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Structure and adsorption properties of sewage sludge-derived carbon with removal of inorganic impurities and high porosity

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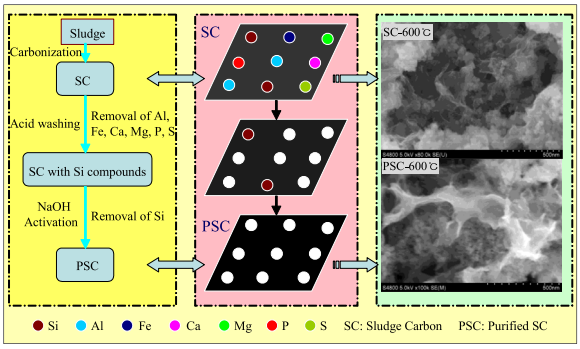
HIGHLIGHTS

- Purified sludge carbon (PSC) with removal of inorganic fractions is obtained.
- Structure and properties of sludge carbon (SC) and PSC are compared.
- Removed impurities are acted as a natural template.
- More hierarchical pores and oxygen-containing groups are formed in PSC.
- PSC as an inexpensive carbon is superior to SC for rhodamine B and phenol adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Purified sludge carbon (PSC) with removal of inorganic 'impurities' (Si, Al, etc.) is prepared from sewage sludge. Morphological structure, textural properties, surface elements and functional groups of sludge carbon (SC) and PSC are compared. S_{BET} and pore volume of PSC are about three times higher than those of SC. PSC with large fluffy cavities remains some memory of SC parent structure. Removed fractions can be considered as a natural template for producing a hierarchical porous structure in PSC. Abundant oxygen-containing groups including hydroxyl and epoxide are generated in PSC, which are favorable for organic contaminant removal from wastewater. Diffraction peaks at $2\theta = 45°$, bending modes of Si–O–Si and Na1s peaks (1070.5 eV) jointly confirm that only a trace of adsorbed impurities ($Na_2O{\cdot}(SiO_2)_x$ ($x \geqslant 1$)) is retained on PSC surface. PSC is superior to SC and comparable to commercial activated carbon for rhodamine B and phenol adsorption capacity.

1. Introduction

Recently, an increasing number of scientific researches has been conducted to find a suitable way for conversion of sludge into sludge carbon (SC) for different applications (Bandosz and Block, 2006; Ding et al., 2012; Lillo-Rodenas et al., 2008; Pan et al., 2011; Rozada et al., 2008). This is an interesting alternative for lightening the atmospheric, water, and soil contamination by sludge (Hofman and Pietrzak, 2012; Ros et al., 2006; Ren et al., 2012; Shen et al., 2008). The feasibility of conversion of this waste to porous SC is associated with the fact that most of sludge is mainly composed of micro-organisms (Gómez-Pacheco et al., 2012; Wang et al., 2011). The bacteria cell wall, the microorganism-secreted slime layer and the

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membrane of prokaryotes are composed of complex organic matters such as peptidoglycan, teichoic acids, and complex polysaccharides, which are not readily biodegradable and still retain in sludge (Shehu et al., 2012; Zou et al., 2012). In carbonization process, pores in SC are formed by the loss of water and the decomposition of organic matters (Bagreev and Bandosz, 2004; Pan et al., 2011; Smith et al., 2009). Furthermore, the induced thermal decomposition of the non-carbon elements, such as the inorganic components that presents in the forms of oxides or salts in sludge, also serves to develop the porous structure through their release as gaseous volatile products (Velghe et al., 2012).

Many studies have affirmatively reported that S_{BET} of SC can be evidently improved by acid washing, which aims at partially removing the inorganic fractions from the carbonaceous framework (Ding et al., 2012; Ros et al., 2006, 2007; Velghe et al., 2012). It is also reported that HCl washing prior to physical, chemical or combined activation is more effective than that of post-activation (Ros et al., 2006). It is reported that the ash contents of SC before and after acid washing are in the range of 65–66 wt.% and 35.8–45.5 wt.%, respectively (Ros et al., 2006, 2007). The main crystalline phases of the ash are reported to be α-quartz (SiO_2), Na–Ca feldspars [albite – $Na(AlSi_3O_8)$ and/or anorthite – $Ca(Al_2Si_2O_8)$], and eventually cristobalite (SiO_2) (Pan et al., 2011; Shen et al., 2008; Xu et al., 2008). No other detailed data about the ash in SC or acid-washed SC is reported so far. However, it is true that after carbonization, the inorganic residues (Al, Fe, etc.) are not thoroughly washed out by the reported acid-washing methods (Ding et al., 2012; Ros et al., 2006, 2007; Velghe et al., 2012). Only by acid washing, most of the SiO_2 (an acid oxide) are inevitably retained in SC.

