel (Wang et al., 2014b) have been used to prepare heterogeneous Fenton catalysts in recent years. However, these efficient catalysts have challenges in terms of technical complexity and high cost of production, which limit their full-scale practical application. Therefore, the main concern researchers face is the development of a novel and efficient catalyst with a simple and low-cost production process, which is beneficial to engineering application. On the other hand, an increasing amount of sewage sludge generated by biological wastewater treatment plants has become an issue of particular concern (Wurz et al., 2011), which would result in a serious pollution problem for the environment in case of inappropriate disposal. It is a better option to reuse residual sewage sludge rather than dispose of it. Thus, greater attention has been focused on converting sewage sludge into activated carbon, based on its high content of organic components, using controlled conditions or some chemical treatments, for use as an adsorbent to remove organic pollutants and heavy metals (Smith et al., 2009). Recently, sewage sludge based activated carbon (SBAC) was reported to be an efficient catalyst for catalytic wet air oxidation of phenolic compounds and ozonation of oxalic acid (Marques et al., 2011; Wen et al., 2012). Meanwhile, some previous studies (Tu et al., 2012, 2013) showed that sewage sludge derived carbon could be used as the support for a low-cost, efficient catalyst in Fenton oxidation of Acid Orange II, which was used as a model target pollutant. However, catalysts are usually used to dispose of real industrial or domestic wastewater in practical processes (Wang et al., 2009). To date, no study on using SBAC as the support of a Fenton catalyst for removal of pollutants in real industrial wastewater has been published, or especially, biologically pretreated CGW. Moreover, most research on the heterogeneous Fenton process has focused on the preparation of highly efficient catalysts and finding the optimum operating conditions. Compared to the classic Fenton reaction, the mechanism of the heterogeneous Fenton reaction is still unclear, to some extent, which inhibits the wide application of the heterogeneous Fenton process.

In the current study, ferric oxides were supported on SBAC (designated as FeOx/SBAC) using a simple impregnation method, and the catalytic activity in Fenton oxidation of real biologically pretreated CGW was investigated. Meanwhile, the effects of important operating parameters on the catalytic activity and the biodegradability and toxicity of treated wastewater were evaluated. Furthermore, a possible reaction pathway and mechanism were proposed. The process was demonstrated to be feasible, and the results provide a reference for subsequent engineering application.

1. Materials and methods

1.1. Materials

The sewage sludge was collected from a biological wastewater treatment plant (Harbin, China) using the hybrid processes of enhanced primary treatment with added polymeric ferric aluminous chloride, followed by secondary biological treatment by activated sludge.

Real biologically pretreated CGW was obtained from the effluent of biological treatment after the ammonia-stripping and phenol solvent extraction processes in the full-scale wastewater treatment facility of the Lurgi coal gasification wastewater at China Coal Longhua Harbin Coal Chemical Industry Co., Ltd. The plant had been operating over 3 years. The concentrations of the main pollutants in raw wastewater were as follows: 140–160 mg/L of COD, 0.05–0.07 of BOD_5/COD value, 30–45 mg/L of total phenols (TP), 45–60 mg/L of total organic carbon (TOC), 50–60 mg/L of total nitrogen (TN) and 20–35 mg/L of NH_4^+-N. The pH ranged between 6.5 and 7.5. The average temperature of raw wastewater over 1 year was around 30°C. Hydrogen peroxide (30%, W/W) and all other chemicals used were of analytical grade if not noted otherwise.

1.2. Preparation of catalyst

The preparation of SBAC was according to the method developed by Wen et al. (2012). Briefly, the dewatered sewage sludge was sieved to a uniform size of <0.1 mm. Then, a 10 g sample was impregnated into 75 mL of 3 mol/L $ZnCl_2$ solution as an activation agent (sludge: $ZnCl_2$ = 1:3, by mass) for 24 hr at room temperature. After the supernatant liquid was completely removed, the sample was pyrolyzed in a muffle furnace flushed with high purity N_2 to maintain oxygen-free conditions until the pyrolyzed products cooled to the room temperature. The furnace temperature was gradually increased at a rate of 18°C/min, and the final temperature of 700°C was maintained for 2 hr, which facilitated the formation of micropores and mesopores due to the cracking of the peptidoglycans (Smith et al., 2009). After being pyrolyzed, the products were washed of inorganic impurities with HCl and then the samples were thoroughly washed with Milli-Q water until the pH of the rinse water became constant, and dried.

SBAC-supported ferric oxide was prepared by a simple impregnation technique (Faria et al., 2009). An amount of

SBAC was immersed in ferric nitrate solution with a desired concentration and the suspension was stirred with 200 r/min at 20°C for 24 hr, and then evaporated in a rotary evaporator at 105°C for 12 hr under vacuum. Then the samples were calcined at 600°C for 3 hr in a muffle furnace in the absence of oxygen to obtain the required catalyst. The calcined sample was washed several times with Milli-Q water to remove the loosely bonded iron metal, then dried and stored in a desiccator until use.

1.3. Experimental procedures

All experiments were carried out in a semi-continuous model reactor (effective volume of 1.2 L), made of cylindrical Plexiglas. First, a fixed amount of FeOx/SBAC was added into the reactor followed by input of real biologically pretreated CGW (1 L) with predetermined pH value, and the reaction started after adding a predetermined dosage of H_2O_2 (except for adsorption experiments, with no H_2O_2). The mixture was homogenized by mechanical agitation (150 r/min) and kept at constant temperature (±1°C) with a controlled water bath, and the pH was adjusted with dilute solutions of NaOH or HCl. Meanwhile, samples were taken from the reactor at regular time intervals and filtered using 0.45 μm acetate fiber filters to separate the catalyst particles prior to analysis. NaOH was added to quench the remaining H_2O_2 since it interferes with some of the analytical techniques (except BOD_5 and toxicity analysis). In the adsorption test, without H_2O_2, all other reaction conditions were kept identical.

