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Preparation of thiol-functionalized activated carbon from sewage sludge with coal blending for heavy metal removal from contaminated water

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ABSTRACT

Sewage sludge produced from wastewater treatment is a pressing environmental issue. Mismanagement of the massive amount of sewage sludge would threat our valuble surface and shallow ground water resources. Use of activated carbon prepared from carbonization of these sludges for heavy metal removal can not only minimize and stabilize these hazardous materials but also realize resources reuse. In this study, thiol-functionalized activated carbon was synthesized from coal-blended sewage sludge, and its capacity was examined for removing Cu(II), Pb(II), Cd(II) and Ni(II) from water. Pyrolysis conditions to prepare activated carbons from the sludge and coal mixture were examined, and the synthesized material was found to achieve the highest BET surface area of 1094 m^2/g under 500 °C and 30 min. Batch equilibrium tests indicated that the thiol-functionalized activated carbon had a maximum sorption capacity of 238.1, 96.2, 87.7 and 52.4 mg/g for Pb(II), Cd(II), Cu(II) and Ni(II) removal from water, respectively. Findings of this study suggest that thiol-functionalized activated carbon prepared from coal-blended sewage sludge would be a promising sorbent material for heavy metal removal from waters contaminated with Cu(II), Pb(II), Cd(II) and Ni(II).

1. Introduction

China's Bohai Rim Region is a densely populated area surrounded by a number of large cities such as Beijing, Tianjin and Tangshan. Large amounts of sewage sludge are generated each year due to treatment of the region's municipal wastewater. For example, in 2013, Beijing and Tianjin produced 0.18 and 0.10 million tons of dry sludge, respectively (Yang et al., 2015). Sewage sludge is a complex mixture containing mainly microbes, minerals, water, pathogens, heavy metals, organic pollutants (Devi and Saroha, 2017; Zhang et al., 2009). Great concerns have been raised in recent years about the disposal of the massive volumes of the generated sewage sludge and its impact on the water quality of Bohai.

Many methods have been used for sewage sludge management that include landfill, incineration and farmland application (Cai et al., 2007). Among these, landfill and farmland application are facing ever increasing pressures because of lack in available sites for landfill and potential farmland pollution (Devi and Saroha, 2017). Incineration is a widely used technology that can substantially reduce the volume of sludge by transforming it into solid incineration ash (Takaoka et al., 2012). Treatment of sludge by this technology, however, tends to form polychlorinated dibenzo-p-dioxins, dibenzofurans (PCDD/Fs) and other unintentional persistent organic pollutants (POPs) (Lin et al., 2015).

Sewage sludge has been utilized to prepare sorbent materials through thermal or activation treatments (Garg, 2013) for contaminants removal from water. Rozada et al. reported (Rozada et al., 2008) that chemical activation followed by pyrolysis of a dried sewage sludge from an urban wastewater treatment plant resulted

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a sorbent having a BET surface area of 472 m^2/g. The derived material was found useful to remove heavy metals following the preferential order of Hg(II) > Pb(II) > Cu(II) > Cr(III). Reported BET surface areas of the derived sorbents by thermal and/or activation treatments using sewage sludges alone typically fall in the domain of 100–600 m^2/g (Hadi et al., 2015), perhaps primarily due to the sludge's relatively low fixed carbon content but high ash fraction. Efforts have been made to improve the surface areas of sludge-derived sorbents by blending raw sludges with additives that have higher fixed carbon contents prior to pyrolysis. For instance, Gu et al. (Gu et al., 2014). introduced reed straw into a sewage sludge and prepared an activated carbon that had 80 m^2/g higher BET surface area than the material obtained without reed straw addition.

Coal is a sedimentary rock having wide applications due to its high heat value and fixed carbon content. For example, coal has been widely used as an auxiliary fuel in treatment and thermal valorization of sewage sludge from wastewater plants (Barbosa et al., 2009). It is hypothesized in this study that, blending coal with sewage sludge prior to sludge carbonization, would significantly increase the surface area of the resulted carbon material because of coal's high fixed carbon content. Subsequent surface functionalization of the carbon material with thiol functional groups would further improve its capacity and strength in binding a range of heavy metals. It has been reported that thiol-functionalization of carbon materials can generally improve their adsorption capability for heavy metal ions (Chai et al., 2010; Kim et al., 2011) due to the strong Lewis acid-base interaction between heavy metal ions and thiol functional groups (Zhang et al., 2012). Synthesizing activated carbon from coal-blended sewage sludge followed by subsequent surface functionalization of the material with thiol groups would help to provide an additional approach for sewage sludge handling, having potential applications in remediation of contaminated sites, such as removing heavy metals from contaminated waters that have hydraulic connections to Bohai Sea. But this has seldom been reported before.

