Improvement of aqueous mercury adsorption on activated coke by thiol-functionalization

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HIGHLIGHTS

- Thiol-functionalized activated coke (SH-AC) was prepared by simple chemical method.
- Thiol groups on activated coke lead to improvement of mercury adsorption capacity.
- The adsorption equilibrium time was shortened greatly by SH-AC compared to AC.
- SH-AC has high selectivity toward mercury adsorption.
- BET, XPS, FTIR, zeta potentials were used to study adsorption mechanisms.

GRAPHICAL ABSTRACT
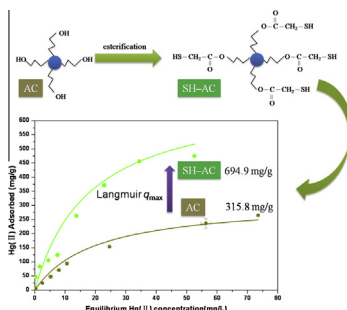
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ABSTRACT

The application of activated coke (AC) in scavenging heavy metals in wastewater has attracted great interest due to its high specific surface area and low cost. In this study, a simple method via esterification with mercapto-acetic acid was developed for the functionalization of activated coke to remove mercury from solution. Results showed that thiol groups were successfully anchored onto the surface of AC. The adsorption equilibrium time was found to be shortened dramatically from 8 h using AC to 15 min using thiol-functionalized AC (SH-AC). The maximum Langmuir adsorption capacity on SH-AC was 694.9 mg g^{-1}, more than twice as much as that on AC. Additionally SH-AC proved its ability to operate over a wider pH range and in the coexistence of other anion species. Higher selectivity was also observed for Hg over multiple metal ions. Zeta potentials, FTIR, and XPS were applied to confirm that the improvement in mercury adsorption was closely related to the anchored thiol groups. The adsorbent also showed high reusability due to its high adsorption capacity after several adsorption–desorption cycles. It can therefore reasonably promise the potential for a more selective and effective but less expensive adsorbent for the treatment of mercury effluent.

1. Introduction

Water pollution by heavy metals has long been brought into public sight along with the high pace of industrialization [1,2]. Unlike organic pollutants, heavy metals are not subject to bio-degradation. Once in the food chain, they are able to accumulate in living organisms and cause extremely high toxicity [2,3]. As one of the most poisonous metals ever discovered, mercury is hazardous to the central nervous system, lungs, kidneys and chromosomes [4]. The chloralkali, pulp paper, fertilizer and similar industries have all contributed greatly to mercury emission into the environment [5].

The aforementioned threats of mercury necessitates the investigation of methods to reduce its presence in contaminated media to innocuous levels and minimize the probability of harmful

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results. A number of removal techniques have been employed such as electrofloatation, chemical precipitation, ion exchange, biosorption, co-precipitation, adsorption, reduction, flocculation and stabilization/fixation technologies, among which adsorption has been proved to be the most practical and economical choice [1,2]. Activated carbon, with its high specific surface area [1,2], has been extensively utilized in the adsorption of heavy metals, including mercury, from a great variety of water solutions, and is effective in adsorption capacity (42.6–724.2 mg/g) [6–8] but high in cost [9,10]. Other materials such as mesoporous silica [11,12], starch [13] and metal oxides [14] have been also improved via chemical modification, only to gain a relatively lower maximum adsorption capacity (131.2–219.8 mg/g) compared to that of activated carbon.

The application of low-cost activated coke in scavenging heavy metals in wastewater as an alternative for costly activated carbon has been investigated. Activated coke is developed from indigenous carbonaceous resources including coal, petroleum, peat, wood, and other biomass [15,16]. Higher in mechanical strength than activated carbon, activated coke can endure attrition and comminution during circulation and handling processes [17,18]. In spite of its lower specific surface area, activated coke usually comprises more macropore and mesopore but less micropore volume than activated carbon, which encourages diffusion of aqueous species into the solid phase [16,19]. Activated coke can suffice for handling numerous pollutants such as H_2S, SO_2, NH_3 and Hg in exhaust gases [15,17,18,20–23] and has been also exploited in treating lignite pyrolysis wastewater, coking pollutants and 2,4,6-trinitrotoluene (TNT) in effluents [16,24,25] from industrial processes.