The acute toxicity of wastewater treated by the catalyst without and with H_2O_2 was assessed by the *Daphnia magna* test following the National Standards of China (GB/T13266-91). *Daphnia* was cultured in laboratory for more than three generations. The treated wastewater was immediately flushed by bubbling with nitrogen gas and heating (50°C) to blow off the residual H_2O_2. An aliquot of wastewater sample (5 mL) was added into each glass beaker (100 mL effective volume) containing 50 mL of synthetic natural water and 10 healthy *Daphnia* neonates. The test beakers were incubated for 48 hr at 20 ± 1°C, and the toxicity was expressed by the immobilization percentage of neonates. The neonates were considered immobile if they remained at the bottom of the test beaker and did not resume swimming within the 15 sec observation period. All toxicity tests were performed in triplicate.

1.4. Analytical methods

Samples were gold-coated and observed under a scanning electron microscope (SEM, HELIOS NanoLab 600i, USA). The specific surface area of catalysts was obtained according to the Brunauer–Emmet–Teller (BET) method from the nitrogen adsorption at liquid nitrogen temperature using a Micromeritics ASAP 2020 system. The micropore volume was calculated by the t-plot method and the macro(meso)pore volume as well as pore diameter were calculated using the Barrett–Joyner–Halenda method. The crystal structure of the catalyst was analyzed by a powder X-ray diffractometer (XRD, RigakuD/max-2000) with monochromatic Cu Kα radiation (45 kV, 50 mA). The ash content of the catalyst was determined by incineration at 850°C and the percentage contents of major elements (excluding C, H, and O) were determined by X-ray fluorescence (XRF) with an X-ray spectrometer (AXIOS-PW4400, Holland). The infrared spectra of treated samples were measured by Fourier transform infrared (FT-IR) spectroscopy (Perkin Elmer Spectrum One B) using the potassium bromide pellet method. The concentration of the dissolved iron in the treated wastewater was analyzed by ICP-AES (Optima 5300DU, Perkin Elmer Inc.). COD, BOD_5, TP and NH_4^+-N were measured according to Standard Methods (APHA, 1998). TOC and TN were determined with a total organic carbon analyzer (TOC-V, Shimadzu Corporation, Japan). The pH values were determined with a pH meter (pHS-3C, Leici, China). All the experiments were repeated three times, and the results were the average of at least three measurements with an accuracy of ±5%.

2. Results and discussion

2.1. Characterization of the prepared FeOx/SBAC

The morphology of the raw sludge and FeOx/SBAC is shown in Fig. 1. Compared to the raw sludge with its dense and smooth surface, there were significant amounts of pores and roughness on FeOx/SBAC, and iron oxides were uniformly distributed on the surface and in the pores of the carbon matrix. The physicochemical properties of SBAC and FeOx/SBAC are listed in Table 1. SBAC exhibits a high specific surface area (S_{BET}, 398.6 m^2/g), the micropore and meso(macro)pore volumes and average pore sizes were 0.141, 0.221 cm^3/g and 3.725 nm, respectively, which illustrated its mesoporous character. It was noteworthy that 14.5% of FeOx (XRF) was loaded on SBAC, resulting in a slight decrease of the S_{BET}, pore volume and average pore size, respectively. This was in good agreement with the fact that iron oxides had been immobilized in the pores of SBAC, leading to a reduction of the surface area. On the other hand, due to the increased amount of mineral matters, there was a higher ash content in FeOx/SBAC than SBAC, and a small amount of Si (2.98%) and Al (1.92%) were found in the bulk of FeOx/SBAC. XRD patterns of FeOx/SBAC showed a wide peak at 23.5° corresponding to the graphite carbon structure (Fig. 1). The diffraction peaks at 30.5°, 35.7°, 44.2°, 53.4° and 62.3° corresponded to the (220), (313), (400), (511), and (440) Bragg diffraction planes of iron(III) oxide (JCPDS, 89-5894) (Karthikeyan et al., 2014), which was assigned the γ-Fe_2O_3 (JCPDS 13-534) or Fe_3O_4 (JCPDS 88-0866). In addition, a previous study had shown that hydroxyl groups constituted the most important functional groups on FeOx/SBAC and pH_{pzc} was 7.6 (Zhuang et al., 2014c).

2.2. Effect of FeOx/SBAC on Fenton oxidation

As shown in Fig. 2, prior to the addition of H_2O_2, only 13.4% of COD was adsorbed on the FeOx/SBAC in 60 min and prolonged adsorption time only slightly increased the removal efficiency (15.4% of COD removal in 120 min). With the addition of H_2O_2, the COD removal efficiency was significantly improved in the raw wastewater (pH around 7). The same removal efficiency with adsorption was reached within only 20 min and 68.3% of COD was removed in 120 min. Hence, it was seen that the increased COD removal efficiency was mainly due to catalytic

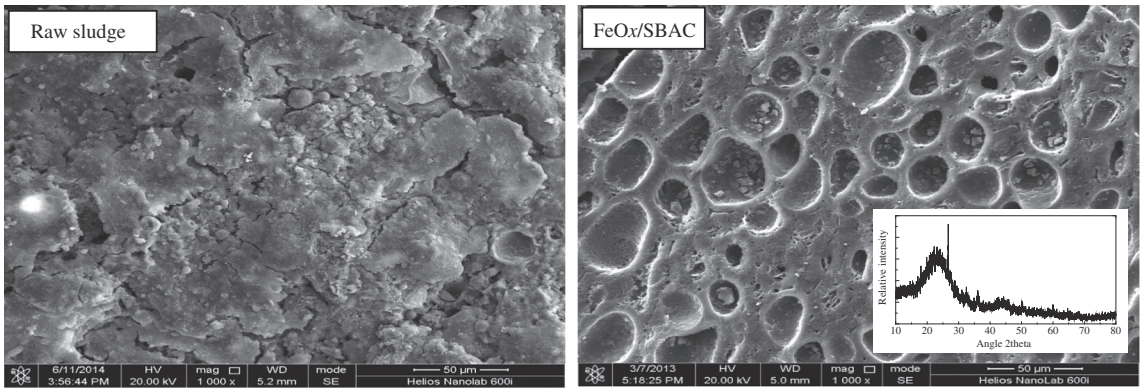

Fig. 1 – Scanning electron microscope of the raw sludge and FeOx/sludge based activated carbon (SBAC) (1000 × magnification; inset, X-ray diffractometer of FeOx/SBAC).

