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Sorption performance and mechanism of a sludge-derived char as porous carbon-based hybrid adsorbent for benzene derivatives in aqueous solution

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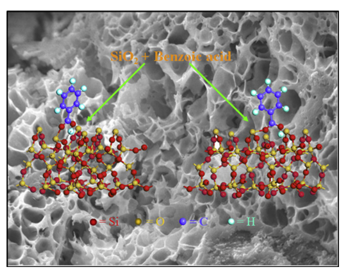
HIGHLIGHTS

- Hierarchical porous sludge char were fabricated by pyrolysis at 500 °C.
- A stronger Si–O bond (1.83 Å and 1.87 Å) between the carboxyl and SiO_2 was found.
- Quantum chemistry calculation confirmed the interaction of Si–O and H–O bonds.
- Multiple model ($Q_T = Q_A + K_P Ce$) was presented in the sludge char sorption process.

GRAPHICAL ABSTRACT



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ABSTRACT

A porous sludge-derived char was prepared by a new one-step pyrolytic process with citric acid–$ZnCl_2$ mixed fabricating-pore agents. The sludge-derived char was confirmed to be a hierarchically porous hybrid adsorbent containing-elemental carbon, -highly carbonized organic species and -inorganic ash with a great surface area of 792.4 $m^2\,g^{-1}$. It was used as a carbon-based hybrid adsorbent for four benzene derivatives including 4-chlorophenol, phenol, benzoic acid and 4-hydroxylbenzoic acid in aqueous solution. Results showed that their sorption isotherms were nonlinear at low concentrations and linear at high concentrations. The sorption performance could be described by a multiple sorption model ($Q_T = Q_A + K_P C_e$). The order of these partition sorption coefficients (K_P) of these benzene derivatives was consistent with their octanol–water partition coefficients ($\log K_{ow}$), but those saturated amounts (Q_A) were inconsistent with their $\log K_{ow}$. The inconstancy was found to be considerably dependent on the preferential interaction of benzoic acid with SiO_2 in the sludge-derived char. Quantum theoretical calculation confirmed that the preferential interaction was attributed to the formation of hydrogen bonds (1.61 and 1.69 Å) and new Si–O bonds (1.83 and 1.87 Å) between the carboxyl of benzoic acid and the SiO_2 surface in the sorption process.

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1. Introduction

Sewage sludge is the main waste generated in the urban wastewater treatment process. In the last decades, there has been growing public concern with problems of its disposal as its production is increasing considerably. The conventional sludge disposal options are landfill bury, land application and incineration, but each option has important limitations with increasing environmental and legislative constraints [1]. The increased environmental burdens of sludge production have prompted a drive for innovative disposal routes for the sewage sludge. Reuse of waste sludge for the carbonaceous production of char has received much attention in recent years [2,3].

Sludge char is a kind of carbon-rich material. It is used in different fields, such as soil amendments, catalysts and so on [4–6], especially adsorption for the treatment of effluent [7]. The use of waste derived adsorbents had been studied as an alternative substitution of activated carbon for the treatment of pollutants [8]. Their applications were governed by developed porous structure [9]. While directly pyrolyzed char at 400–600 °C are generally rigid solid with a surface area smaller than 60 $m^2 g^{-1}$ [10], many efforts have been paid to increase their porosity. For example, Rozada et al. increased surface area (S_{BET}) of char from 60 to 472 $m^2 g^{-1}$ with $ZnCl_2$ as the thermal fabricating-pore agent [10]. Martin et al. prepared sludge-derived carbon with a S_{BET} of 253 $m^2 g^{-1}$ with H_2SO_4 as the thermal fabricating-pore agent [11]. Liu et al. found that activated carbons from 0.2 wt.% pyrolusite-supplemented surplus sludge had up to a 75% higher BET surface area than that from the original surplus sludge [12]. It is noticed that the current investigations on the improvement mainly focus on the use of inorganic fabricating-pore agents but scarcely on the use of organic fabricating-pore agents. Among the different pore-fabricating methods, $ZnCl_2$ was the most widely used inorganic fabricating-pore agents due to its efficient effect on fabricating micropores and mesopores [10,13]. An advanced adsorbent should possess a hierarchically porous architecture where rich shorter micropores are connected by surface of abundant meso- or macropores throughout the whole structure because a large pore size distribution can provide the potential to adsorb a broad spectrum of pollutants, and especially macropores and mesopores enhance the transport properties throughout the adsorbents [14]. Therefore, it is an attractive research topic to improve the porous architecture and the surface area of sludge-derived char adsorbent for environmental application.

