Influence of activated carbon characteristics on toluene and hexane adsorption: Application of surface response methodology

Mª Teresa Izquierdo [a],[*], Alicia Martínez de Yuso [b], Raquel Valenciano [b], Begoña Rubio [a], Mª Rosa Pino [b]

[a] Instituto de Carboquímica, ICB-CSIC, c/Miguel Luesma, 4. 50018 Zaragoza, Spain
[b] Universidad San Jorge, Autovía A23 Zaragoza-Huesca km 510, 50830 Villanueva de Gállego, Zaragoza, Spain

ARTICLE INFO

ABSTRACT

The objective of this study was to evaluate the adsorption capacity of toluene and hexane over activated carbons prepared according an experimental design, considering as variables the activation temperature, the impregnation ratio and the activation time. The response surface methodology was applied to optimize the adsorption capacity of the carbons regarding the preparation conditions that determine the physicochemical characteristics of the activated carbons.

The methodology of preparation produced activated carbons with surface areas and micropore volumes as high as 1128 m^2/g and 0.52 cm^3/g, respectively. Moreover, the activated carbons exhibit mesoporosity, ranging from 64.6% to 89.1% the percentage of microporosity. The surface chemistry was characterized by TPD, FTIR and acid–base titration obtaining different values of surface groups from the different techniques because the limitation of each technique, but obtaining similar trends for the activated carbons studied. The exhaustive characterization of the activated carbons allows to state that the measured surface area does not explain the adsorption capacity for either toluene or n-hexane. On the other hand, the surface chemistry does not explain the adsorption results either. A compromise between physical and chemical characteristics can be obtained from the appropriate activation conditions, and the response surface methodology gives the optimal activated carbon to maximize adsorption capacity. Low activation temperature, intermediate impregnation ratio lead to high toluene and n-hexane adsorption capacities depending on the activation time, which a determining factor to maximize toluene adsorption.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Non-methane volatile organic compounds (NMVOCs) are atmospheric pollutants coming from the use of solvents in the industry and the storage, distribution and use of fossil fuels. NMVOCs have direct effect on human health. Moreover, they participate in reactions in the atmosphere with other pollutants contributing to the formation of tropospheric ozone calling them ozone precursors [1].

According to the European Environmental Agency (EEA) 34% of NMVOCs come from energy related sectors with a further 39% from the solvents sector [2].

Toluene and n-hexane are NMVOCs commonly used as solvents in the industry. Toluene can be considered as representative of aromatic hydrocarbons solvents. It is mainly used to dissolve paints and adhesives. Hexane can be considered as representative of aliphatic hydrocarbons. Hexane is mainly used in the

formulation of glues for shoes and leather products as well as for cleansing and degreasing all sorts of items.

The proposed NECD (National Emission Ceilings Directive) target required a 60% reduction of NMVOCs emissions below 1990 emissions by 2010. No new ceiling has been established up to now. According to the NEC Directive Status Report published by the EEA [3], NMVOC projections for the EU-27 are 10% below the aggregated emission ceiling given in Annex I for 2010, but still 5% above the Annex II ceiling. Thus, allowable technology is needed to control the NMVOCs emission to the atmosphere to comply with the current NMVOCs emission regulations.

Carbons have recognized adsorption capacity and versatility for different applications [4]. The adsorption of NMVOCs over carbons can operate under a wide range of conditions. Especially remarkable are the capability of working at low NMVOCs concentration [1]. Moreover, they have the advantage of the recovery of these compounds by desorption to be used again [5].

The efficiency of a given carbon to adsorb a given NMVOC is characterized by the quantity adsorbed at a given adsorbate pressure. The adsorption capacity of a carbon will depend on surface area, pore volume and microporosity [4]. Another

* Corresponding author.
  E-mail address: mizq@icb.csic.es (M.T. Izquierdo).

important factor for the removal of polar compounds is surface chemistry [4,6]. In addition to the influence of adsorbent characteristics on adsorption capacity, the composition of gas stream might be specially influencing the NMVOC removal capacity of carbons.

The preparation of activated carbons from biomass and agricultural wastes is widely known [4,7]. However, some aspects have been developed in lower extent: the production of activated carbons related to their utilization [4], the recovery of solvents and NMVOC removal in low concentration streams.

In this context, the objective of this study was to evaluate the adsorption capacity of toluene and hexane over activated carbons prepared by chemical activation of almond shells with phosphoric acid, according to an experimental design described in [8]. According to the compilation of information carried out in this work, no study has been done on the optimization of the adsorption capacity on activated carbons from almond shells. To achieve this objective, the response surface methodology was applied to predict the physicochemical characteristics of the activated carbons that optimize the adsorption capacity.

2. Experimental methods

2.1. Preparation of activated carbons

Activated carbons have been obtained from the chemical activation with phosphoric acid of almond shells at different impregnation ratios and temperature and time of carbonization. Almond shell used as starting material is an agricultural residue from Teruel province, Spain. This material was crushed to a particle size of 0.3–0.5 mm. Average ash content of almond shell was 2.5%.