activity *via* Fenton oxidation rather than adsorption by FeOx/SBAC. Meanwhile, only 3.1% of COD was oxidized by H_2O_2 alone after 120 min, indicating the significance of FeOx/SBAC as catalyst in the heterogeneous Fenton reaction. In addition, when Fe_3O_4 powder (around 30 mg/L, close to the Fe oxide content of loaded FeOx/SBAC) was used as a substitute catalyst to catalyze the Fenton reaction, only 22.5% of COD was removed in 120 min. Notably, the COD removal efficiency was improved by 42.7% with simultaneous use of H_2O_2 and FeOx/SBAC in contrast to that using H_2O_2 plus Fe_3O_4, which shows a strong synergistic effect. However, as the dominant refractory compounds (around 47.2% of COD) in raw wastewater, phenolic compounds had a faster degradation rate than total COD in the heterogeneous Fenton process, which was attributed to the fact that phenol and its derivatives have k_{O3} and K_{OH} values of about 1.8×10^6 $(mol/L)^{-1}$ sec^{-1} and 6.1×10^9 $(mol/L)^{-1}$ sec^{-1}, respectively. Fig. 2b shows that approximately 50% of TP was rapidly degraded within 20 min, and more than 90% was degraded with FeOx/SBAC in Fenton oxidation after 120 min. However, only 42% of TP was oxidized by H_2O_2 plus Fe_3O_4 under the same reaction conditions. Meanwhile, TOC removal results showed that 61.3% of pollutants were directly mineralized to carbon dioxide for FeOx/SBAC in Fenton oxidation, while other reactions showed less TOC elimination (Fig. 2c) which could possibly be attributed to the generation of more $^{\cdot}OH$ in the heterogeneous Fenton process. In addition, a previous study (Tu et al., 2012) pointed out that the inorganic components (mainly SiO_2 and Al_2O_3) in the sewage sludge-derived char had co-catalytic effects on the degradation of AOII in a heterogeneous Fenton-like process. However, the current results indicated that the catalytic activity of SBAC was very limited; taking the effect of adsorption of SBAC into account, only a small part of COD (around 5%) was oxidized in 120 min. This difference was attributed to the fact that the catalyst in the previous study had lower specific surface area (less than 20 m^2/g) and higher content of SiO_2 and Al_2O_3 (more than 5.5%, respectively). The results indicated that the stronger catalytic activity of FeOx/SBAC could possibly be attributed to its very large specific surface area (302.5 m^2/g), and adsorption of reactants by a catalyst was recognized as a crucial catalytic factor (Wang et al., 2014a).

2.3. Effects of operating parameters on catalytic activity of FeOx/SBAC

2.3.1. Effect of pH

The Fenton reaction is sensitive to high pH in the solution, which affects the treatment capacity by quickly decomposing H_2O_2 into oxygen without the formation of a significant quantity of $^{\cdot}OH$ (Martins et al., 2010). The effect of initial pH on the removal of pollutants was investigated and the results are shown in Fig. 3a. The results indicated that FeOx/SBAC had remarkable catalytic activity at neutral and basic pH (COD removal efficiency was 72%, 70.5%, 68.4%, 63.7% and 56.4% at pH 2, 3, 5, 7 and 9 in 120 min, respectively). It was demonstrated that the heterogeneous Fenton process with FeOx/SBAC can efficiently remove the refractory pollutants of industrial wastewater over a wide pH range. This might be ascribed to FeOx/SBAC having a huge specific surface area and high pH_{pzc} (7.6), which facilitated the exposure of iron oxides to H_2O_2 at high pH and enhanced the rate of generation of $^{\cdot}OH$, further weakening the effect of solution pH. From an economic point of view, it was an interesting result that the raw wastewater (6.5–7.5) pH was close to the optimal heterogeneous Fenton reaction pH. Thus, the operational costs associated with pH correction could be avoided, and the optimal pH value was raw wastewater pH.

Table 1 – Summary of physicochemical properties of SBAC and FeOx/SBAC.

Sample	S_{BET} (m^2/g)	$V_{meso(macro)}$ (cm^3/g)	V_{micro} (cm^3/g)	Pore size (nm)	Ash (wt.%)	Fe (wt.%)	Si (wt.%)	Al (wt.%)
SBAC	398.6	0.221	0.141	3.725	14.64	0.78	2.49	1.74
FeOx/SBAC	302.5	0.211	0.115	3.325	20.75	14.5	2.98	1.92

S_{BET}, The specific surface area; $V_{meso(macro)}$, meso(macro)pores volumes; V_{micro}, micropore volume.

