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The effects of adsorbing organic pollutants from super heavy oil wastewater by lignite activated coke

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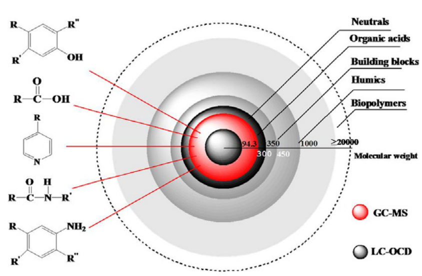
HIGHLIGHTS

- LAC adsorption can increase pH and B/C of SHOW that benefit for biodegradation.
- FTIR, Boehm titrations, GC–MS, and LC–OCD were employed for mechanisms analysis.
- The organic pollutions that removed are HOCs, complicated structures or toxic.
- The mechanisms of adsorption are due to hydrogen bonding and the functional groups.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption of organic pollutants from super heavy oil wastewater (SHOW) by lignite activated coke (LAC) was investigated. Specifically, the effects of LAC adsorption on pH, BOD_5/COD_{Cr}(B/C), and the main pollutants before and after adsorption were examined. The removed organic pollutants were characterized by Fourier transform infrared spectroscopy (FTIR), Boehm titrations, gas chromatography–mass spectrometry (GC–MS), and liquid chromatography with organic carbon detection (LC–OCD). FTIR spectra indicated that organic pollutants containing —COOH and $—NH_2$ functional groups were adsorbed from the SHOW. Boehm titrations further demonstrated that carboxyl, phenolic hydroxyl, and lactonic groups on the surface of the LAC increased. GC–MS showed that the removed main organic compounds are difficult to be degraded or extremely toxics to aquatic organisms. According to the results of LC–OCD, 30.37 mg/L of dissolved organic carbons were removed by LAC adsorption. Among these, hydrophobic organic contaminants accounted for 25.03 mg/L. Furthermore, LAC adsorption was found to increase pH and B/C ratio of the SHOW. The mechanisms of adsorption were found to involve between the hydrogen bonding and the functional groups of carboxylic, phenolic, and lactonic on the LAC surface. In summary, all these results demonstrated that LAC adsorption can remove bio-refractory DOCs, which is beneficial for biodegradation.

1. Introduction

Activated coke (AC) can be produced from various natural carbonaceous materials, such as lignite [1] [termed lignite activated coke (LAC)], petroleum coke [2], wood [3], and other biomasses [4].

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Table 1
Characteristics of SHOW.

Parameter	Concentration (mg/L)	Parameter	Concentration (mg/L)
COD_{Cr}	467.8	Cl^-	460.1
BOD_5	79.53	SiO_2	140.3
Oil	24.19	Ca^{2+}	33.21
NH_3-N	10.53	Mg^{2+}	14.62
TN	14.31	Total salt	3060
TP	0.206	pH	7.098
SS	50.77	TOC	152.3

In particular, LAC represents a potential alternative material for activated carbon and is a less expensive adsorbent. Previously, LAC has been extensively applied to treat the toxic gas-phase materials such as H_2S [3], SO_x, NO_x [4,5], and Hg° [6], and the bio-refractory wastewaters contaminated with trinitrotoluene [7], coke [8], and heavy oil [9]. Though LAC is generally utilized as an advanced treatment after biodegradation processes, the capacity for LAC to improve the biodegradability of SHOW, and especially its effect on the properties of wastewater, have not been extensively reported.

After most mineral oils and surfactants have been demulsified and flocculated in SHOW, chemical oxygen demand (COD) is generally lowered to 500 mg/L. However, large amounts of heavy oils and surfactants still exist, so a further treatment of SHOW is needed. Correspondingly, biological methods have become increasingly popular in the treatment of oilfield wastewater due to their high efficiency, cost effectiveness, and environmental friendliness [10–13]. However, pretreatment of SHOW is needed to improve its biodegradability [14,15] and high toxicity [16].

LAC has a lower iodine sorption value (300–500 mg/g) compared with many other active carbons. It is also characterized by mesopores with a diameter of 403 μm and a pore volume of 0.271 cm^3/g. Thus, these pores can selectively absorb large molecules and long-chain organic compounds. The adsorption capacity of LAC for COD is approximately 100 mg/g [9]. It can remove organic compounds in effluents and alleviate biodegradation load.

