Enhanced performance of calcium-enriched coal ash for the removal of humic acids from aqueous solution
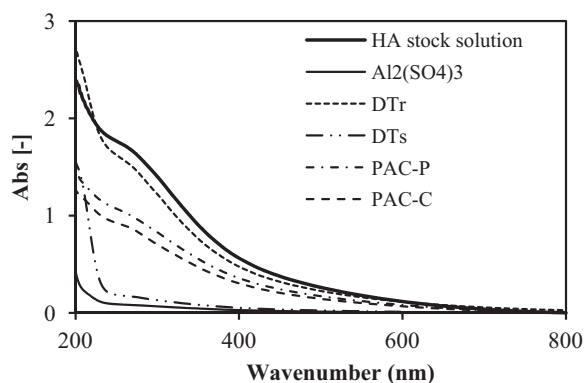
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HIGHLIGHTS

- The adsorption and coagulation characteristics of HA in aqueous solution has been examined.
- A shell-added DT_s is markedly superior to PACs for HA removal.
- The presence of anhydrite and lime in DT_s dramatically increases HA removal.
- Low solution pH and high DT_s dosage are favorable for the removal of HA.
- There is an optimal temperature of approximately 313 K for the HA removal by DT_s.

GRAPHICAL ABSTRACT

ABSTRACT

This study is designed to follow-up our previous work, in which we demonstrated synergistic and in-situ desulfurization effects during co-disposing shell wastes and an aqueous condensate (AQ) derived from biomass carbonization in combination with coal combustion. The potential use of Ca-enriched coal ash as a coagulant for removing humic acid (HA) from aqueous solution is explored in this study. The HA removal performance of raw and shell-added Datong (DT) coal ashes from aqueous solution is examined and compared with that of commercial aluminum sulfate (alum) and powdered activated carbons (PACs). It is found that shell-added DT ash (DT_s) is markedly superior to both PACs and raw DT ash (DT_r) and is even comparable to alum in terms of HA removal. The excellent HA removal performance of DT_s was mainly attributable to the formation of anhydrite and lime during coal combustion. The removal efficiency of HA strongly depends on temperature, initial pH, and DT_s dosage. From the results obtained in this study, it is revealed that the calcium-enriched coal ash can be used as an efficient and cost-effective coagulant to treat surface and/or waste waters that are polluted with humic substances.

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1. Introduction

Humic acid (HA) is one of the main components of humic substances, which represent 50–90% of organic matters in water from terrestrial sources, lakes, and rivers [1]. The existence of HA in water resources limits the use of microfiltration for surface water treatment, because the membrane will be contaminated by HA [2]. Moreover, HA is troublesome not only for causing color, odor, and taste problems but also for forming trihalomethanes and other halogenated organic compounds that exhibit mutagenic properties during the chlorination step in drinking water treatment [3–5]. These toxic disinfection by-products have proven to be a serious

threat to human health. Therefore, the removal of HA from water is of the utmost importance.

For the removal of HA from water, a number of methods have been reported to date, including adsorption [6–11], oxidation [12,13], coagulation [14–16] and filtration [17]. Among these, adsorption and coagulation are the most promising processes for removing HA from the aqueous phase, due to their high removal efficiencies. However, the high cost and non-regenerability of commercial adsorbents and coagulants greatly hinder their practical large-scale applications. Therefore, it is desirable to find an alternative low-cost material for the adsorption or aggregation of HA in aqueous solution.

Coal ash is a solid waste generated during the combustion or gasification of coal for power generation or syngas production. The current annual production of coal ash worldwide is estimated at approximately 750 million tons [18]. Presently, a substantial amount of these wastes is disposed in landfills and/or lagoons at a significant cost [19], and only 16% of the total ash worldwide is potentially utilized for various applications such as cement production, synthesis of zeolite, mine backfill, and road sub-base [19]. In recent years, considerable investigations have reported on the utilization of coal ash as a low-cost adsorbent for removing some pollutants, such as heavy metals, dyes, and phenolic compounds in a wastewater stream or flue gas [20–23]. Wang et al. [24,25] reported the utilization of fly ash and its derived unburned carbon for the removal of HA from aqueous solution. They concluded that higher surface area and pore volume of fly ash and unburned carbon would result in higher adsorption of HA. However, to date, no information has been given with respect to the effect of calcium-rich coal ash on the removal of HA from aqueous solution.

In our previous paper [26], we have demonstrated synergistic and in-situ desulfurization effects during co-processing the binary mixtures of calcium-rich coal and an aqueous condensate (AQ) from biomass carbonization. The same effects can also be achieved when co-processing a calcium-deficient DT coal with an AQ solution containing dissolved shell wastes.