The overall objective of the current study is to examine the possibility of utilizing coal-blended sewage sludge to synthesize functionalized activated carbons that can be potentially used in future remediation of contaminated sites, such as heavy metals removal from contaminated waters. Specific objectives were to: (1) optimize the pyrolysis conditions to prepare activated carbon from coal-blended sewage sludge; (2) synthesize thiol-functionalized activated carbon prepared under the optimal conditions; and (3) examine its capability to remove Cu(II), Pb(II), Cd(II) and Ni(II) from aqueous solution. A series of activated carbons from coal-blended sewage sludge were prepared to determine the optimal pyrolysis conditions, including the pyrolysis temperature and pyrolysis time. Thiol-functionalized activated carbon was then synthesized and its capacity in removing the selected heavy metals from aqueous solutions was examined by conducting batch equilibrium adsorption experiments.

2. Materials and methods

2.1. Materials

The sewage sludge (SS) used in this study was a digested sludge sample collected from a wastewater treatment plant in Beijing. To prepare the sample, SS was first homogenized and dried at 105 °C for 24 h. The sample was then allowed to cool at room temperature, ground and finally passed through a 200-mesh sieve. The coal sample was a bituminous coal from Datong, Shanxi Province, China. The coal sample was prepared similarly. Chemical reagents thioglycollic acid, $NaHSO_4 \cdot H_2O$ and $Na_2S \cdot 9H_2O$ were purchased from Acros Organics. Zinc chloride, hydrochloric acid, nitric acid, acetic acid, ethanol and N,N-Dimethylformamide (DMF) were purchased from Sinopharm group, China.

2.2. Preparation of activated carbon from coal-blended sewage sludge

To prepare the activated carbon, the sewage sludge and coal samples were first thoroughly mixed at a ratio of 1:1. The mixture was then impregnated with $ZnCl_2$ by soaking the sample in 5 M $ZnCl_2$ solution (1:4 g/mL). The suspension was allowed to shake for 24 h at 100 rpm. Finally, the mixture was separated by centrifugation at 9000 rpm and the solid product was dried for 24 h at 105 °C. In the carbonization stage, the obtained product was evenly spread on a boat and heated in a tubular furnace (Tianjin Zhonghuan, China) to the desired temperature ranging from 500-800 °C at a ramp of 10 °C/min. The whole carbonization process was controlled under anaerobic condition by flowing N_2 at a rate of 100 mL/min. At the end of preset pyrolysis time (15-120 min), the carbonized sample was cooled down to room temperature in the furnace. The sample was then washed sequentially with 3 M HCl and hot distilled water (70–80 °C) several times to remove any residual chemicals. The material was finally dried at 105 °C for 24 h, crushed to size <200-mesh, and stored in desiccator before use. Activated carbons thus prepared from coal-blended sewage sludge were labelled as CSAC.

2.3. Preparation of thiol-functionalized CSAC (SH-CSAC)

Thiol-functionalized CSAC (SH-CSAC) was prepared following the procedures reported by Chai et al. (Chai et al., 2010). with minor modification. Thiol-functionalization of CSAC consisted of two separate stages: surface oxidation of CSAC by nitric acid and grafting thiol functional groups on the oxidized carbon surface. In the oxidation step, 5 g of CSAC was first transferred to flask containing 100 mL concentrated nitric acid and the mixture was allowed to refluxed for 6 h at 93 °C. After cooling to room temperature, the mixture was centrifuged to separate CSAC from the liquid phase. The product was then thoroughly washed with deionized water till pH 6 and vacuum dried at 60 °C for 24 h. In the functionalization step, 5 g of HNO_3-treated CSAC was mixed with 12.5 mL of DMF in a flask. The, 25 mL of thioglycollic acid and 0.125 g of catalyst $NaHSO_4 \cdot H_2O$ was added to the flask and the mixture was heated at 120 °C and allowed to react for 3 h under constant stirring. The obtained product was then further treated for 60 min in a flask containing 30 g of $Na_2S \cdot 9H_2O$ and 125 mL of 95% ethanol to convert any oxidized −SH functional groups on CSAC surfaces back to thiol groups. At the end of reaction, the mixture was washed thoroughly with deionized water and vacuum dried at 60 °C for 24 h. Finally, the product was crushed, allowed to pass through a 200-mesh sieve and stored in the desiccator before use (labelled as SH-CSAC).

2.4. Sorbent characterization

The synthesized materials were characterized by BET surface area (Brunauer – Emmett - Teller), SEM (scanning electron microscope), Fourier transform infrared spectroscopy (FTIR) and XPS (X-ray photoelectron spectroscopy). The specific surface area of the synthesized material was calculated by the BET equation using the N_2 adsorption/desorption data collected by Quadrasorb SI-MP. The