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Pretreatment of coal gasification wastewater by adsorption using activated carbons and activated coke

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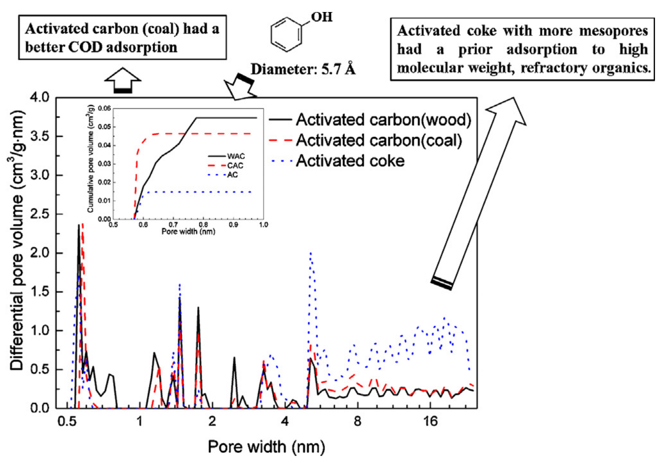
HIGHLIGHTS

- Three adsorbents were used to pretreat coal gasification wastewater.
- Pore size distribution of different adsorbents was investigated.
- Activated carbon (coal) had a better COD adsorption performance.
- Activated coke had a prior adsorption to aromatic refractory compounds.
- Mesopores percentage of activated coke was 63%.

GRAPHICAL ABSTRACT



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ABSTRACT

Powdered (below 125 μm) activated carbons made by wood (WAC) and coal (CAC) and activated coke (AC), whose BET surface areas were 551, 335 and 484 m^2/g, respectively, were studied to adsorb organic pollutants from coal gasification wastewater (CGWW). This study initially focused on the equilibrium sorption isotherms of adsorbents for the removal of chemical oxygen demand (COD) from CGWW. Molecular weight (MW) distribution and fluorescence excitation emission matrix (FEEM) were used to determine the difference of CGWW quality. Water qualities of CGWW before and after adsorption by adsorbents were also investigated. The isotherm results showed that Langmuir model fit the adsorption isotherms of activated carbons, while Freundlich model was better for that of AC. CAC and AC had a higher adsorption capacity under lower and higher COD concentration, respectively. It was also found from MW distribution and FEEM results that AC had a prior adsorption to high MW aromatic, refractory compounds in CGWW, which is good for the following biological treatment and suitable for pretreatment. This was because that the mesopores percentage of AC was 63%, which was higher than WAC and CAC.

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1. Introduction

Coal gasification is a promising technology for supplying clean coal gas in China, where coal is the main energy resource and coal combustion is treated as one of the main contributions to air pollution. However, the coal gasification processes, especially the widely used Lurgi process, generate wastewaters that contain complex inorganic and organic pollutants, such as ammonia, phenolic compounds, cyanide, thiocyanate, polycyclic aromatic hydrocarbons, heterocyclic compounds and long-chain hydrocarbons, most of which are refractory and toxic [1].

Ammonia-stripping and solvent extraction is usually used as pretreatment processes which are effective for the reduction of ammonia and phenolic compounds of coal gasification wastewater (CGWW), while the content of refractory organic compounds in the effluent of solvent extraction remains high [2]. Biological treatment, such as conventional activated sludge, anoxic-oxic, and anaerobic-anoxic-oxic, is usually used to treat CGWW [3–6]. Due to their capability to improve biodegradation of CGWW, considerable attention has been directed to the anaerobic processes, e.g. anaerobic filter [7], anaerobic granular activated carbon reactor [8] and upflow anaerobic sludge bed [9,10]. Since high amount of organic toxic components in CGWW may be toxic to biological system, it is very important to pretreat the wastewater before it is treated by anaerobic digestion or biological treatment. Many methods, such as acidification demulsion [11] and advanced oxidation [12] have been investigated as the pretreatment process of CGWW. However, these methods are either technically complicated or economically unfavorable, which make them difficult to be practically used.

