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Adsorption of sulfur dioxide using nickel oxide/carbon adsorbents produced by one-step pyrolysis method

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ABSTRACT

In this study, we present the preparation of nickel oxide/carbon using sewage sludge as precursor and nickel nitrate as activating agent by one-step pyrolysis method. The nickel oxide could be self-assembled on the surface of sewage sludge based carbon materials. The surface modified carbon adsorbent was characterized by Brunauer–Emmett–Teller (BET) surface area, scanning electron microscopy (SEM), Fourier-transform infrared spectra (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and energy dispersive spectrum (EDS) to illustrate the successful deposition of nickel oxide on the carbon adsorbent. The effect of the surface activation treatment on the adsorption performance of the carbon adsorbents was investigated. The results indicated that the prepared nickel oxide/carbon adsorbents produced beneficial effects on sulfur dioxide adsorption performance due to the existence of nickel oxide and nickel particles. Furthermore, the Fourier-transform infrared spectra and thermogravimetric method are used to illustrate the possible adsorption mechanism.

1. Introduction

Growing concerns about the environment have resulted in the development of new environmentally friendly technologies, new materials, and new ways to reduce and minimize wastes [1,2]. The abundance of raw sewage sludge produces one of the major environmental problems. Various methods have been proposed for its disposal [1–4]. A more efficacious and safer alternative is the pyrolytic carbonization of sludge to obtain useful adsorbents [5–9]. Since 1976, several patents have been issued on the carbonization of sewage sludge and various applications of the final materials [3,4]. The carbonization process has been studied in detail using different chemical agents and various conditions [10–12]. Materials obtained by the various treatments have surface areas between 100 and 500 m^2/g, and could be used as cheap and good adsorbents for heavy metals, dyes and toxic gases containing sulfur [10–12]. But their performance as adsorbents have been demonstrated to be much worse than that of activated carbons.

Differences in capacities result from differences in porosity, surface chemistry, and inorganic constituents of the adsorbents. Recently, much attention has been paid in the modification of carbon adsorbents to improve their affinity with certain pollutants [13–15]. Chemical and thermal methods are commonly employed for this purpose. By chemical treatment, some functional groups could be introduced onto the carbon surface by incubating the carbon materials with various chemicals, including acid/base, strong oxidants, salts or surfactants [16–21]. Thermal treatment could also be used to change the surface chemistry characteristics of the adsorbents, and it is also considered to be more effective for the adjustment of the porous structure [16].

The incorporation of the metal particles on the surface of carbon materials could be considered as another way to alter/enhance their surface chemistry properties, but preserving the properties of the carbon matrix. The excellent sorption ability of these materials is linked to the catalytic action of metals, which present in various forms in the final products [22–25]. Their chemical forms along with their location on the surface are reported as important factors to govern the pollutant removal capacities. The former investigation was focused on the modification of metal on the activated carbon by carbonation firstly and then activation methods. The activated carbons are prepared mostly by two-step physical activation method and one-step chemical activation. Physical activation involved carbonization of the raw material and activation with steam, air or CO_2. Chemical activation involves impregnation of the raw material with chemical agents including phosphoric acid, sulfuric acid, potassium hydroxide and zinc chloride in an inert atmosphere. In our study, the raw sewage sludge materials are carbonized firstly to prepare pyrolytic carbons, which are then impregnated with nickel nitrate salt solution. The nickel oxide could be self-assembled on the formed sewage sludge based carbon by the one step direct pyrolysis method to form the nickel oxide/carbon.

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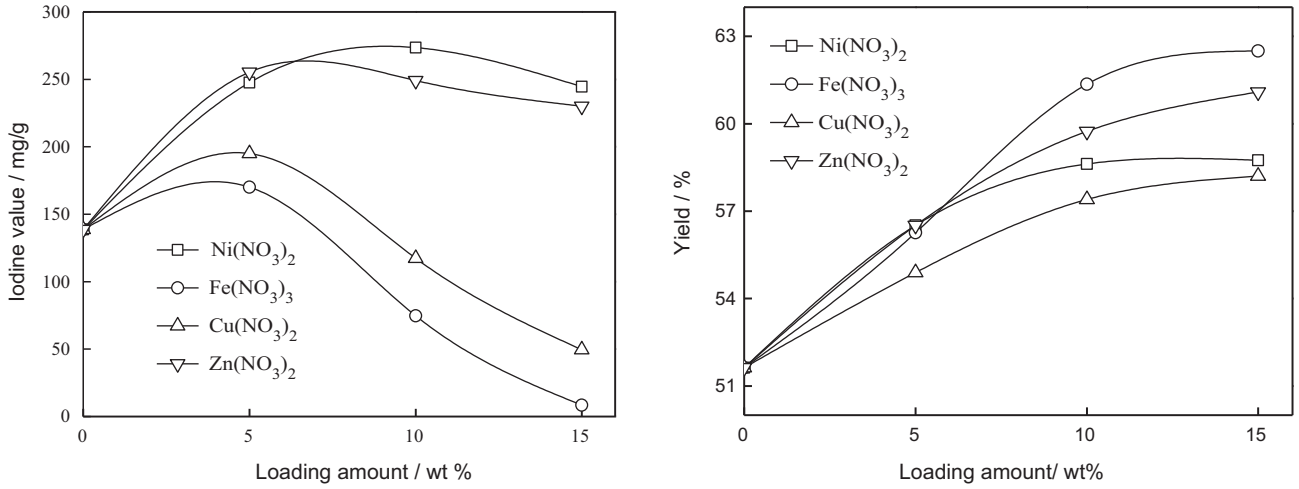

Fig. 1. The effect of loading amount of different activation solution on the iodine value and yield of carbon adsorbents.