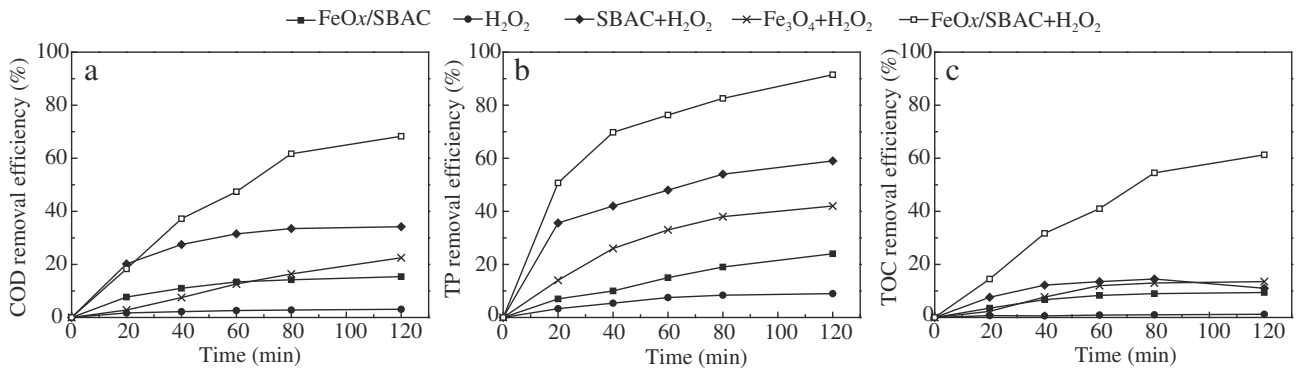

Fig. 2 – Effect of FeOx/SBAC on the pollutant removal performance in the Fenton process, (a) COD removal; (b) TP removal; (c) TOC removal.

2.3.2. Effect of temperature

Fig. 3b depicts the effect of temperature on COD removal efficiency in Fenton oxidation with FeOx/SBAC. In accordance with Arrhenius kinetics, increasing temperature improves the rate of chemical degradation processes. As expected, COD removal was enhanced with increasing temperature in the heterogeneous Fenton process, however the growth rate slowed down noticeably when temperatures exceeded the temperature (30°C). In fact, COD removal only increased by 2.0% when the temperature rose from 30 to 50°C, and even dropped by 4.6% when it further rose to 70°C, which was attributed to the fact that the increasing temperature also accelerated the decomposition of H_2O_2 into useless oxygen and water. Meanwhile, the need to control temperature means more operational costs in real application, therefore the raw wastewater temperature (30°C) was used in the following work.

2.3.3. Effect of FeOx/SBAC dosage

As Fig. 3c shows, the pollutants were hardly removed in the absence of FeOx/SBAC (only 3.1% of COD removal with H_2O_2 alone). The addition of FeOx/SBAC significantly enhanced the pollutant removal performance, acting as a catalyst to accelerate the decomposition of H_2O_2 into reactive radicals. When dosing FeOx/SBAC in the range from 0.0 to 1.0 g/L, the COD removal efficiency increased faster than in the range from 1.0 to 3.0 g/L. The COD removal efficiency at 1.0 g/L of

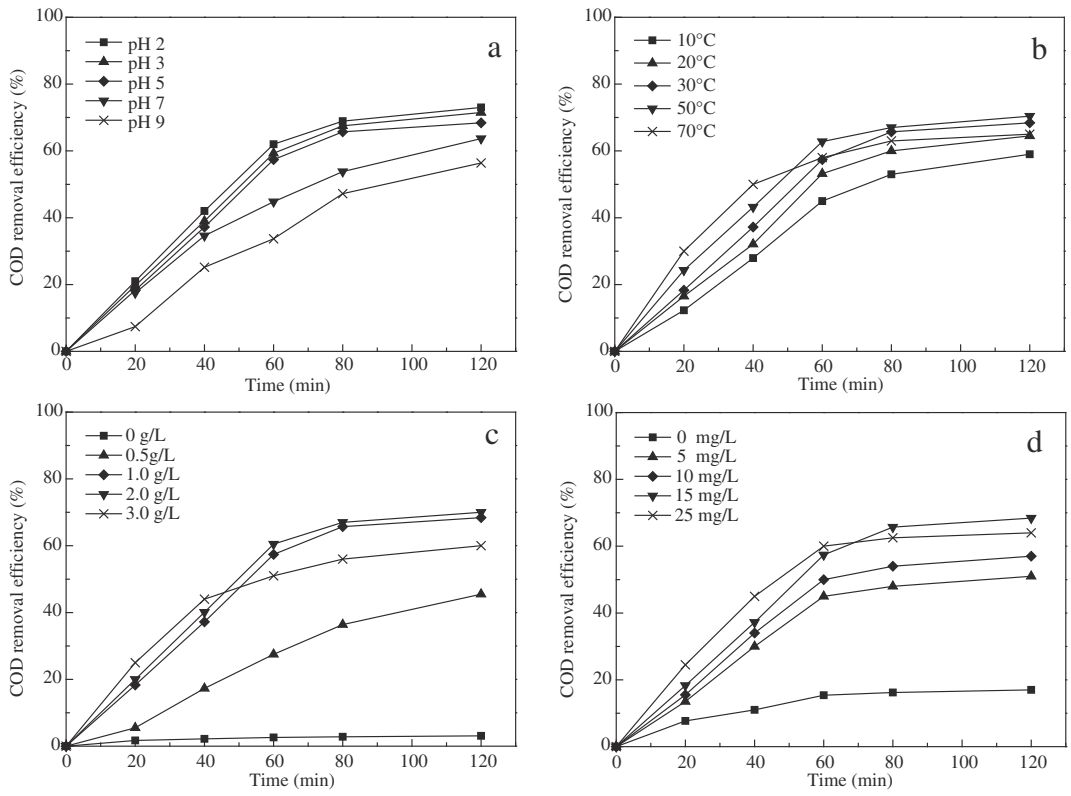

Fig. 3 – Effects of (a) initial pH, (b) temperature, (c) FeOx/SBAC dosage, (d) H_2O_2 dosage on COD removal.

FeOx/SBAC was 65.3% higher than that in H_2O_2 alone. However, no significant differences were observed when the dose of FeOx/SBAC increased from 1.0 to 2.0 g/L, and efficiency even slightly deceased at 3 g/L. Thus, the optimal amount of catalyst of 1.0 g/L was a tradeoff between efficient catalytic activity and cost.

