



Improvement of biodegradability for coking wastewater by selective adsorption of hydrophobic organic pollutants



Xubiao Yu^{a,b,c,*}, Chaohai Wei^b, Haizhen Wu^d, Zhengming Jiang^b, Ronghua Xu^b

^a Faculty of Architectural, Civil Engineering and Environment, Ningbo University, Ningbo 315211, PR China

^b The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, PR China

^c The Belle W. Baruch Institute of Coastal Ecology and Forest Science, Clemson University, Georgetown 29440, USA

^d School of Bioscience and Bioengineering, South China University of Technology, Guangzhou, Guangdong 510006, PR China

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ABSTRACT

As a typical industrial wastewater, coking wastewater is characterized as high organic load, complicated composition and strong biological inhibition. Based on the analysis between organic composition and toxicity contribution of coking wastewater, a selective removal for targeting hydrophobic contaminants was conducted by organic modified acid-vermiculites (Chlorotrimethylsilane modification, CTMS-V; and Chlorotriethylsilane modification, CTES-V), powdered activated carbon (PAC) and XAD-16 polymer adsorbent. Binary solution containing hydrophilic (phenol) and hydrophobic (diethyl phthalate, DEP) compounds was employed to evaluate the performance of selective adsorption then coking wastewater was further tested. Results of binary adsorption indicated that the average adsorption percentages of DEP for PAC, XAD-16, CTMS-V and CTES-V were $32.6 \pm 11.1\%$, $50.8 \pm 17.4\%$, $68.7 \pm 22.6\%$, $75.5 \pm 27.4\%$ (mean \pm standard deviation, $n = 5$) at varying phenol:DEP ratios (10–100, mol:mol). Coking wastewater treated by PAC, XAD-16, CTMS-V and CTES-V had a decrease of chemical oxygen demand (COD) at $24.6 \pm 3.0\%$, $11.3 \pm 1.5\%$, $4.4 \pm 0.08\%$ and $6.8 \pm 1.1\%$. For biochemical oxygen demand (BOD₅), PAC and XAD-16 gave a decrease of $47.5 \pm 5.6\%$ and $7.8 \pm 1.4\%$, whereas CTMS-V and CTES-V gave an increase of $36.7 \pm 4.1\%$ and $57.2 \pm 4.6\%$, respectively. The resulting BOD₅:COD were 0.21 ± 0.03 , 0.31 ± 0.04 , 0.42 ± 0.05 and 0.50 ± 0.05 after treatment by PAC, XAD-16, CTMS-V and CTES-V, respectively. Post incubation of treated coking wastewater showed that the residual TOC after ten-day incubation were $73.1 \pm 1.5\%$, $77.9 \pm 3.5\%$, $73.2 \pm 3.7\%$ and $59.2 \pm 3.0\%$ for PAC, XAD-16, CTMS-V and CTES-V, respectively. The non- π functional surface (i.e., $-\text{CH}_3$ and $-\text{CH}_2\text{CH}_3$) of modified acid-vermiculites played a critical role for capturing hydrophobic compounds from the solution with high concentration of hydrophilic competitive compounds.

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1. Introduction

Coking wastewater is generated in the process of coke making, especially the destructive distillation of coal under temperatures around 1000–1100 °C without oxygen. Due to the pyrolysis of coal, complicated composition of aromatic compounds such as phenols [1], amines [2], polycyclic aromatic hydrocarbons (PAHs) [3] and heterocyclic compounds [4] are generated as by-products and released to the water of coke quenching and gas washing. Coking wastewater is characterized as high organic load, complicated composition [5], strong bio-inhibition [6] and genotoxicity [7] for traditional biological treatment. The refractory contaminants such as PAHs and heterocyclic compounds have significant toxic and inhibitory effects on microbial activity such as anaerobic [8] and

nitrification [6] processes, thus coking wastewater was commonly reported with a low biodegradability (BOD₅:COD < 0.3) [9]. The traditional industrial wastewater treatment, i.e., physicochemical pretreatment followed by activated sludge, encountered a series of challenges, e.g., long HRT, difficulty of sludge acclimation, weak resistance to impact load and high construction cost, for eliminating the hazardous compounds from coking wastewater. Many strengthening techniques were developed to overcome this problem. Enhanced biological treatments include zeolite-biological aerated [4,10], thermophilic anaerobic digestion [11] and biofilm systems [12], etc. The physicochemical improvements include supercritical water oxidation [13], electrochemical degradation [14], Fenton oxidation [5] and adsorption [15]. In addition, techniques combined with biological and physicochemical treatment were also studied [16,17].

