Journal of Analytical and Applied Pyrolysis 124 (2017) 42–50

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Analysis of devitalization mechanism and chemical constituents for fast and efficient regeneration of spent carbon by means of ultrasound and microwaves

Chunyang Li[a,b,c,d], Libo Zhang[a,b,c,d], Hongying Xia[a,b,c,d,*], Jinhui Peng[a,b,c,d], Song Cheng[a,b,c,d], Jianhua Shu[a,b,c,d], Qi Zhang[a,b,c,d], Xin Jiang[a,b,c,d]

[a] State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming, Yunnan 650093, China
[b] Yunnan Provincial Key Laboratory of Intensification Metallurgy, Kunming University of Science and Technology, Kunming, Yunnan 650093, China
[c] National Local Joint Laboratory of Engineering Application of Microwave Energy and Equipment Technology, Kunming, Yunnan 650093, China
[d] Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China

ARTICLE INFO

Article history:
Received 1 January 2017
Accepted 28 February 2017
Available online 2 March 2017

Keywords:
Spent carbon
Organic compounds
Molecular force
Covalent bond
Regeneration

ABSTRACT

The spent carbon that contained kinds of organic compounds was investigated and characterized by techniques of nitrogen adsorption, SEM, FT-IR and Raman, GC–MS and TG-DSC. Results found that the combination forms between amounts of miscellaneous organic compounds and carbon molecules were the molecular force and covalent bond, these combined types mainly caused the devitalization of spent carbon, and they influenced the surface chemistry properties of carbon deeply. GC–MS analysis illustrated that the spent carbon contained organic and inorganic compounds of alkanes, benzenes, ketones, alcohols, sulfide, nitrogen and halogens substituent compounds. Majorities of organic compounds were endothermic through the TG-DSC analysis. For obtaining the faultless-structure carbon, the spent carbon was regenerated by using techniques of ultrasound and microwaves. Regeneration experiment of different types compounds was implementing by stepwise stratificational way. The regeneration carbon's adsorption property was much better than the conventional regeneration technics', the regeneration rate achieved 83%. The BET surface area, total volume and average diameter of regenerated carbon were 1080 m^2/g, 2.5 cm^3/g and 4.7 nm, respectively, it was much better than spent carbon's.

1. Introduction

The huge surface area and superb adsorption properties are the good nature for porous carbonaceous materials, like activated carbon, it have been facilitating the application in many fields [1]. The extensively uses for activated carbon includes the purification of waste gas and effluent, as catalyst supports for treating waste water, as adsorbents for the solvent recovery or decoloring, all of those applications are aiming at the fast and convenient production, environmental protection and reusing resource [2–5]. However, the increasing accretion of pollutants adsorbed on the surface of activated carbon will lead to continuing discounts both in adsorption capacity and structure properties of activated carbon, being as spent carbon. Once exhausted of their adsorption capacity, spent activated carbons can be landfilled, incinerated, thermally regenerated for reuse or replaced by fresh activated carbon [6,7]. If discarded, the landfilled carbon potentially creates a hazardous waste problem. Use of activated carbon only once is not only inefficient but generates excessive waste to the environment. Researches also are fond that the life cycle of activated carbon is short relatively in treating wastes, therefore, the carbon must be regenerated [8]. The further researches are also showed that inactivation phenomenon of spent carbon is temporary and convertible, if the regeneration work done well, it could be reutilized completely according to the deep inactivation mechanism [9,10]. For further reason of environment and economic, the removal of pollutants and regeneration utilization of spent carbon also become important and challengeable to the researchers, which response to the modern ideas of recycling resource positively [11].

Thermal, chemical, microbiological and vacuum are the four basic regeneration techniques according as common categories

* Corresponding author at: State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming, Yunnan 650093, China.
E-mail address: hyxia@kmust.edu.cn (H. Xia).

http://dx.doi.org/10.1016/j.jaap.2017.02.025
0165-2370/

[12–16]. By far the most extensively used technique is thermal regeneration under steam or an inert atmosphere. Unfortunately, the thermal regeneration process by conventional heating is time consuming and after successive heating and cooling cycles, the carbon becomes damaged. Therefore, the innovative regeneration methods by microwaves, ultrasound or electrical currents are developed and applied in many fields [17–19]. Microwave assisted regeneration is one of the most popular methods because of the obvious advantages: interior heating, higher heating rates, selective heating, greater control of the heating process and good treatment effects [20]. Ultrasound assisted regeneration have the good penetrability, to some degree its physico-chemical effects are highly significant for the spent carbon, like leading to the main thixotropicity for transition of gel-sol, making macromolecule organics depolymerized [21]. The foremost goal for spent carbon regeneration is to eliminate those pollutants and to restore the previous adsorption capacity, carbon structure is as important as adsorption capacity. For being successful carbon, porous structure of spent carbon should not alter, carbon substantial mass should not loss, neither, carbon structure and adsorption capacity are closely linked, and both are the good natural properties that activated carbon must have [7,22]. The pollutants occupied in carbon are multifarious usually, they might be divided into two mainly categories: organic wastes and inorganic wastes. Compared with traditional thermal regeneration technics, microwave and ultrasound methods could directly act on waste compounds of spent carbon, depolymerizing macromolecule chains that bond between carbon molecule and kinds of organic compounds, providing enough mechanical energy to clean the corpuscles that concealed in deep carbon aperture [23–26].

