Journal of the Taiwan Institute of Chemical Engineers 45 (2014) 1733–1738

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Effect of thermal regeneration of spent activated carbon on volatile organic compound adsorption performances

Irfan Khursheed Shah [a,*], Pascaline Pre [b,1], B.J. Alappat [a,2]

[a] Department of Civil Engineering (Environmental Engineering Group), Indian Institute of Technology Delhi, Hauz Khas, 110016 New Delhi, India
[b] GEPEA UMR-CNRS 6144, Ecole des Mines de Nantes, Department of Environment and Energy Systems, La Chantrerie, 4, rue Alfred Kastler, BP 20722, 44307 Nantes Cedex 3, France

ARTICLE INFO

Article history:
Received 10 July 2013
Received in revised form 29 November 2013
Accepted 12 January 2014
Available online 13 February 2014

Keywords:
Activated carbon
Regeneration
Thermo gravimetric analysis
Thermal swing adsorption
Volatile organic compounds

ABSTRACT

Thermal swing adsorption (TSA) is widely used as a process in industry for gas purification and air treatment. This study enlightens the effects of thermal regeneration of an activated carbon spent with volatile organic compounds (VOCs) on its adsorption capacities. Ketone group VOCs (acetone and methyl ethyl ketone (MEK)) were selected for this study as they are sensitive to oxidation reactions at low temperature, and for this reason, are responsible for many reported fire accidents on industrial units. Cyclic adsorption–desorption experiments were performed using a thermo-gravimetric analyzer (TGA). First cycle adsorption capacity of acetone and MEK at 20 °C was 5.06 mol/kg and 6.41 mol/kg, respectively. The regeneration was performed with air at temperature ranging from 80 °C to 160 °C. Multiple cycles were successively repeated to assess the variations in the material adsorption performances. For acetone, it was found that after first regeneration cycle conducted at 80 °C, the adsorption capacity was restored at nearly 95%, and remained unchanged after 8 successive cycles. For MEK, continuous degradation of the adsorption capacities was observed, which was more drastic when the temperature was low and reached 3.4 mol/kg after 8 cycles. This could be related to the partial decomposition of the chemisorbed MEK molecules. Effect of air humidity was furthermore examined and a protocol was developed to guarantee good regeneration efficiency of MEK spent activated carbon at a moderate temperature.

1. Introduction

Volatile organic compounds (VOCs) cover a great variety of molecules including alkanes, ketones, aromatics, paraffins, olefins, alcohols, ethers, esters, halogenated and sulfur hydrocarbons [1,2]. Owing to their high vapor pressure under normal conditions, they are easily vaporized into the atmosphere and greatly contribute to air pollution. VOC emissions into environment are anthropogenic as well as biogenic. Anthropogenic emissions have various sources, and result mainly from transport and industrial activities. They are especially used as solvents, degreasers or cleaning agents in many processes of oil, chemical and food industries [3–5]. VOCs are toxic [6] and participate in the formation of tropospheric ozone [7], photochemical smog in urban air [8,9] and also promote acid rain [10]. Therefore reduction of VOC emissions from ambient air is deemed as crucial.

Adsorption onto activated carbon (AC) is among the most current technologies used for air purification and solvent recovery purposes. In 2005, the per capita consumption of ACs per year was 0.5 kg in Japan, 0.4 kg in the U.S., 0.2 kg in Europe, and 0.03 kg in the rest of the world [11]. World demand for virgin AC is forecast to reach 2.3 million metric tons by 2017. Besides the strong demand for water and liquid treatment applications, the gas phase application for air purification is poised for unprecedented growth in the future, with a forecast compound annual growth rate of over 22% through 2017 [12]. Consumption of ACs for industrial use has now become an indicator of development and environmental management efficiency.

Regeneration of ACs has multiple benefits regarding the environmental impact, the economics and the operational ease of the adsorption processes [13]. In many cases, spent carbon adsorbents are to be treated as hazardous waste and need to be incinerated [14]. Spent ACs may be toxic and flammable [15] or explosive [16]. Exposed to ambient air, they may adsorb moisture or undergo oxidation reactions causing local heating and desorption of adsorbed pollutants [17], thus creating a hazardous environment. Spent AC dumping also causes nuisance due to odor release.

* Corresponding author. Tel.: +91 9419212898.
E-mail addresses: asirfan@yahoo.com (I.K. Shah), Pascaline.Pre@mines-nantes.fr (P. Pre), bjalappat@yahoo.com (B.J. Alappat).
[1] Tel.: +33 02 51 85 82 68.
[2] Tel.: +91 1126596254.

http://dx.doi.org/10.1016/j.jtice.2014.01.006
1876-1070/

Regeneration can be proved as double rewarding as it allows stabilization of exhausted ACs and helps in recovering material resources, thereby minimizing demands of both solvents and virgin adsorbents [18].

Optimization of the AC bed regeneration process in terms of efficiency and energy requirement appears as an important deal for the improvement of VOC capture technologies. Whereas the adsorption step has been extensively studied in the literature with the aim to answer some practical issues such as selection of the carbon adsorbent, bed design, effect of gas inlet conditions on abatement performances, thermal regeneration of AC beds has been scarcely investigated despite its efficiency is a key parameter for adsorption process [19,20]. Indeed the regeneration rate of the AC bed, as well as the duration of the thermal swing adsorption (TSA) cycle, impacts directly the size and the number of columns of the purification unit. Moreover, thermal decomposition of oxygenated compounds adsorbed onto the carbon surface may cause bed ignition hazards. So a mean to prevent fire bed accidents is to better understand and control the VOC–AC system reactivity during bed heating.