After chemical activation, SC is usually water-washed to remove the chemical activating agents, such as KOH, NaOH, $ZnCl_2$, K_2CO_3/Na_2CO_3, K_2S, H_3PO_4, etc. (Gómez-Pacheco et al., 2012; Lillo-Rodenas et al., 2008; Ren et al., 2012; Rozada et al., 2008; Wang et al., 2008). Meanwhile, part of the silicon compounds in SC is removed, because the conjugation reaction (for example, $SiO_{2(s)} + 2NaOH_{(s)} \rightarrow Na_2SiO_{3(s)} + H_2O_{(L)}$) between base reagents (such as Na, K) and Si compounds is happened (Asquini et al., 2008; Zou et al., 2013). It should be noted that the stable (deeper) silicates may not be reacted with the activating agent in the activation process and most of Si^{4+} 'impurities' can not be thoroughly removed from SC by simple water-washing. Many studies have already implied that the disparity in SC's properties is mainly attributed to the difference in the removed proportion of their ash (Bandosz and Block, 2006; Ros et al., 2006, 2007). So far, the ambiguity in the characteristics and purity of 'as-prepared' SC still needs to be clarified. The specially designed SC with thorough removal of inorganic fractions (Si, Al, etc.) must present unique characteristics in S_{BET}, surface groups and security against toxic leaching. Furthermore, the removed 'impurities' (soluble residues, Si^{4+}, Al^{3+}, etc.) can be reclaimed for other valuable applications (nano-SiO_2 and nano-$Al(OH)_3$ has been successfully synthesized from the sludge-derived water–glass and sodium aluminates, respectively) (Zou et al., 2012, 2013). This hence leaves room for further refinements.

To the best of our knowledge, there is no study investigating the characteristics of inorganic-free SC (with removal of basic oxides (Al_2O_3, Fe_2O_3, CaO, MgO, etc.) and acidic oxide (SiO_2)). The aim of this work is to prepare the purified-SC (PSC) with pure carbon, high surface area and pore volume, and abundant surface functional groups, which is expected to have higher pollutants uptake capacity than that with 'impurities'. Difference of physicochemical properties between PSC and SC, effect of 'impurities' removal on formation of porous structure and surface groups of PSC, and relationship between PSC (carbon) and chemical composition (inorganic fractions) are discussed. Adsorption isotherms and kinetics for adsorption of Rhodamine (RhB) and phenol by commercial activated carbon (CAC), PSC and SC are also investigated. The value of this work is to provide a beginning that others can build upon as the panorama of PSC, nano-$Al(OH)_3$ (or Al_2O_3) and nano-SiO_2 reclamation develops worldwide.

2. Experimental

2.1. Materials

Sludge was obtained from the Wen–chang Wastewater Treatment Plant, Daowai District, Harbin, China. The sludge was treated by air-dry method and was ground into sizes below 100 μm. The elements analysis of sludge is conducted by following the reported method (Zou et al., 2013). 0.3 g dried sludge, 1 mL deionized water and l0 mL HNO_3 (water/HNO_3 of l:1, v/v) was sequentially added into a conical flask (CF) covered with a triangular funnel, which was then heated on the electrothermal board for l0 min. After cooling, 5 mL HNO_3 was added into the CF, which was then heated for 30 min. This step was repeated several times, until no smoke was generated. The brownish yellow smoke was generated from the sludge oxidation by HNO_3. Two milliliter deionized water and 1 mL hydrogen peroxide was added into the CF, which was heated for 5 min. This step was also repeated several times (less than 10 times), until the reaction was no longer violent. Then, 10 mL hydrochloric acid (37 wt.%) was added into the CF for 15 min heating. After cooling, 40 mL deionized water was added into the CF, which was heated until 10 mL water was remained. Ion concentrations in the collected solution were measured by using a Perkin–Elmer Optima 5300DV Inductively Coupled Plasma Atomic Emission Spectrometer (ICP–AES, Waltham). The elements analysis data of sludge is shown in Table S1 (Supplementary data). All chemical reagents used in this study were analytical grade and were used without further purification.

2.2. Preparation of SC and PSC

Sludge was carbonized from 20 to 500–1000 °C (at intervals of 100 °C) at a rate of 5 °C/min in a tubular furnace under N_2 atmosphere (50 mL min^{-1} of flowing N_2 gas). The samples were soaked at final temperature for 60 min and naturally cooled until they reached room temperature in N_2 atmosphere (Zou et al., 2012). The carbonized powder was acid-washed with liquid/solid (L/S, mass ratio) ratio of 20: 1 at 80 °C. The samples were thoroughly washed with 2 M HCl for 120 min, and then with de-ionized water for 10 min (L/S ratio of 5: 1 at 80 °C) until pH of the washing water was achieved 6–7. Centrifuge was used to separate the supernatant liquid and the SC (3500 rpm). Dried SC was mixed with activating reagent at a NaOH:SC ratio of 1:1 (by dry mass). Then the mixture was heated (5 °C min^{-1}) to 500–1000 °C (at interval of 100 °C) with dwell time of 120 min in a tubular furnace under N_2 atmosphere (60 mL min^{-1} of flowing N_2 gas). The obtained sample was water-washed with L/S ratio of 10:1 at 80 °C (water bath and magnetic stirring) for 5 h. The washing process was repeated for another 10 min (L/S ratio of 5:1 at 80 °C) until pH of the washing water was achieved 6–7 (Zou et al., 2013). The PSC samples were separated (3500 rpm for 5 min) from the washing water and then dried at 100 °C for 12 h. It should be noted that no wastewater was discharged in this process and all the washing water was reclaimed for other use (Zou et al., 2012, 2013). There were some heavy metals (very small amounts) in the washing water, which could be easily removed in the reported process (Zou et al., 2012, 2013).

2.3. Analysis methods

The N_2 adsorption/desorption isotherms were measured at 77 K using a Micromeritics Tristar II. The specific surface area of the materials was calculated by the Brunauer–Emmett–Teller (BET)