In this research, spent carbon used in zinc sulfate solution contained different organic compounds. Polymerization ring-opening mechanism and the carbon functional groups have been explored deeply, and applied successfully in regeneration process. According to the accurate assay, alkanes, benzenes, ketones, alcohols and sulfide, nitrogen and halogens substituent compounds groups show good polymerization ratio, i.e., higher percentage of polymers exactly is the reason that resulted the spent carbon's inactivation [27,28]. Ultrasound and microwave technic are applied respectively to clean and eliminate those compounds, so good adsorption capacity carbon and relatively-perfect structure carbon could be obtained.

2. Experimental

2.1. Materials and instruments

Spent carbon was taken from zinc hydrometallurgical plant (Yunnan, China).

The pore structure properties of spent carbon and regenerated carbon was detected by nitrogen adsorption-desorption apparatus at 77 K (Quant chrome, Autosorb-1-C), data of BET surface area, average pore diameter, total pore volume and size distribution could be obtained and fitted precisely [29].

Morphology of the spent carbon and regenerated carbon was observed by field emission scanning electron microscopy (SEM; Philips XL30ESEM-TMP). FT-IR spectra was used to determine potential chemical functional groups in spent carbon (Nicoleti S10; USA). Raman spectrometer was used to supplement detecting nopolar functional groups in spent carbon (INAIA; RENISHAW).

2.2. GC–MS

The chemical constituent and types of organic compounds in spent carbon was analyzed by GC–MS (TRACE DSQ; DB5; USA).

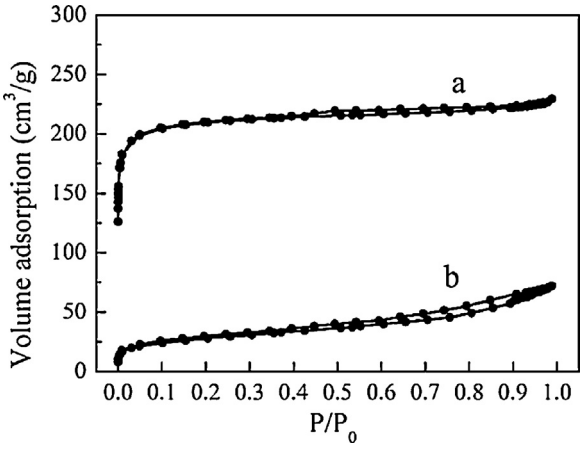

Fig. 1. N_2 adsorption-desorption isotherms.

High molecule weight compounds separated by subjecting the samples to pass through the GC columns of the dementions: 30 M*0.25 mm*0.25 μm, Helium is used as carrier gas at constant flow rate of 1.0 mL/min, starting temperature is 40 °C, keeping this state for 3 min and then heating as rate of 10 °C/min to 200 °C, then heating as 40 °C/min to 280 °C, remaining 5 min. Chromatographic peaks are identified with NIST mass spectral data library and the retention times are compared with standard compounds listed in Wiley Registry of MASS SPECTRAL DATA 8th EDITION and NIST 2008 Mass Spectral Libraries V2.2 [30].

2.3. Regeneration experiment of spent carbon

Researches indicated that organic compounds dissolved in ethanol easily and quickly. Similarity principle was applied in spent carbon. 500 g spent carbon was dissolved accurately in enough ethanol solution, impregnating with ultrasound bath assisted for several minutes in room temperature, then filtrating in vacuum condition, the filtrate would be taken for another analysis and characterization, while the filter residue was adding and mixing with moderated powdered NaH_2PO_3. Setting the different parameters in high temperature-microwave reaction furnace, putting the filtrated spent carbon in it, recording the commensurate data of parameter. The experimental procedure was operated to obtain the parallel data, average value was needed to have an accurate result.

3. Results and discussion

3.1. Porous structure analysis

Nitrogen adsorption-desorption isotherm was the standard procedure to determine carbonaceous adsorbent porosity. Fig. 1 showed the isotherms of spent carbon (curve b) and regenerated carbon (curve a). Both rising trends were gentle and slow relatively, hysteresis loops were observed in two curves, high P/P_0 class ranged from 0.4 to 0.9. It was reasonable to say that isotherms were the combined types of I and II, according to the IUPAC [31]. N_2 adsorption-desorption for curve b was very low, indicating that spent carbon was not good at adsorption because of devitalization, its porous structure was jammed and broke by organic compounds. Curve a was the isotherm for regenerated carbon, before $P/P_0 < 0.1$, the trend of N_2 adsorption was fast-growing, after that it became slow, but kept ascending obviously, demonstrating that reversible single layer adsorption was possible and it accumulated later in middle and high P/P_0 class.

The pore width distribution of spent carbon and regenerated carbon were shown in Fig. 2, thick line substantiated the pore width