2.3.4. Effect of H_2O_2 dosage

H_2O_2 plays the role of the source of ·OH in the Fenton oxidation process. The effect of different H_2O_2 dosages on COD removal was examined, as shown in Fig. 3d. Only 17% of COD was removed without H_2O_2, indicating that pollutant adsorption onto the FeOx/SBAC was slight. It was noted that initial small concentration increases of H_2O_2 could enhance the COD removal when H_2O_2 dosage was increased to 15 mg/L (68.4% of COD removal); however, when this dosage was exceeded, the removal rate did not increase, and even decreased slightly at 25 mg/L (dropped by 4.4%). This might be caused by the competition of the excessive H_2O_2 for adsorption on the surface of FeOx/SBAC, which limited the pollutant concentration on the catalyst surface. Meanwhile, the excessive H_2O_2 could reduce ·OH as a radical scavenger (Huang et al., 2012). In addition, higher amounts of H_2O_2 can lead to lower utilization efficiency, and the subsequent experiments were performed using 15 mg/L of H_2O_2.

2.4. Biodegradability and toxicity assessment

The real biologically pretreated CGW contains considerable amounts of toxic and inhibitory compounds with low biodegradability (around 0.06 of BOD_5/COD value), which are difficult to break down by microorganisms. A clear biodegradability improvement was observed after Fenton oxidation of the raw wastewater with FeOx/SBAC, as shown in Fig. 4a. With the prolonging of oxidation time, the BOD_5/COD value increased gradually from 0.06 to 0.15 (FeOx/SBAC alone) and 0.43 (FeOx/SBAC with H_2O_2), respectively. No observable biodegradability increase was observed in H_2O_2 alone, indicating that the oxidation by H_2O_2 could be considered negligible. Esplugas et al. (2004) pointed out that effluent could be considered totally biodegradable with BOD_5/COD higher than 0.4. It was evident that only Fenton oxidation with FeOx/SBAC achieved this threshold, which was in agreement with the elimination of more than 60% of TOC (Table 2). In contrast to the rapid COD removal, BOD_5/COD slowly increased in the initial 20 min, which might be due to the formation of intermediates more refractory than the parent compounds. Consequently, these intermediates were efficiently removed and then BOD_5/COD increased by the generation of more ·OH, which is the most powerful oxidant in water. Fig. 4b demonstrates that the acute toxicity was remarkably reduced as the Fenton oxidation proceeded. The toxicity inhibition decreased by 25% and 60% using FeOx/SBAC without and with H_2O_2, respectively, and the corresponding effluent inhibition rates were 50% and 26.7%, which suggested that the highly toxic pollutants were degraded by heterogeneous Fenton oxidation into less toxic or even non-toxic substances. Therefore, it was revealed that properly extended catalytic oxidation could enhance biodegradation, which was beneficial to the performance of the subsequent biological treatment (Zhuang et al., 2014b).

In summary, the heterogeneous Fenton oxidation with FeOx/SBAC significantly improved the pollutant removal performance as advanced treatment of real biologically pretreated CGW. Table 2 shows that the average removal efficiencies of COD, TP and TOC were 68.3%, 95.3% and 60.8%, respectively, and the corresponding effluent concentrations were 47.5, 1.9 and 19.7 mg/L, respectively, which (including BOD_5) all met class-I criteria of the Integrated Wastewater Discharge Standard (GB18918-2002, China). In fact, even NH_4^+-N and TN were also partially removed or transformed, and the NH_4^+-N of the treated wastewater met the class-II criteria of the Integrated Wastewater Discharge Standard.

2.5. Possible reaction pathway and mechanism

In order to further investigate the possible role of ·OH, the effect of a radical scavenger (*tert*-butanol) on TP and TOC removal in the heterogeneous Fenton oxidation process was evaluated. *tert*-Butanol ($K_{OH} = 5 \times 10^8$ $(mol/L)^{-1}$ sec^{-1}) is a strong radical scavenger, as indicated by its higher reaction rate constant with ·OH. *tert*-Butanol reacts with ·OH, generating inert intermediates, causing termination of the radical chain reaction. Thus, *tert*-butanol is a suitable indicator for a radical type reaction. Fig. 5 shows that the presence of

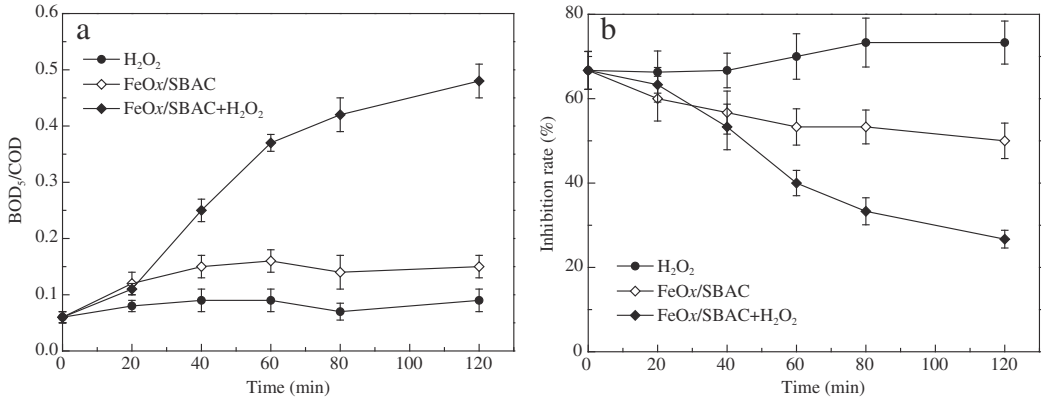

Fig. 4 – Changes of biodegradability and acute toxicity in Fenton oxidation, (a) the biodegradability of the treated wastewater; (b) the acute toxicity of the treated wastewater.

Table 2 – Pollutant evolution in the raw and treated wastewater by FeOx/SBAC without and with H_2O_2. Experimental conditions: initial solution pH: 7, temperature: 30°C, FeOx/SBAC: 1 g/L, H_2O_2: 15 mg/L (if used).

