Coal cinder filtration as pretreatment with biological processes to treat pharmaceutical wastewater

Wei Zheng, Xiao-ming Li, Zhi-ming Hao, Dong-bo Wang, Qi Yang and Guang-ming Zeng

ABSTRACT

This study aims at coupling coal cinder filter with biological process to improve pharmaceutical wastewater quality and reduce the disposal cost. In the coal cinder filter, the removal efficiencies of COD, BOD_5, SS and color were 90 ± 2%, 72 ± 2%, 95 ± 2% and 80 ± 2%, respectively. The results attribute to the big specific surface area and strong adsorption ability. Coal cinder filter removes a large portion of the pollutants in the influent wastewater, which would strongly stable the effluent waste water quality, and reduce the load of follow-up biological treatment process. The average removal efficiencies for COD, BOD_5, SS and color of the combined process were about 99.7 ± 3%, 98.2 ± 4%, 98.5 ± 3% and 96.3 ± 2%, respectively, with the average effluent quality of COD 16 ± 1 mg/L, BOD_5 11 ± 1 mg/L, SS 10 ± 0.6 mg/L and color 22 ± 1 (multiple), which are consistent with the national requirements of the waste pollutants for pharmaceutical industry of chinese traditional medicine discharge standard (GB 21906-2008). The results indicated that the combined procedure could offer an attractive solution for pharmaceutical wastewater treatment with considerable low cost.

Key words | activated sludge, adsorption, coal cinder, filtration, pharmaceutical wastewater

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INTRODUCTION

The existence of pharmaceutical substances in the aquatic environment and their possible effects on living organisms are a growing concern (Heberer 2002). The treatment of pharmaceutical wastewater to the desired effluent standards has always been difficult due to the wide variety of the products that are produced in a drug manufacturing plant. Variable wastewater composition and fluctuations in pollutant concentrations cannot be treated by conventional treatment plants (Carballa *et al.* 2004). Activated sludge process is a well-known process for removing various organic contaminants and organic carbon. However, the properties of pharmaceutical wastewater make it hard to be effectively eliminated by traditional biological treatment (Ternes 1998; Castiglioni *et al.* 2006). As a result, alternative treatment processes before and/or after biological treatment seem promising and even critical where pollution is present or anticipated. So, many researchers have been done a large number of investigations on advanced oxidation processes (Balcıoğlu & őtker 2003; Cokgor *et al.* 2004; Tekin *et al.* 2006; Badawy *et al.* 2009; Benitez *et al.* 2009; Yang *et al.* 2009*a,b*; Zhao *et al.* 2009) and adsorption (Ternes *et al.* 2002; Urase & Kikuta 2005; Westerhoff *et al.* 2005; Bui & Choi 2009) for the treatment of pharmaceutical wastewater. Activated carbons are widely used because of

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their high adsorption abilities (Zhou *et al.* 2005; Yu *et al.* 2008; Reddinga *et al.* 2009). However, the price of activated carbons is relatively high, which may limit their usage. This has led many researchers to search for lower cost materials such as coal cinder (Yang *et al.* 2009), fly ash (Gupta *et al.* 2002, 2003; Gupta & Ali 2004), alga (Gupta *et al.* 2006; Gupta & Rastogi 2008, 2009), eggshell waste (Zheng *et al.* 2007; Liao *et al.* 2010) and agricultural wastes (Li *et al.* 2008; Zheng *et al.* 2008).

Coal cinder is an inorganic waste produced in coal combustion. It is a relatively coarse, gritty material and has a particle size generally within the range of 0.1–10 mm. Cinder contains much SiO_2, Al_2O_3, which is porous non-crystalline material. It can also be used to immobilize cells or as filter media for advanced wastewater treatment because of the high specific surface (Yang *et al.* 2009*a*,*b*). Moreover, converter slag and coal cinder are staple solid wastes in China and their utilization is also making sense to waste reuse. Therefore, the main objective of this work was to test the feasibility of coal cinder filtration with biological processes to treat pharmaceutical wastewater and give the reference to the practice.

MATERIALS AND METHODS

Characteristics of cinder

The coal cinder was obtained from the boiler house of Hunan University, and the particle size was between 4 and 15 mm. The property and composition of coal cinder was presented in Table 1. Si-, Al-, Fe- and Ca-oxides constituted 48, 34.5, 7.8 and 4.7% of the coal cinder, respectively (Table 1).