The characteristics of coking wastewater, especially the chemical composition, should be fully considered before developing enhanced techniques. It has been reported that the

* Corresponding author at: Faculty of Architectural, Civil Engineering and Environment, Ningbo University, Ningbo 315211, PR China.

E-mail address: xubiao@clmson.edu (X. Yu).

easy-biodegradable contaminants such as phenols and amines account for the major part of coking wastewater, whereas the hydrophobic bio-inhibitory contaminants such PAHs, pyridine and indole only account for a minor part of total organic compounds [18]. Generally, phenols account for about 80% of the total COD amount in coking wastewater [18,19]. Song et al. analyzed coking wastewater from six coking plants [20]. Results showed that the sum of concentration of phenols and anilines was $23.8 \pm 3.0 \text{ mg L}^{-1}$, but the sum of 16 PAHs's concentration was $0.66 \pm 0.10 \text{ mg L}^{-1}$. Our previous analysis of coking wastewater showed that the concentration of phenols was $178.5 \pm 15.2 \text{ mg L}^{-1}$ [1], but the total amount of 18 PAHs (identified by US EPA) was in the range of 98.5 ± 8.9 – $216.0 \pm 20.2 \text{ } \mu\text{g/L}$ [21]. However, even though the amount of hydrophobic contaminants is much lower than that of hydrophilic compounds, their toxicity and inhibition for biodegradation were significantly higher.

Adsorption is a quick and simple technique that has been widely used for pretreating industrial wastewater and polishing the biological effluent [22,23]. For coking wastewater, adsorbents such as activated carbon [2], activated coke [15] and bottom ash [24] have been studied. Most of these adsorbents were evaluated by the adsorption capacity for COD or TOC, but little emphasis has been put on the removal of critical toxic compounds and the improvement of biodegradability. For example, adsorption of organic compounds by carbonaceous adsorbents was driven by the π - π electron donor-acceptor (EDA) mechanism [25,26], thus it is difficult to employ them to remove hydrophobic aromatic pollutants with the competition of hydrophilic aromatic compounds. Ren et al. studied the competitive adsorption of phenol, aniline and *n*-heptane from tailrace coking wastewater [2]. Their results demonstrated that the hydrophobic compound (*n*-heptane) has a weak affinity toward activated carbon with the competition of hydrophilic compounds (phenol and aniline). Recent studies reported that the hydrophobic compounds such as PAHs had a strong affinity to the suspended microbial particles. Burmistrz and Burmistrz [27] investigated the fate of 16 PAHs and results indicated that 70% of PAHs in raw coking wastewater were adsorbed by suspended solid during biological treatment. Results of Zhang et al. [3] showed that 56–76% removal of high molecular weight PAHs was contributed by adsorption of sludge. Therefore, a hydrophobic adsorbent without the π - π EDA mechanism could be effective for this task.

In this study, the hypothesis of improving biodegradability of coking wastewater by targeted removal of hydrophobic components was examined by different adsorbents. Non- π hydrophobic adsorbents modified by acid-vermiculite were used to selectively remove hydrophobic compounds. For comparison, powdered activated carbon (PAC), a widely used adsorbent in coking wastewater treatment, was selected as a representative of π functional adsorbents. The XAD-16 polymer adsorbent containing both the π and non- π functional group was also tested for detecting the mechanism involved in selective adsorption of hydrophobic compounds. Binary adsorption of phenol (hydrophilic) and diethyl phthalate (hydrophobic) was conducted to evaluate the capability of hydrophobic-targeted adsorption. Finally, coking wastewater was treated with different adsorbents and its biodegradability after treatment was investigated.