The objective of present work is to investigate the role of metal oxides in nickel oxide/carbon for the sulfur dioxide adsorption performance. In this study, nickel oxide/carbon is prepared by direct preparation method. The changes of the surface physical and chemical properties after activation are characterized and analyzed. The sulfur dioxide adsorption capacity of the prepared carbon adsorbent is measured according to breakthrough test. Furthermore, the possible adsorption mechanism is deduced based on the Fourier-transform infrared spectra and thermogravimetric results.

2. Materials and methods

2.1. Preparation of the carbon adsorbents

The precursor materials are surplus sludge obtained from the sewage treatment pant. The raw sludge is dried at 105 °C for 24 h to achieve constant weight, and then comminuted. The carbon adsorbents are prepared by carbonization of sewage sludge at 550 °C for 1 h. Detailed procedures are described as follows: 10 g sewage sludge materials are loaded in quartz pipe after pretreatment, and then are carbonized at 550 °C for 1 h under nitrogen atmosphere. Then, the samples are cooled.

2 g pyrolytic carbon samples are pretreated with nitrate and then impregnated with different mass ratio of $Ni(NO_3)_2$, $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Zn(NO_3)_2$ solution to obtain certain loading amount. After stirring for 24 h, samples are dried in oven and then calcined under N_2 flow at 400 °C to form the metal oxides/carbon.

2.2. Characterization of the carbon adsorbents

The methylene blue (MB) capacity and iodine value are determined by China National Standards (GB/T12496.8-1999 and GB/T12496.10-1999) to examine the adsorption capability of the prepared samples.

The morphologies of the samples are obtained with the scanning electron microscopy (SEM) (Hitachi, S-3000N) using an accelerating voltage of 20 kV. The structures of samples are analyzed with Fourier transforms infrared spectroscopy (FTIR) (Bruker Tensor 27 spectrometer in the range of 500–4000 cm^{-1} on sample pellets made with KBr). Brunauer–Emmett–Teller (BET) surface areas and pore volumes are measured on a Micromeritics ASAP 2020 sorptometer using nitrogen adsorption at 77 K. Thermal analysis is carried out using Thermal Analyzer (New Castle, DE, USA). The heating rate is 10 °C/min in a nitrogen atmosphere at 100 mL/min flow rate. The samples are heated up to 800 °C. The main elements content are analyzed by energy dispersive spectrometer (EDS).

2.3. SO_2 breakthrough capacity

Dynamic tests are carried out at room temperature to evaluate the capacity of the adsorbents for SO_2 removal under dry condition. 1 g adsorbent samples are packed into a glass column (internal diameter 9 mm). Dry air containing 0.12% (1200 ppm) SO_2 is then passed through the column of adsorbent at 100 mL/min. The SO_2 breakthrough is monitored using a MultiRae Plus monitoring system with an electrochemical sensor. The test is stopped at the breakthrough concentration of 20 ppm (sensor limit). The adsorption capacities of each adsorbent in terms of milligrams of SO_2 per gram are calculated by integration of the area above the breakthrough curves and from the SO_2 concentration in the inlet gas, flow rate, breakthrough time, and mass of adsorbent. For each sample, the SO_2 test is repeated at least twice.

3. Results and discussion

3.1. The optimization of preparation condition

The pyrolytic carbon is prepared under the optimum condition using sewage sludge as the precursor. The carbonation experiment is operated at 550 °C for 1 h. Then, the different metal nitrate is impregnated with the above pyrolytic carbon. After the calcination, the relative metal oxide is deposited on the carbon surface. The iodine adsorption and the yield are used to evaluate the performance of carbon adsorbents.

In order to optimize the reaction conditions, the effect of the loading amount of different activation solution on the iodine value are studied, which are shown in Fig. 1. With the increase of loading amount, the iodine value increase firstly and then decrease. 10% $Ni(NO_3)_2$ show the best adsorption capacity. The other activating agents with 5% loading amount have the best adsorption capacity. In the meanwhile, the yield of metal oxide/carbon increase as the increase of activation agents amounts. Compared with the other activation solution, the $Ni(NO_3)_2$ solution shows the highest iodine adsorption capacity. It can be seen that adsorption capacity has the sequence of $Ni(NO_3)_2 > Fe(NO_3)_3 > Cu(NO_3)_2 > Zn(NO_3)_2$. Therefore, the $Ni(NO_3)_2$ solution is selected as the activation agent in the following studies.