Table 1 | Property and composition of the coal cinder

Property and composition	Cinder
Al_2O_3 (%)	34.5
SiO_2 (%)	48
Fe_2O_3 (%)	7.8
CaO (%)	4.7
MgO (%)	0.3
C (%)	4.7
Porosity (%)	65
Specific surface area (cm^2/kg)	2,500–4,000
pH	8.2
Particle size (mm)	4–15

Experimental setup and operation

Figure 1 shows the process constructed to treat wastewater from a pharmaceutical company. The sewage sludge was was obtained from the secondary sedimentation tank of the second municipal wastewater treatment plant in Changsha, China. The initial concentrations of seed sludge were established to be approximately 3,500 and 2,400 mg-MLSSL/L in the hydrolysis-acidification tank and biological contact oxidation tank. An acclimatization period of 2 months was imposed for both systems to obtain a steady state operation. Then, both hydrolysis-acidification tank and biological contact oxidation tank were operated directly at room temperature. The company is located at Wuhan city, Hubei province. Discharged pharmaceutical wastewater was transferred to coal cinder yard using pump. The filtered wastewater was delivered through pipeline to collecting well pass through bar rack. The hydraulic retention time (HRT) was kept at 8 h in hydrolysis-acidification tank and biological contact oxidation tank. The main functions and design parameters for each unit were described as following:

- Collecting well: The collecting well has dimensions of 2.5 m × 2 m × 4 m, holding approximately 20 m^3 of working volume and 0.5 h of average HRT.
- Grit chamber: Because the effluent of coal cinder filter exists a certain amount of grit, which should be removed by grit chamber before biological process. The collecting well has dimensions of 6 m × 3 m × 1.5 m, holding 24 m^3 of working volume and 0.6 h of average HRT.
- Hydrolysis-acidification tank: The hydrolysis-acidification tank has dimensions of 15 m × 5 m × 4 m, with average HRT of about 8 h, hanging elastic semi soft packing, with strand silk diameter 0.35 mm and specific surface area 200 m^2/m^3, were filled as microorganism carriers in the tank. its main operational parameters are: a sludge retention time (SRT) of 8 d and an average organic loading rate (OLR) of 3.5 kg COD/(m^3 d). The sludge age was 18 d.

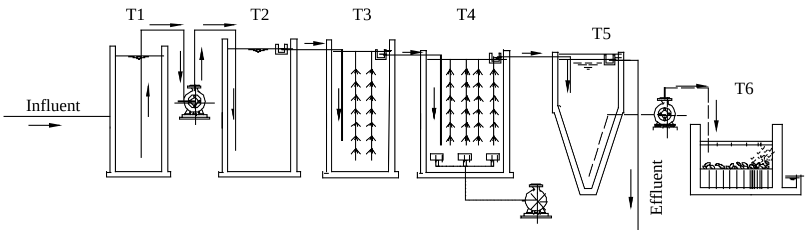

Figure 1 | Schematic diagram of experimental set-up. T1: collecting well; T2: grit chamber; T3: hydrolysis-acidification tank; T4: biological contact oxidation tank; T5: Secondary sedimentation tank; T6: sludge drying bed.

- Biological contact oxidation tank: The biological contact oxidation tank was divided into three cells, each having dimensions of 5 m × 5 m × 4 m, with average 2.7 h. The average organic loading rate (OLR) of 2 kg $BOD_5/(m^3\ d)$.
- Secondary sedimentation: The secondary sedimentation tank has dimensions of 10 m × 2.5 m × 2 m, with average HRT of about 1.5 h.
- Sludge drying bed: The excess sludge was transferred to sludge drying bed. The sludge drying bed has dimensions of 10 × 4 m.

Wastewater characteristics

The wastewater was mainly generated from the processes of product manufacturing and equipment cleaning, containing a variety of organic and inorganic constituents, such as spent solvents, catalysts, reactants and a small amount of intermediates or products. The characteristics of the pharmaceutical wastewater and discharge standard are showed in Tables 2 and 3. The COD of the wastewater was quite high, nitrogen and phosphorus concentrations (not shown) were not adequate for biological treatment. Hence, NH_4Cl and KH_2PO_4 were added to obtain COD/N/P ratio as 100/5/2.

Table 2 | Characteristics of the pharmaceutical wastewater

Characteristic items	Concentration	Mean
COD (mg/L)	4,000–6,000	5,200
SCOD (mg/L)	2,800–5,100	4,500
BOD_5 (mg/L)	300–1,500	600
SS (mg/L)	600–700	660
Color (multiple)	550–700	600
pH	6.5–8	7.1
Temperature (°C)	19–25	22

Control and monitoring

DO, pH and flow rates were recorded daily using the in-line controllers. Dissolved oxygen (DO) was monitored with electrochemical probe method (JPB-607, Shanghai) and maintained higher than 2.0 mg/L in the biological contact oxidation tank. The influent and effluent of each tank were sampled one time per day, except BOD_5 (one time per two days).