2. Materials and methods

2.1. Materials

In this study, the natural vermiculite used for preparing clay-based adsorbents was provided by DingSheng Mining Co. LTD from Shijiazhuang, China. The chemical composition of this clay obtained by X-ray fluorescence (XRF) was 39.95% SiO_2 , 16.36%

Al_2O_3 , 16.77% Fe_2O_3 , 9.19% MgO , 5.24% K_2O , 1.28% CaO , 1.76% TiO_2 , 0.14% Na_2O , 0.20% MnO , 0.05% Cl , and 8.70% loss ignition. The powdered activated carbon (PAC) was supplied by Xinhua Activated Carbon Co. LTD, Shanxi Province, China. The parameters of PAC provided by the supplier are as follows: specific surface area: $1100 \text{ m}^2/\text{g}$; iodine adsorb: $>1000 \text{ mg/g}$; average particle size: $\sim 60 \text{ } \mu\text{m}$; ash content: $<5\%$. The Amberlite XAD-16 hydrophobic polymer resin was purchased from Sigma-Aldrich (USA) and the porous parameters provided by the supplier are as follows: specific surface area: $900 \text{ m}^2/\text{g}$; average pore diameter: 10 nm ; total pore volume: 1.82 mL/g .

The organic modifier for acid-vermiculite: Chlorotrimethylsilane (CTMS, CAS: 75-77-4) and Chlorotriethylsilane (CTES, CAS: 994-30-9) were purchased from Aladdin-Reagent Co. (China); Phenol ($\log K_{OW}$: 1.50, CAS: 108-95-2) and diethyl phthalate (DEP, $\log K_{OW}$: 2.47, CAS: 84-66-2) were used as the representatives of hydrophilic and hydrophobic compounds, which were purchased from Sigma-Aldrich Co. (USA). Deionized water ($>18.0 \text{ M}\Omega$) used in the experiment was produced by Milli-Q pure water system (USA).

2.2. Coking wastewater

Coking wastewater tested in this study was collected from the wastewater treatment plant (WWTP) of Shaoguan Steel Company, located in Guangdong province of China. The company's affiliated coking plant has a coke production capability of 1.32 million metric tons per year and generates about 2000 m^3 coking wastewater per hour. The biological treatment of the WWTP was designed as an anoxic-oxic-hydrolytic-oxic (A/O/H/O) system coupled with biological fluidized bed. Physicochemical pretreatments (i.e., air-floatation for oil removal, ferrous precipitation for cyanide and sulfide removal) and post-treatment (i.e., coagulation for suspended microbial products) were also employed for enhancing treatment effect. Ten liters of raw coking wastewater were collected from the intake of WWTP using acid-washed, glass bottles that were pre-rinsed with sample wastewater. The water samples were kept on ice during transportation from WWTP to the laboratory. Table 1 shows the main characteristics of coking wastewater studied in this work.

2.3. Preparation of adsorbents

The preparation of vermiculite-based adsorbents tested in this study followed the previous methods [28]. Fig. 1 presents the synthetic route of CTMS and CTES modified acid-vermiculite. The main reaction of surface silanization took place through the condensation reaction between CTMS/CTES and surface silanol groups (Si-OH) of acid-vermiculite. The resulting hybrid organic-inorganic materials were abbreviated to CTMS-V and CTES-V, respectively.

2.4. Characterization of adsorbents

FTIR spectras of adsorbents were recorded on a Nicolet 6700 spectrometer (ThermoNicolet, USA) in the 4000 – 400 cm^{-1} region using KBr platelets. The nitrogen adsorption-desorption isotherms of the samples were measured using a Micrometrics ASAP 2020 M apparatus (Micrometrics, USA) at $-196 \text{ }^\circ\text{C}$. Prior to analysis, the samples of vermiculite were degassed for 4 h at $250 \text{ }^\circ\text{C}$ below 10^{-2} Pa . The parameters of specific surface areas and pores structure were calculated using the Micrometrics software. Pore size distribution of the porous materials was calculated using the Howarth-Kawazoe (HK) formalism for micropores and Barret-Joyner-Halenda (BJH) method from the desorption branch for mesopores, respectively. Thermal gravimetric analysis was conducted by TG 209 F1 Thermogravimetric Analyzer (Netzsch, Germany).

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