Parameters	Raw wastewater mg/L	Without H_2O_2		With H_2O_2	
		mg/L	%	mg/L	%
COD	150.0 ± 10.5	126.9 ± 10.3	15.4	47.5 ± 3.9	68.3
TOC	50.0 ± 5.8	54.4 ± 3.8	9.4	19.7 ± 2.1	60.8
NO_3^--N	10.8 ± 1.2	9.9 ± 1.5	7.7	19.5 ± 1.4	–
NH_4^+-N	25.5 ± 3.1	19.9 ± 2.7	21.6	10.1 ± 1.2	60.5
TN	55.0 ± 4.7	52.1 ± 4.2	5.4	40.9 ± 4.7	25.7
TP	40.0 ± 5.5	33.7 ± 3.2	15.7	1.9 ± 0.2	95.3
BOD_5	8.7 ± 0.6	–	–	20.3 ± 1.1	–

tert-butanol negatively affected the catalytic activity of FeOx/SBAC in the Fenton process. TP and TOC removal efficiency was decreased from 95.3% and 60.8% without *tert*-butanol to 50.5% and 25.5%, respectively, when 100 mg/L of *tert*-butanol was added. The results indicated that the main reaction pathways of the heterogeneous Fenton process involved the participation of the highly reactive radical $^{\cdot}OH$. It was noteworthy that there was no obvious difference in the reduction of TOC with (12.5%) and without *tert*-butanol (14.5%) in the initial 20 min. This phenomenon might be caused by the generation of $O_2^{\cdot-}/HO_2^{\cdot}$ radicals, which have strong oxidation activity and are not appreciably suppressed by *tert*-butanol. As the oxidation reaction proceeded, and the more highly refractory intermediates were formed, $^{\cdot}OH$ played the key role in the elimination of refractory compounds because it had a stronger effect than $O_2^{\cdot-}/HO_2^{\cdot}$. It can be speculated that FeOx/SBAC could catalyze H_2O_2 to form $^{\cdot}OH$ and $O_2^{\cdot-}/HO_2^{\cdot}$. A possible reaction pathway was proposed (Eqs. (1)–(4)).

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + O_2^{\cdot-}/HO_2^{\cdot} + H^+ \quad (1)$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\cdot}OH + OH^- \quad (2)$$

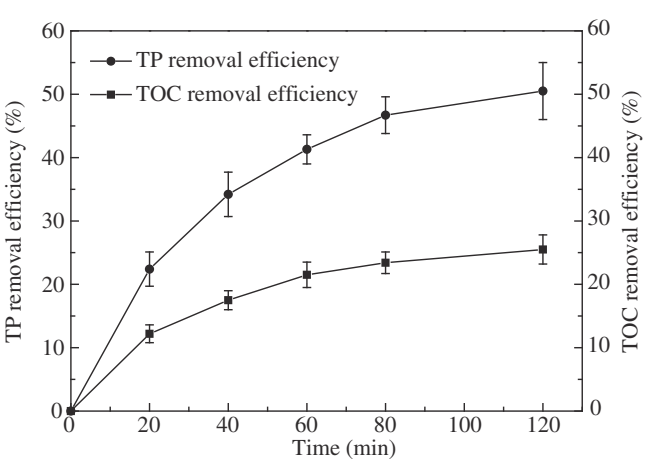

Fig. 5 – Effect of radical scavenger on TP and TOC removal.

$$Fe(III) + 2\,{}^{\cdot}OH \rightarrow Fe(II) + O_2^{\cdot-}/HO_2^{\cdot} + H^+ \quad (3)$$

$${}^{\cdot}OH + H_2O_2 \rightarrow O_2^{\cdot-}/HO_2^{\cdot} + H_2O \quad (4)$$

Meanwhile, the sites where the oxidation took place were still unclear. To evaluate the interfacial mechanism of heterogeneous Fenton oxidation, the evolution of FT-IR spectra of FeOx/SBAC at adsorption saturation without and with H_2O_2 was investigated (Fig. 6). FT-IR spectral analysis showed that FeOx/SBAC after saturated adsorption had some significant trends and peaks: the strong peaks near 3400 cm^{-1} were attributed to phenolic OH groups; an obvious set of peaks emerging in the region from 2800 to 3000 cm^{-1} was attributed to the presence of hydrocarbon chains; peaks around 1600–1700 cm^{-1}, with $\nu(-NO_2)$, and $\nu(C{=}O)$ associated with $\nu(-CONH-)$ *i.e.*, amino groups; the peaks near 900–1100 cm^{-1} were assigned to aliphatic structures having a high level of functional groups rich in oxygen (Zhu et al., 2012); in the lower region of the spectra, the more intense absorption peaks near 500–800 cm^{-1} could be out-of-plane O–H bending, attributed to the presence of substituted aromatics. The results suggested that the characteristics of the peaks and the raw wastewater quality were highly consistent. However, there was no obvious distinction in most wavelength regions between FeOx/SBAC with saturated adsorption and after heterogeneous Fenton oxidation treatment. In contrast to the remarkable removal of pollutants in the Fenton oxidation effluent (Fig. 2, reduction of 60.5% TOC), the results indicated that the surface of FeOx/SBAC generated reactive oxygen species that mainly attacked the unabsorbed organic compounds near the interface region, *i.e.*, the E–R kinetic mechanism.