Chemicals and analysis

All chemicals used were of AR grade, and water for all solutions preparation had been treated by purification system beforehand. Reagents used in the work were purchased from Damao Chemical Reagent Co., Ltd., China, including $K_2Cr_2O_7$, H_2SO_4, NaOH, NH_4Cl and KH_2PO_4. Chemical Oxygen Demand (COD) was determined by using microwave assisted potassium dichromate ($K_2Cr_2O_7$) oxidation method (Dharmadhikari *et al.* 2005). Soluble Chemical Oxygen Demand (SCOD) was measured after centrifugation (4,000 rmp). A WTW OxyTop system (WTW, Germany) was used for determine the quantities of oxygen consumed in the 5th day in various mixtures (from 10 to 90%) at neutral pH, at 20°C (Achak *et al.* 2009). The Suspended Solid (SS) was measured according to

Table 3 | Discharge standard of waste pollutants for pharmaceutical industry chinese traditional medicine

Characteristic items	Concentration
COD	100 (mg/L)
BOD_5	20 (mg/L)
SS	50 (mg/L)
Color	50 (multiple)
pH	6–9

standard method (APHA 1995). The color of wastewater was determined with standard dilution multiple method (Wei 2002). pH were determined according to a Multiline 330i phmeter which was standardized using buffer solutions of different pH values (4.01, 7.00, 10.00). The coal cinder had a surface area of 2,500–4,000 (cm^2/kg), which were determined by low temperature nitrogen absorption using a Micrometrics ASAP 2000 Surface Area Analyser (School Natural Resources). The particle size analysis was carried out using standard sieves. All the respirometric data presented in this work corresponds to the arithmetic average of the results derived from two repeated experiments. The reproducibility of the results and the match (within 8%) between successive experiments was excellent.

RESULTS AND DISCUSSION

Performance of coal cinder filtration

Figure 2 shows the variations of COD, BOD_5, SS and color by coal cinder filtration. SS and COD effluent was remarkably stable and with a highest removal efficiency of 95 ± 2% and 90 ± 2%, respectively. The color and BOD_5 were also stable and with a removal efficiency of 80 ± 2% and 72 ± 2%, respectively. The ratios of SCOD/TCOD increased from 0.86 to 0.94. The results attribute to the bigger specific surface area and stronger adsorption ability (Yang *et al.* 2009*a*,*b*). Coal cinder filter decreases the influent wastewater pollutants greatly, which strongly stable the effluent wastewater quality, and reduce the load of follow-up biological treatment process. The COD, BOD_5, SS and color after flush cinder were 500 ± 28 mg/L, 180 ± 8 mg/L, 70 ± 4 mg/L and 65 ± 3 (multiple), respectively.

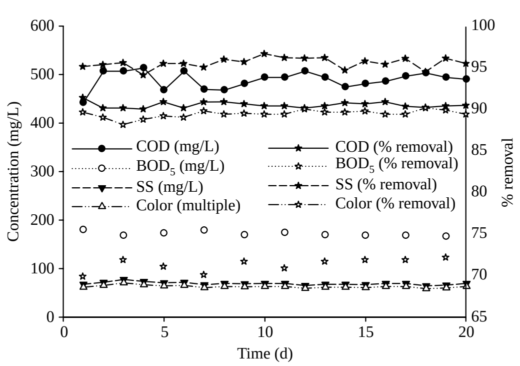

Figure 2 | Variations of COD, BOD_5, SS, color by coal cinder filtration. Experimental conditions: Influent wastewater: COD, BOD_5, SS and color were 4,200–4,500 mg/L, 600–630 mg/L, 650–680 mg/L and 600–620 (multiple); temperature: room temperature; Hydraulic retention time: 1–1.5 h.

High surface area contributed to its close packing in columns thereby serving as primary barriers to solids in the aqueous medium. This reduction can be also explained by shifting of SS on the level of filter in spite of the high content of the pharmaceutical wastewater of SS. Adsorption was the main mechanism to color in coal cinder filter. Biological growth within the filter medium will reduce the organic in the wastewater.

Performance of hydrolysis-acidification tank

Because the pollutants in the effluent are generally refractory compounds which are very difficult to deal with by ordinary activated sludge method, it is thus expected that anaerobic hydrolysis acidification process would be an effective pretreatment for aerobic treatment of refractory wastewater. The hydrolysis acidification process in the present work was: (1) to improve the biodegradability of the wastewater; (2) to destroy the chromophoric groups by removing its chroma; (3) to act as a buffer for the influent load fluctuation.