An experimental design was used to obtain the conditions to prepare the activated carbons. The parameters introduced were impregnation ratio (defined as phosphoric acid, wt./precursor, wt.), temperature and time of carbonization. A total of 12 activated carbons were prepared according the experimental design. Samples were labelled indicating temperature of carbonization, followed by impregnation ratio and activation time. Example: AT400R05t120 (A: almond shell; T400: activation temperature of 400 °C; R05: impregnation ratio of 0.5; t120: activation time of 120 min).

The procedure to prepare the activated carbons is as follows: mixing the almond shell with a determined amount of phosphoric acid of 89 wt.% concentration to reach impregnation ratios in the range 0.5–1.5. The suspension was shaken at room temperature during 1 h. The impregnated samples were further thermally treated at different temperatures ranging from 400 °C to 800 °C by passing through a flow of N_2 (which was kept during both heating and cooling), and maintained at the selected temperature during a time ranging from 30 to 120 min. Solid pyrolysis residues were water washed in Soxhlet until pH > 6. The resulting activated carbons were dried at 100 °C until constant weight and stored under Ar.

More details of the experimental design and procedure of preparation of the activated carbons can be found elsewhere [8].

2.2. Characterization

Samples were characterized by temperature programmed desorption (TPD), infrared spectroscopy (FTIR), Boehm titration and N_2 adsorption.

The TPD runs were carried out with a custom built set-up, consisting of a tubular quartz reactor placed inside an electrical furnace. In a typical TPD experiment the sample was heated up to 1100 °C in Ar flow at a heating rate of 10 °C/min. The amounts of CO and CO_2 evolved at each temperature were measured continuously with a quadrupole mass spectrometer from Pfeiffer. The calibrations for CO and CO_2 were carried out by standards diluted in Ar. In a typical run 0.5 g of carbon was placed in a horizontal quartz tube reactor under a stream of 30 ml/min of Ar.

Infrared spectra of the activated carbons were obtained in a Bruker Tensor 27. A small amount of sample finely ground is placed directly on the equipment. The spectra were normalized and the baseline was corrected with the own software of the apparatus.

The selective neutralization method was used to evaluate the acidic character of the surface of the activated carbons according to Boehm's procedure [9]. The amounts of various acidic oxygen functional groups (carboxyls, lactones, phenols and carbonyls) were measured by selective neutralization using bases of different strength. Approximately 0.5 g of each sample was mixed with 50 ml of a 0.1 N solution of a base (NaOH, Na_2CO_3, $NaHCO_3$, $NaOC_2O_5$). The suspension was shaken for 24 h at room temperature. After that time, the solution was filtered and an aliquot was taken. The amount of each base neutralized by the activated carbon was determined by back-titration using HCl 0.1 N solution.

Textural characterization was performed by N_2 adsorption–desorption at 77 K. Isotherms were obtained in an apparatus ASAP 2020 from Micromeritics. Prior to the analysis, samples were outgassed at 200 °C up to a vacuum of 10^{-5} mm Hg. The volume of adsorbed nitrogen was measured from a relative pressure of 10^{-7} up to 0.995. Surface area was determined by BET method [10] applied to the adsorption branch of the isotherm. Pore volume corresponding to micropores was calculated using Dubinin–Radushkevich (DR) equation applied to the adsorption branch of the N_2 isotherm [11]. DR equation was also applied to obtain characteristic energy (E_0) and the mean pore with (L_0), estimated taken nitrogen density as 0.808 cm^{-1} and affinity coefficient as 0.33 and the relationship between E_0 and L_0 taken from [12]. Pore volume corresponding to mesopores was calculated with Barret–Joyner–Halenda (BJH) equation applied to the desorption branch of the N_2 isotherm [13]. The total pore volume was taken from the measure of adsorbed nitrogen at a relative pressure of 0.995. The percentage of microporosity can be obtained as the ratio between total micropore volume (calculated by applying Dubinin–Radushkevich equation to the adsorption branch of the N_2 isotherm) and volume adsorbed at relative pressure of 0.995 [14]. Pore size distribution (PSD) was evaluated by density functional theory (DFT) method [15].

2.3. Toluene and n-hexane adsorption

The adsorption–desorption isotherms of toluene or n-hexane vapours in static mode were obtained using a gravimetric analyser from VTI Corporation (Miami, USA). This apparatus is fully computer controlled and measures adsorption and desorption on a gravimetric microbalance. The sample temperature (298 K) is constantly monitored throughout the duration of the experiments and the variation was found to be 0.5 K. A pressure transducer in the range of 0–100 mm Hg (accurate to ±0.12%) is used to monitor de vapour pressure in the system. Approximately 100 mg of a sample of activated carbon was placed into a bucket made from stainless steel mesh and was outgassed in situ at 423 K under vacuum to a constant weight. Pressure steps in the range of p/p_0 values 0–0.95 were used to obtain the isotherms. After the equilibrium was reached, the organic vapour pressure was increased to the next set pressure value, and the subsequent uptake was measured until equilibrium was re-established.