Adsorption technique is widely used for wastewater treatment due to its efficient ability to separate dissolved/undissolved chemical compounds and easy operation. Activated carbons are most widely used as the adsorbent in the wastewater treatment. However, activated carbons present high adsorption capacity coupled with high costs [13]. A cheap adsorbent is the prerequisite for practical application of adsorption process [14]. Besides, activated carbons with higher microporous volumes exhibited higher adsorption affinities to low molecular weight (MW) organic matter, but are expected to be less efficient in adsorption of large size molecules than those adsorbents with higher mesopore and macropore volumes [15]. Activated coke (AC) made mainly from lignite, which is cheaper and with higher mesopore volumes, has become an alternative to activated carbon in the treatment of gaseous emissions. In recent literatures, activated coke has been used to treat wastewater containing refractory contaminants which are usually high MW [16]. However, to the best of our knowledge, few studies on the adsorption pretreatment of CGWW by AC were reported before.

The aim of this study was to investigate the different adsorption properties of activated carbons and AC by the batch experiments and find out the most suitable adsorbent for pretreatment of CGWW. Chemical oxygen demand (COD), total organic carbon (TOC), UV_{254}, and decolorization were used as the indexes for evaluating the treatment efficiency. Fluorescence excitation emission matrix (EEM) of CGWW before and after adsorption was also detected for further understanding the adsorption difference among absorbents in this study.

2. Experimental

2.1. Materials

2.1.1. CGWW

The actual Lurgi CGWW used in the experiment was provided by Yima coal gasification factory located in Henan province, China. It had been pretreated by ammonia stripping and phenols solvent extraction processes. The average COD, TOC and biochemical oxygen demand (BOD_5) concentrations were 823, 330 and 381 mg/L. And the pH of CGWW was around 7. As can be seen, concentrations of pollutants in the wastewater were low because of high performance of pretreatment when wastewater was obtained.

2.1.2. Adsorbents

Activated carbons made by wood (WAC) and coal (CAC) were purchased from Guangzhou Zhongjun Company. The AC produced from lignite was obtained from State Grid Electric Power Research Institute, China. The particle size of all adsorbents was below 125 μm.

2.2. Adsorption experiments

The isotherm adsorption property of the adsorbents was investigated by batch experiment. 150 mL of raw CGWW was added into a series of 250 mL triangular flasks, into which different doses (0–0.9 g) of adsorbents were put. Sealed flasks were agitated in an air-bath shaker bath (HZ-9610 K, China) at 25 °C and initial pH for 24 h at a shaking speed of 200 rpm to reach adsorption equilibrium. Effect of adsorbent dosage on adsorption performance was investigated at the same time.

For the need of sampling, 500 mL triangular flasks filled with contrast amount of adsorbent mixed with 400 mL raw CGWW were used for evaluating adsorption properties of different adsorbents. The procedure was basically identical to that of equilibrium experiment.

2.3. Analytical methods

2.3.1. Fluorescence EEM

Before optical analysis, samples were first equilibrated to room temperature after filtration through a 0.45 μm membrane filter, and then the pH of filtered samples was adjusted to 7–7.1 with 0.1 mol/L hydrochloric acid under room temperature, in order to minimize the temperature and pH effect. Fluorescence EEM spectra were obtained using a fluorescence spectrophotometer (F-7000, Hitachi Inc., Japan) at a photomultiplier tube voltage of 700 V. EEM analysis was conducted at a scan rate of 2400 nm/min, with sampling interval at 5 nm on both excitation (Ex) and emission (Em) modes. Ex and Em slit bandwidths were set at 5 nm, whereas the scanning field was set at emission spectra from 200 nm to 400 nm and excitation spectra from 250 nm to 500 nm.

A Milli-Q water EEM was subtracted from the raw EEMs to remove the Raman scattering. Inner filter affect was compensated based on the absorbance profile of the same sample. Any negative values in the data were set equal to zero before the EEMs were Raman calibrated by normalizing to the area under the Raman scatter peak (Ex = 350 nm) of a Milli-Q water. Normalized EEMs were plotted in MATLAB using the contour function.

2.3.2. Molecular weight distribution

Water samples were fractionized using ultrafiltration performed in a 250 mL stirred pressure filtration cell (Amicon) with flat membrane filters (Millipore) under a pressure of 3–5 bar realized by a nitrogen gas cylinder. The active layer of the filters is made of polyethersulfone. Their MW cutoff limits were 100, 10 and 1 kDa. The molecular size distribution of the fractions related to TOC was estimated by calculating the values of the individual filtrates.

2.3.3. BET surface area and pore size distribution

The BET surface area and pore size distribution of all the adsorbents were measured using N_2 adsorption and desorption test at 77 K (ASAP 2020, Micromeritics, USA). Samples were outgassed at