The hydrolysis-acidification process in the present work was expected to reduce partially the refractory substance in the wastewater, and to destroy the chromophoric groups in the pharaceutical wastewater, thus to offer beneficial conditions for the subsequent biological oxidation. Figure 3 shows the behavior of the main variables of the process in hydrolysis acidification tank. It can be seen from Figure 3, the concentration of BOD_5 increased with time, due to partial persistent pollutants transformed into readily biodegradable substances. The ratios of BOD_5/COD increased from 0.35 to 0.72. The main removal mechanism of the color is indicated to be adsorption (Sahinkaya *et al.* 2008; Wang *et al.* 2008). It can be seen that after the hydrolysis-acidification process, the COD, BOD_5, SS and color in pharmaceutical wastewater were reduced to 195 ± 5% mg/L, 140 ± 3% mg/L, 22 ± 5% mg/L and 43 ± 5% (multiple), respectively.

Performance of biological contact oxidation tank

Because the concentration of influent is very low, so the wastewater was fed without dilution. The COD loading rate

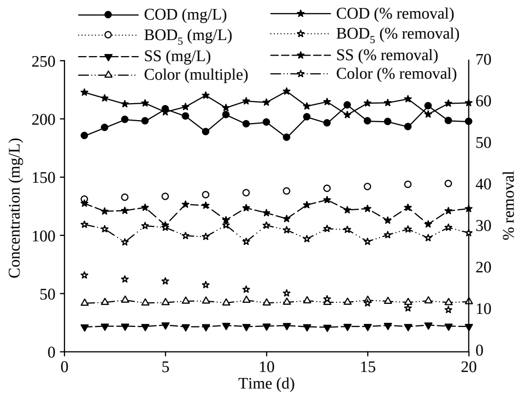

Figure 3 | Variations of COD, BOD_5, SS, color in hydrolysis-acidification tank. Experimental conditions: Influent wastewater: COD, BOD_5, SS and color were 420–440 mg/L, 160–180 mg/L, 60–70 mg/L and 60–70 (multiple); temperature: room temperature; Hydraulic retention time: 8 h.

at steady-state operation was 0.5 mg COD/mg MLVSS d. It can be seen from Figure 4, the effluent COD, BOD_5, SS concentration and color (multiple) averaged 18 ± 4 mg/L, 11 ± 4 mg/L, 10 ± 1 mg/L and 23 ± 1 corresponding to 91 ± 2%, 95 ± 1%, 51 ± 5% and 44 ± 5% removal, respectively. The pollutants were degraded by biomembrane of filled packing in biological contact oxidation tank, and microbes of biomembrane took in organic matter in wastewater for nourishment by contact with the wastewater. In our study, we have directly used biological contact oxidation tank in which HRT was 2.7 h. One of the reasons of obtaining high COD and BOD_5 removal efficiencies was the influent concentration was low. The color removal efficiency is not so effective and the main removal mechanism is indicated to be adsorption. The aerobic biological COD removal is a process where part of the substrate is directly used for biomass growth and the rest is oxidised for energy production.

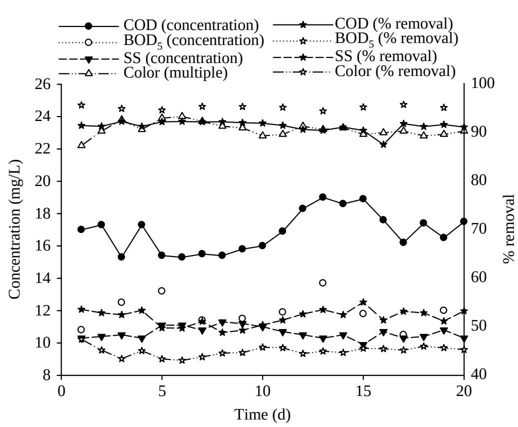

Figure 4 | Variations of COD, BOD_5, SS, color in biological contact oxidation tank. Experimental conditions: Influent wastewater: COD, BOD_5, SS and color were 180–210 mg/L, 130–140 mg/L, 20–23 mg/L and 40–44 (multiple); temperature: room temperature; Hydraulic retention time: 2.7 h.

CONCLUSIONS

A combined coal cinder filter with biological treatment process on a full-scale of 800 t/d was studied and the performance of the system was measured. The results showed that the average removal efficiencies of COD, BOD_5, SS and color were 90 ± 2%, 72 ± 2%, 95 ± 2% and 80 ± 2%, respectively, with the average effluent quality of COD 16 ± 1 mg/L, BOD_5 11 ± 1 mg/L, SS 10 ± 0.6 mg/L and color 22 ± 1 (multiple). The results shows that adsorption on coal cinder filter showed an important potential to remove COD, BOD_5, SS and color were 90 ± 2%, 72 ± 2%, 95 ± 2% and 80 ± 2%, respectively. The effluent quality was better than the requirement of the standards for pharmaceutical wastewater discharge in China. The results indicated that the combined procedure could offer an attractive solution for pharmaceutical wastewater treatment with considerable low cost.

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