2.6. Catalytic stability of FeOx/SBAC

Catalyst stability is essential for its industrial application since it has to maintain its activity over long operation times. The reusability of FeOx/SBAC in Fenton oxidation of biologically pretreated CGW was evaluated. Fig. 7 shows that, compared to

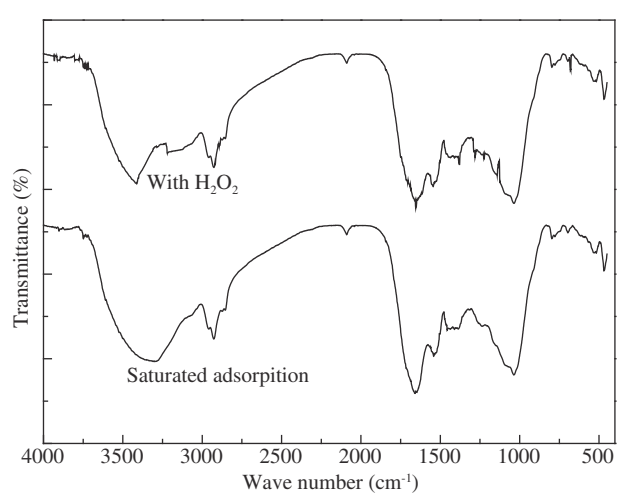

Fig. 6 – Evolution of FT-IR spectra on pollutant-saturated FeOx/SBAC with and without H_2O_2.

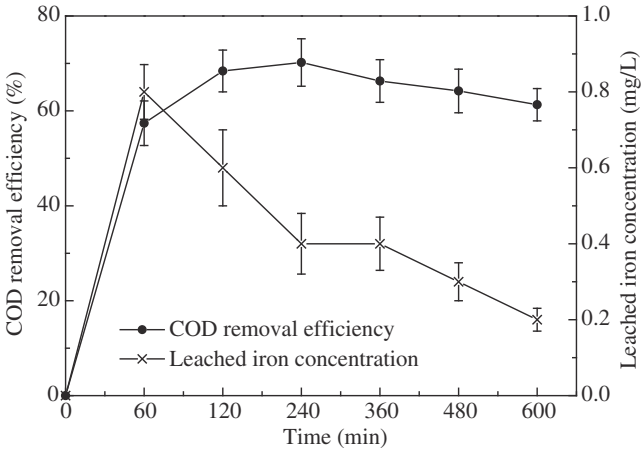

Fig. 7 – Catalytic performance of FeOx/SBAC in successive heterogeneous Fenton oxidation runs.

the activity achieved by fresh catalyst, no remarkable change was observed in activity after successive 600 min runs (5 cycles of reuse), and the COD removal efficiency was only decreased by 7.1%, remaining higher than 61.3% throughout five successive runs. Meanwhile, the stability of the catalyst was also evaluated by measuring the concentration of leached iron ions in aqueous solution during the successive catalytic runs. As Fig. 7 shows, the leaching of iron from the catalyst after every reaction cycle was investigated, and the results showed that the leached iron was 0.8, 0.6, 0.4, 0.3 and 0.2 mg/L, respectively, lower in all cases than the 2 ppm iron in water for the European standard. Meanwhile, the contribution of homogeneous reactions induced by the leached iron at such a level was very slight. Importantly, SBAC was prepared by recycling of residual sewage sludge of biological wastewater treatment. Thus, the results demonstrated that heterogeneous Fenton oxidation with FeOx/SBAC showed efficient and stable pollutant removal performance of advanced treatment of real biologically pretreated CGW, with the advantages of low cost, eco-friendliness and sustainability, facilitating engineering application.

3. Conclusions

Sewage sludge from a biological wastewater treatment plant was converted into SBAC with $ZnCl_2$ as activation agent, and was used as the support for iron oxides to prepare a catalyst to improve the performance of Fenton oxidation of real biologically pretreated CGW. The results indicated that FeOx/SBAC significantly enhanced the pollutant removal performance of the Fenton process, and the treated wastewater was more biodegradable and less toxic than raw wastewater. On the basis of significant inhibition by a radical scavenger in the heterogeneous Fenton process and the evolution of FT-IR spectra of pollutant-saturated FeOx/SBAC without and with H_2O_2, it was deduced that the catalytic activity was responsible for generating hydroxyl radicals, and a possible reaction pathway and interface mechanism were proposed. Moreover, FeOx/SBAC showed superior stability over successive catalytic runs. Thus, this process, with the advantages of being economical, efficient and sustainable, holds promise for engineering application.

Acknowledgments

This work was supported by the State Key Laboratory of Urban Water Resource and Environment (Harbin Institute of Technology) (No.2015DX02).

REFERENCES

An, J.J., Zhu, L.H., Zhang, Y.Y., Tang, H.Q., 2013. Efficient visible light photo-Fenton-like degradation of organic pollutants using in situ surface-modified $BiFeO_3$ as a catalyst. J. Environ. Sci. (China) 25 (6), 1213–1225.

APHA (American Public Health Association), 1998. Standard Methods for the Examination of Water and Wastewater. 20th ed. (Washington DC, USA).

Chakinala, A.G., Bremner, D.H., Gogate, P.R., Namkung, K.C., Burgess, A.E., 2008. Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing. Appl. Catal. B Environ. 78 (1-2), 11–18.

Esplugas, S., Contreras, S., Ollis, D.F., 2004. Engineering aspects of the integration of chemical and biological oxidation: simple mechanistic models for the oxidation treatment. J. Environ. Eng. 130 (9), 967–974.

Faria, P.C.C., Órfão, J.J.M., Pereira, M.F.R., 2009. Activated carbon and ceria catalysts applied to the catalytic ozonation of dyes and textile effluents. Appl. Catal. B Environ. 88 (3-4), 341–350.

Fukuchi, S., Nishimoto, R., Fukushima, M., Zhu, Q.Q., 2014. Effects of reducing agents on the degradation of 2,4,6-tribromophenolin a heterogeneous Fenton-like system with an iron-loaded natural zeolite. Appl. Catal. B Environ. 147, 411–419.

Huang, R.X., Fang, Z.Q., Yan, X.M., Cheng, W., 2012. Heterogeneous sono-Fenton catalytic degradation of bisphenol A by Fe_3O_4 magnetic nanoparticles under neutral condition. Chem. Eng. J. 197, 242–249.