Nevertheless, the adsorption capacity of activated coke toward heavy metals is still limited by its non-polar character, which hinders interactions between charged metal species and the solid surface [2]. Thus, suitable chemical modifications on activated coke are sought to boost its adsorption capacity for heavy metals. A great diversity of chemicals have been explored which include mineral and organic acids, bases, oxidizing agents, organic compounds, etc. [26]. Due to mercury's high affinity toward sulfur [27], the introduction of sulfur onto the material surface may be considered as a feasible way to elevate the adsorption capacity of activated coke. Various methods have been used to achieve such purpose [28–32]. Lin et al. [28] soaked activated carbon prepared from waste tires in a sodium sulfide solution at 140 °C for 24 h, which proved to raise adsorptive capacity of mercury chloride vapor from 8.35×10^{-2} mg/g to 1.20×10^{-2} mg/g in a self-designed bench-scale adsorption. Krishnan [31] prepared sulfurized activated carbon by steam activation at 400 °C in presence of SO_2 or H_2S to achieve a maximum mercury adsorptive capacity of 188.7 mg/g. Wu [32] has modified adsorbent cotton with thiol groups via chemical reaction to gain an excessive aquatic lead adsorptive capacity of 17.89 mg/g. Chemical pyrolysis methods are complicated and energy-consuming, which were usually used in vapor-phase mercury treatment. And simple chemical reactions are still new and few of them are applied in mercury wastewater treatment.

In this study, a simple method using esterification with mercapto-acetic acid was developed for the functionalization of activated coke to treat mercury wastewater. The materials required are quite easily available and the procedures are relatively simple to carry out. The adsorption properties such as pH effect, the effect of coexisting metals, adsorption kinetics and adsorption isotherm were studied. The surface characteristics of the adsorbent before and after functionalization and the adsorption mechanisms were investigated through zeta potentials, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis.

## 2. Materials and methods

2.1. Materials

The raw powders of activated coke were received from China Electric Power Research Institute. Mercapto-acetic acid (97+%) was obtained from Alfa Aesar. Mercuric nitrate was of analytical grade and obtained from Jiangyan Huanqiu Reagent Factory. The guaranteed pure nitric acid, hydrochloric acid, sulfuric acid and potassium hydroxide as well as analytically pure potassium nitrate, potassium chloride, potassium bicarbonate, potassium sulfate, potassium phosphate, potassium borohydride, potassium bromide, potassium bromate, hydroxylamine hydrochloride, nickelous nitrate, chromic nitrate, cupric nitrate, cadmium nitrate and lead nitrate were all purchased from Sinopharm Chemical Reagent Co., Ltd. The standard solutions of Hg(II), Cr(III), Ni(II), Cu(II), Cd(II), and Pb(II) were obtained from the National Research Center for Certified Reference Materials, China. Ultrapure water (18 MΩ cm) produced with a Millipore Milli-Q water purification system was used for all experiments if not specially stated.

The 100 mg/L stock solution of each heavy metal was prepared by dissolving the appropriate mass of the relevant nitrate salt in ultrapure water and stored way from light. Working solutions were obtained by diluting the stock solution right before the experiment. For the determination of mercury, the $KBrO_3$–KBr solution as oxidizer and KBH_4–KOH solution as reducer were prepared before use by dissolving 2.784 g $KBrO_3$ and 10 g KBr in 1 L ultrapure water and dissolving 0.1 g KBH_4 in 1 L 0.2% KOH solution, respectively.

2.2. Adsorbent functionalization

The raw powders of activated coke (AC) were sieved to obtain a particle size lower than 0.15 mm. The powders were then stirred in 0.01 mol/L HNO_3 for 72 h, filtered and washed with deionized water until the filtrate reached a neutral pH value. Then the solid was dried in a convection oven at 80 °C for 15 h and stored in a desiccator for further experiments, designated as activated coke (AC).

The method for thiol-functionalization of AC was developed in previous research [28,32]. A mixture of 5.0 ml mercapto-acetic acid, 3.5 ml acetic anhydride and 25 μL concentrated sulfuric acid was prepared in a brown glass wide-mouthed bottle with ground glass stopper. Then 5.0 g AC was added to react according to Eq. (1) in the bottle, which was sealed and heated in the convection oven at 80 °C for 13 h. The suspension was filtered and washed with deionized water until the wash water had a pH value higher than 4. Then the product was freeze-dried inside a lyophilizer at a temperature lower than −50 °C for 24 h and stored in a desiccator, and designated as thiol-functionalized activated coke (SH-AC).

$$\equiv AC-OH + HO-CH_2-C(=O)-SH \xrightarrow[H_2SO_4,\ 80\,^\circ C]{Acetic\ Anhydride} \equiv AC-O-C(=O)-CH_2-SH + H_2O \tag{1}$$
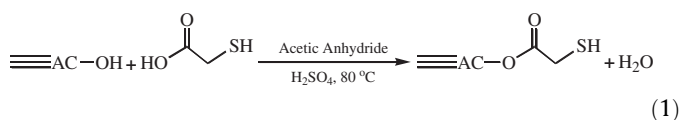
2.3. Adsorbent characterization

The specific surface area, pore volume and pore diameter of adsorbents were obtained by the nitrogen adsorption/desorption isotherm method using an ASAP 2000 surface analyzer (Micromeritics Co., USA). The BET method was applied in the calculation of specific surface area.

The contents of carbon, hydrogen, nitrogen and sulfur of the adsorbent were measured on a CHNS Elemental Analyser (Vario Macro, Germany). Samples sealed in small tin vessels were