In this paper, the thermal regeneration of AC spent with ketone group compounds is considered. As ketones may be decomposed into peroxides and carboxylic acids at temperature as low as 100 °C under oxidative conditions, regeneration of AC beds spent with this kind of organic molecules is especially sensitive to fire hazards [21]. The purpose of this study was to examine the effect of different operating conditions applied during thermal desorption by dry and wet air of an AC spent with acetone and methyl ethyl ketone.

2. Materials and methods

Adsorption and desorption data were measured onto a commercial AC, supplied by Arkema – CECA, hereafter referred as BGX. The textural properties, such as BET surface area (S_{BET}) and micropore volume, were determined from N_2 adsorption–desorption isotherms at 77 K using a volumetric apparatus (ASAP 2010, Micrometrics). Prior to textural characterization, the samples were degassed at 350 °C for 48 h. The S_{BET} of the BGX was 1500 m^2/g and was derived from the Brunauer, Emmett and Teller (BET) model using adsorption isotherm in the relative pressure range between 0.2 and 0.9. The micropore volume was found as 0.62 cm^3/g and was calculated from the Horwarth Kawazoe theory [22], in the pore size range between 0.4 and 2 nm. The mesoporosity of the sample was 0.67 cm^3/g, and was determined by mercury porosimetry, and corresponds to pore sizes between 8 and 50 nm.

Surface functional groups on activated carbon surface were identified by Fourier Transform Infrared spectroscopy. FTIR analysis of the AC samples was conducted using Vertex 70 spectrophotometer.

The adsorbent was spent with acetone and methyl ethyl ketone (MEK). The affinity of a carbon adsorbent toward a gas compound depends on its molecular properties like the polarisability, the vapor pressure and the molar volume [23].

The adsorption–desorption cycles were conducted with a TG-DSC apparatus (Setaram; TG-DSC 111). Brooks's smart mass flow controller with digital control was employed to control the gas flow feeding the cell containing material. Experimental setup used for the study is shown in Fig. 1. Both during the adsorption and desorption steps, the carrier gas flow rates were fixed at 5 L/h. Adsorption of VOC onto the sample contained in the cell was carried out at constant temperature, 20 °C, whilst thermal desorption was conducted in the temperature range between 80 °C and 160 °C. During the adsorption step, the inlet air flow was continuously loaded with a constant VOC concentration at 50 g/m^3. The VOC concentration was maintained by continuous injection of the liquid solvent at constant and predetermined speed, via a syringe infusion pump. Prior to the first adsorption–desorption cycle, the virgin sample was subjected to N_2 flow into the cell maintained at 120 °C for 1 h in order to remove humidity traces possibly contained in the material.

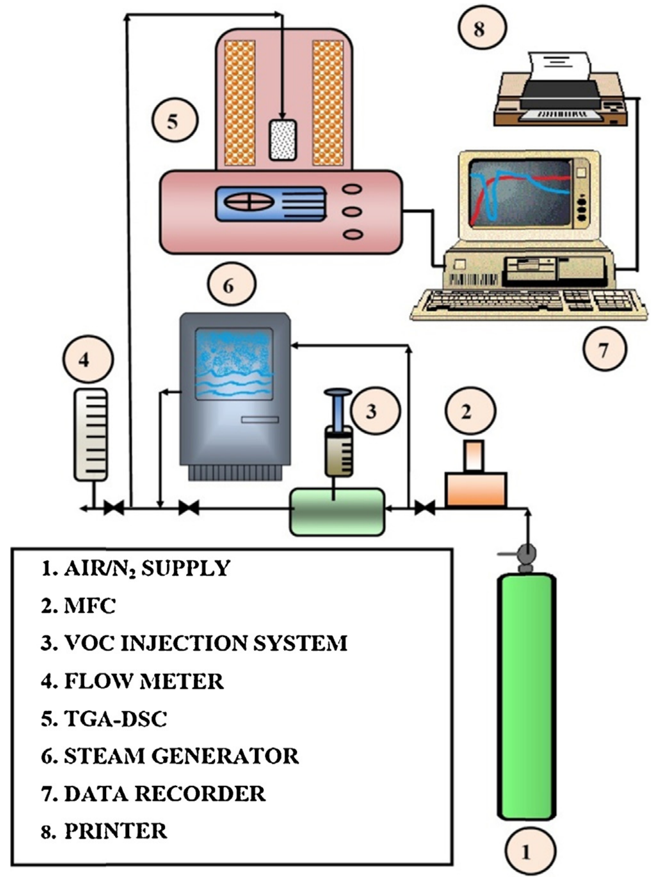

Fig. 1. Schematics of the experimental set-up.

During adsorption, the mass gain was continuously recorded untill equilibrium was achieved. Equilibrium adsorption data were determined when no more change in the sample mass was recorded after 1 h. The regeneration step was afterwards undertaken by flowing air stream into the cell.

Desorption experiments were carried out by controlling the temperature of the sample and the relative humidity (RH) of the gas. The total duration of the regeneration tests was 2 h. Experimental conditions of the tests are specified in Table 1.

For all tests, except test 8, the inlet flow rate and regeneration temperature along whole duration of desorption step were maintained constant. During test 8, desorption was initially carried out for 10 min with a 40% RH gas stream at 120 °C, and completed at the same temperature under dry gas flowing. Successive adsorption–desorption cycles were repeated for each test.

Table 1
Experimental conditions for different tests.

Test	Adsorbed VOC	Conditions of regeneration	Number of cycles
1	Acetone	80 °C–0% RH	9
2	MEK	80 °C–0% RH	10
3	MEK	120 °C–0% RH	10
4	MEK	160 °C–0% RH	10
5	MEK	120 °C–5% RH	3
6	MEK	120 °C–10% RH	3
7	MEK	120 °C–15% RH	3
8	MEK	120 °C–40% RH during 10 min – 0% RH after	3