Karthikeyan, S., Sekaran, G., 2014. *In situ* generation of a hydroxyl radical by nanoporous activated carbon derived from rice husk for environmental applications: kinetic and thermodynamic constants. Phys. Chem. Chem. Phys. 16 (9), 3924–3933.

Karthikeyan, S., Titus, A., Gnanamani, A., Mandal, A.B., Sekaran, G., 2011. Treatment of textile wastewater by homogeneous and heterogeneous Fenton oxidation processes. Desalination 281, 438–445.

Karthikeyan, S., Judia Magthalin, C., Mandal, A.B., Sekaran, G., 2014. Controlled synthesis and characterization of electron rich iron(III) oxide doped nanoporous activated carbon for the catalytic oxidation of aqueous ortho phenylene diamine. RSC Adv. 4, 19183–19195.

Marques, R.R.N., Stüber, F., Smith, K.M., Fabregat, A., Bengoa, C., Font, J., et al., 2011. Sewage sludge based catalysts for catalytic wet air oxidation of phenol: preparation, characterization and catalytic performance. Appl. Catal. B Environ. 101 (3-4), 306–316.

Martins, R.C., Amaral-Silva, N., Quinta-Ferreira, R.M., 2010. Ceria based solid catalysts for Fenton's depuration of phenolic wastewaters, biodegradability enhancement and toxicity removal. Appl. Catal. B Environ. 99 (1-2), 135–144.

Murray, C.A., Parsons, S.A., 2004. Advanced oxidation processes: flowsheet options for bulk natural organic matter removal. Water Sci. Technol. Water Supply 4 (4), 113–119.

Shu, H.Y., Chang, M.C., Chen, C.C., Chen, P.E., 2010. Using resin supported nano zero-valent iron particles for decoloration of Acid Blue 113 azo dye solution. J. Hazard. Mater. 184 (1-3), 499–505.

Smith, K.M., Fowler, G.D., Pullket, S., Graham, N.J.D., 2009. Sewage sludge-based adsorbents: a review of their production, properties and use in water treatment applications. Water Res. 43 (10), 2569–2594.

Tu, Y.T., Tian, S.H., Kong, L.J., Xiong, Y., 2012. Co-catalytic effect of sewage sludge-derived char as the support of Fenton-like catalyst. Chem. Eng. J. 185–186, 44–51.

Tu, Y.T., Xiong, Y., Descorme, C., Kong, Y., Tian, S.H., 2013. Heterogeneous photo-Fenton oxidation of Acid Orange II over iron–sewage sludge derived carbon under visible irradiation. J. Chem. Technol. Biotechnol. 89 (4), 544–551.

Ventura, A., Jacquet, G., Bermond, A., Camel, V., 2002. Electrochemical generation of the Fenton's reagent: application to atrazine degradation. Water Res. 36 (14), 3517–3522.

Wang, W., Han, H.J., 2012. Recovery strategies for tackling the impact of phenolic compounds in a UASB reactor treating coal gasification wastewater. Bioresour. Technol. 103 (1), 95–100.

Wang, J.B., Zhou, Y.R., Zhu, W.P., He, X.W., 2009. Catalytic ozonation of dimethyl phthalate and chlorination disinfection by-product precursors over Ru/AC. J. Hazard. Mater. 166 (1), 502–507.

Wang, W., Han, H.J., Yuan, M., Li, H.Q., Fang, F., Wang, K., 2011. Treatment of coal gasification wastewater by a two-continuous UASB system with step-feed for COD and phenols removal. Bioresour. Technol. 102 (9), 5454–5460.

Wang, L., Yao, Y.Y., Zhang, Z.H., Sun, L.J., Lu, W.Y., Chen, W.X., et al., 2014a. Activated carbon fibers as an excellent partner of Fenton catalyst for dyes decolorization by combination of adsorption and oxidation. Chem. Eng. J. 251, 348–354.

Wang, W., Liu, Y., Li, T.L., Zhou, M.H., 2014b. Heterogeneous Fenton catalytic degradation of phenol based on controlled release of magnetic nanoparticles. Chem. Eng. J. 242, 1–9.

Wen, G., Pan, Z.H., Ma, J., Liu, Z.Q., Zhao, L., Li, J.J., 2012. Reuse of sewage sludge as a catalyst in ozonation—efficiency for the removal of oxalic acid and the control of bromate formation. J. Hazard. Mater. 239–240, 381–388.

Wurz, A., Kuchta, K., Onay, T.T., 2011. Review on municipal sewage sludge management in Turkey and Europe. Int. J. Global Warm. 3 (1-2), 116–128.

Zhu, L., Qi, H.Y., Lü, M.L., Kong, Y., Yu, Y.W., Xu, X.Y., 2012. Component analysis of extracellular polymeric substances (EPS) during aerobic sludge granulation using FTIR and 3D-EEM technologies. Bioresour. Technol. 124, 455–459.

Zhuang, H.F., Han, H.J., Jia, S.Y., Zhao, Q., Hou, B.L., 2014a. Advanced treatment of biologically pretreated coal gasification wastewater using a novel anoxic moving bed biofilm reactor (ANMBBR)-biological aerated filter (BAF) system. Bioresour. Technol. 157, 223–230.

Zhuang, H.F., Han, H.J., Jia, S.Y., Hou, B.L., Zhao, Q., 2014b. Advanced treatment of biologically pretreated coal gasification wastewater by a novel integration of heterogeneous catalytic ozonation and biological process. Bioresour. Technol. 166, 592–595.

Zhuang, H.F., Han, H.J., Hou, B.L., Jia, S.Y., Zhao, Q., 2014c. Heterogeneous catalytic ozonation of biologically pretreated Lurgi coal gasification wastewater using sewage sludge based activated carbon supported manganese and ferric oxides as catalysts. Bioresour. Technol. 166, 178–186.