The objective of this study was to investigate the capacity of the LAC removing organic pollutants in SHOW. The factors evaluated included pH and B/C. A systematic characterization of the effects of LAC on the main pollutants was also conducted. Regarding the latter, GC–MS and LC–OCD were used to characterize the organic compounds removed. In addition, the mechanisms that improved the biodegradability of LAC to treat SHOW were analyzed. These results provided the basis for the full-scale usage of LAC in treatments of SHOW.

2. Materials and methods

2.1. SHOW

The SHOW used in the experiments was obtained from a heavy oil wastewater treatment plant, the Liaohe oilfield (Liaoning province, China), which had already been treated by demulsification and flocculation. The SHOW received was a colorless and transparent liquid with no peculiar smell and it had a COD value of less than 500 mg/L. Table 1 summarizes the important chemical and physical parameters of the SHOW used.

2.2. LAC

LAC prepared by lignite was obtained from the Beijing Guodianfutong Technology Development Co., Ltd. The particle size and surface area for the LAC ranged from 0.074 mm to 0.83 mm and from 500 m^2/g to 600 m^2/g, respectively. In addition, the total pore volume ranged from 0.48 cm^3/g to 0.52 cm^3/g and the average pore diameter was 2.61 nm, as measured by N_2 adsorption isotherms using an ASAP 2010 micromeritics instrument (Table 2).

Prior to the adsorption experiments, the LAC was heated in an electric furnace. Then it was washed for several times with distilled water until visibly clear water was obtained in order to remove the organic gases [9]. The LAC was then dried in an oven at 378 K for 72 h and then cooled to the room temperature in an air-tight glass bottle. The LAC remained was stored in an air-tight glass bottle until needed.

2.3. Adsorption experiments

LAC powder (0.5 g) was added into each sealed 1000 mL glass bottle, which contained 500 mL of heavy oil wastewater. Then the bottles were placed in an air-bath shaker at 150 rpm and 303 ± 0.2 K for 360 min. The initial pH was unchanged. The samples were subsequently filtered and the resulting filtrate was analyzed. All of the experiments were performed in duplicated.

2.3.1. Effect of LAC dosage on pH

Various doses of LAC powder (1.0, 2.0, 3.0, 3.5, and 4.0 g/L) were added to each 1000 mL sealed glass bottle, which contained 500 mL of heavy oil wastewater. Experiments were performed in an air-bath shaker at 150 rpm and 303 ± 0.2 K for 360 min, and the initial pH was unchanged.

2.3.2. Effect of LAC dosage on B/C

Various doses of LAC powder (1.0, 2.0, 3.0, 4.0, and 5.0 g/L) were added to each 1000 mL sealed glass bottle, which contained 500 mL of heavy oil wastewater. These experiments were also performed in an air-bath shaker at 150 rpm and 303 ± 0.2 K for 360 min, and the initial pH remained unchanged.

2.4. Analytical methods

Biochemical oxygen demand after 5 days (BOD_5) was determined according to Chinese standards (GB 7488-87). COD was used to evaluate SHOW treatment efficiency and pH was determined by the dichromate method (Water Quality-Determination of the Chemical Oxygen Demand-Dichromate method, GB11914-89) with a pH meter (pH-3D, Leici Corporation, China). Mineral oil concentration was measured by infrared spectroscopy (F2000, Jilin China). Oil components in the wastewater were determined by a national standard method (GB/T16488-1996). Ions were detected by an ion chromatograph (DionexIonpac, USA). Concentrations of Cl^-, Mg^{2+}, and Ca^{2+}, as well as other pollutants, were determined by a national standard method [17].

The removal rates and adsorption of COD at equilibrium were calculated according to the following formulas:

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where η (%) is the removal rate, C_0 (mg/L) is the COD concentration in the raw SHOW, C_e (mg/L) is the COD concentration after adsorption, q_e (mg/g) is the amount of maximum COD adsorbed per unit mass by the LAC, V (L) is the volume of the SHOW, and W (g) is the LAC weight.

2.5. Characterizations

A HITACHI S-450 scanning electron microscope (Hitachi, Japan) operated at 10 kV was employed to observe the surface morphology of the LAC before adsorption [18].