This study is a follow-up to our previous paper [26]. The focus of this study is to explore a potential use of calcium-enriched coal ash as a coagulant for removing HA from water, providing an additional benefit to co-processing calcium-enriched coal and an aqueous condensate from biomass carbonization. Two commercial powdered activated carbons (PAC) and aluminum sulfate (alum) were selected for comparison. In addition, a series of batch experiments was conducted to study the influence of ash dosage, initial pH and temperature on the removal of HA.

2. Experimental

2.1. Materials

A bituminous coal from Shanxi Datong (DT) was used as the starting material for ash preparation. The raw DT ash was obtained by directly burning DT coal at 1123 K in a muffle furnace with air circulation. The resulting ash is denoted DT_r. The calcium-modified DT ash was prepared by firstly blending DT coal and AQ containing dissolved shell wastes. The detailed procedures have been reported elsewhere [26]. Briefly, approximately 300 mg of Manila clam shell powder was previously dissolved in 3 mL of AQ. Then, 2.5 g of the above solution containing dissolved shells was added to the crucible and mixed with 5.0 g of DT coal. The resulting mixture (denoted as DT/AQ-MS in Ref. [26]) was then burned under the same conditions as above. The ash sample obtained in this way is denoted DT_s hereafter.

In adsorption experiments, two commercially available PACs, referred to as PAC-C and PAC-P, were used as reference materials

for the removal of HA from aqueous solution. PAC-C was prepared from a woody material by chemical activation with phosphoric acid, and PAC-P was obtained from an anthracite coal by physical activation with steam at 1173 K. Alum ($Al_2(SO_4)_3 \cdot 18H_2O$) was purchased as analytical grade from Xinxing Chemical Reagent Ltd. (Shenyang, China) and employed in coagulation tests.

The HA sample was purchased as a powder product from Guangfu Fine Chemical Research Institute (Tianjin, China) and used as received.

2.2. Analyses

The chemical compositions of the coal ash were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and were reported as the percentage of the total weight for each metal elemental oxide. The amount of Ca^{2+} ions (mg/L) released from coal ash in deionized water or in a HA filtrate was also obtained by ICP-AES analysis.

The chemical forms of the mineral constituents in coal ashes were determined by X-ray diffraction analysis (XRD) on a Rigaku diffractometer (50 kV, 300 mA, Cu Kα radiation). The scattering angles ranged from 10° to 90°, with a scanning speed of 2° per minute.

The surface and pore structures of coal ash and PACs, including the BET surface area (S_{BET}), average pore size (D) and total pore volume (V_t), were determined by an automated adsorption apparatus (Micromeritics, 3Flex). The BET surface area and pore volume were obtained by applying the BET equation and $p/p_0 = 0.95$ to the adsorption data, respectively. The pore size distributions (PSDs) were derived using the Horvath–Kawazoe (H–K) method for micro-pores and the Barrett–Joyner–Halenda (BJH) method for meso- and macro-pores.

2.3. Humic acid solution

The preparation and calibration methods of HA solutions have been reported elsewhere [27]. A stock HA solution was previously prepared by dissolving 120 mg of dry HA powder in 250 mL of a sodium hydroxide solution (1.2 g/L) and stirring on a magnetic stirrer hot plate at 353–363 K for 30 min. The obtained solution was then filtered using a 0.45 μm polycarbonate membrane to remove the insoluble matters. The amount of dissolved HA in the filtrate was calculated by subtracting insoluble residuals from the initial mass of HA. The final concentration and pH of HA stock solution was 39.85 mg/L and 8.96, respectively. This solution was further diluted to get several sub-solutions with HA concentration ranging from 0.5 to 39.85 mg/L for determining a calibration curve.

2.4. HA adsorption and coagulation tests

In the present study, HA removal tests were conducted in batch mode. The characteristics of HA adsorption on PACs and coagulation by alum or calcium-modified coal ash were studied at pH 7.0 and room temperature. For each test, 10 mg of adsorbent or coagulant and 10 mL of HA working solution were added to a 20 mL glass bottle and shaken for 5 min. All solutions were kept in a static state and taken out at different time intervals. The sampling solution was filtrated with a 0.45 μm polycarbonate membrane to remove solid adsorbents for analysis.

Apart from the above comparison tests, DT_s was selected to study the effects of initial pH, temperature, and dosage on the removal of HA from aqueous solution. The individual procedure is described as follows:

To study the effect of initial pH on HA removal efficiency, a predetermined quantity of H_2SO_4 (0.1 mol/L) or NaOH (0.1 mol/L) was added to the solution to achieve a target pH in the range of 4–10.