The sorption performance of an advanced adsorbent is also dependent on its chemical composition in addition to its porous architecture. Although the chemical composition of sludge char is complex and moreover related to the sludge feedstocks, most of the sludge chars generally have high content of inorganic compounds because dried sludge usually contains 26–46% ash content [15,16]. It is reasonably expected that the complex and heterogeneous natures of the hybrid sludge char can lead to different sorption mechanisms from common carbonaceous materials. Although sludge chars have been used to adsorb of a wide range of pollutants, such as NO_2, H_2S, phenol, nitrobenzene [17–20], there are only a few of investigations on their sorption mechanisms, and moreover the limited investigations on the mechanisms primarily focus on the effects of surface area, porous size, surface charges and oxygen- and nitrogen-containing groups etc. on adsorptions [21,22], while little information is available for the roles of non-carbon inorganic species as major components of the sludge char in the sorption processes. Therefore, it is more significant to explore what happen for the non-carbon inorganic species in sorption for engineering fabrication and practical environmental applications of sludge char.

In the view of the aforementioned two issues, we start a project to improve and understand the sorption performance of sludge char as a carbon-based hybrid adsorbent for removing organic pollutants. It is expected that a lot of macro-pores could be fabricated by the thermal decomposition of CA, which will provide more inner-space for $ZnCl_2$ to fabricate abundant meso- and micropores [23]. In this paper, the improvement focuses on enriching the porous architecture and increasing surface area of the sludge char by one step coupling utilization of inorganic and organic fabricating pore agents ($ZnCl_2$-citric acid). The understanding centers on the effect of inorganic species SiO_2 in the sludge char on the adsorption of organic pollutants in aqueous solution by both experimental approach and theoretical simulation because silica is usually one of most non-carbon components in sludge char [18]. Four benzene derivates, 4-chlorophenol, benzoic acid, phenol and 4-hydroxylbenzoic acid, are utilized as adsorbates because they are typical environmental organic pollutants frequently found in wastewaters [20,24]. The main objective of this investigation is to provide a preparation method of hierarchically porous sludge char and a new understanding towards sorption performance and mechanism of sludge char as an effective carbon/inorganic hybrid adsorbent based on experimental approach and quantum theory.

2. Materials and experiment

2.1. Materials

Dewatered sewage sludge was collected from Wanglong wastewater treatment plant in Guangzhou, China, subsequently dried in air at 105 °C, grounded in less than 0.149 mm for further utilization. The properties of the sludge were presented in Table S1. The combustible content was high to 80.58%, indicating that the sludge contained large amounts of organic materials, which had the potential to produce sludge carbon. The SiO_2 content in the sludge was 12.40%, as the mainly component in the ash content. 4-Hydroxybenzoic acid (OH-BA), phenol (PHEN), benzoic acid (BA), 4-chlorophenol (Cl-PHEN), $ZnCl_2$ and citric acid (CA) were purchased from Fuchen chemical reagent Co., Tianjin, China (chemical grade).

2.2. Preparation of sludge derived char

2.2.1. Preparation of SC and SC_{Zn}

40.0 g powder sludge was added into 100 mL water solution containing 0–2 mol $ZnCl_2$ and stirred overnight to form homogenous sol–gels. The sol–gels were dried and put into ceramic ark, and heated in a programmable tube electric furnace at a rate of 20 °C min^{-1} to 500 °C in the presence of N_2 holding for 1 h [25]. After cooling to room temperature, the product was ground to less than 80 mesh, washed with hydrochloric acid solution to remove metal ions, then rinsed with deionized water until the pH reached 7 and finally dried at 105 °C over night. The product without adding $ZnCl_2$ and the product with the maximum BET surface area after adding $ZnCl_2$ was named as SC and SC_{Zn}, respectively.

2.2.2. Preparation of SC_{CA}

40.0 g sludge was added into 100 mL solution containing 0–2 mol CA and stirred overnight to form homogenous sol–gels. The sol–gels were dried and carbonized, subsequently washed with hydrochloric acid solution as described above. The product with the maximum BET surface area was named as SC_{CA}.

2.2.3. Preparation of SC_{CA-Zn}

40.0 g sludge was firstly added into 100 mL solution containing 0–2 mol CA and 0.5 mol $ZnCl_2$, stirring overnight to form homogenous sol–gels. The sol–gels were dried and carbonized, subsequently washed with hydrochloric acid solution as described