Direct Nitrogen Enrichment of Activated Carbon Produced from Synthetic or Natural Precursor

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Introduction

The specific application of activated carbons (AC) as adsorbents for gases and vapours depends on the properties of pollutants to be removed, but the performance of the AC depends on various properties. If their porosity is the main parameter in gas adsorption, the chemical nature of their surface plays a significant role in liquid phase interactions and in their usefulness as catalyst support materials. Of particularly interest are the AC containing heteroatoms, such as oxygen, hydrogen, phosphorus, sulphur and nitrogen. Generally, the AC containing various nitrogen groups,present more basic character and increased adsorption of acidic agents is expected. These AC found widespread applications as adsorbents for hydrogen sulphide, sulphur dioxide, sulphur and carbon dioxide and as catalysts for selective oxidation of hydrogen sulphide [1,2].

The AC containing nitrogen surface groups are usually obtained, at first, from raw materials with high nitrogen content or by the introduction of nitrogen functions into the raw materials commonly used for AC production or,finally, by a chemical modification of AC already formed. The reagents most often used for the nitrogen introduction into the AC structure are ammonia, amines, urea and their derivatives [2].

This work presents preliminary information on the direct nitrogen incorporation into the activated carbons during the carbonisation / activation step. A particular attention was given to the porosity, nitrogen content and surface functionality change. Enriched AC were prepared by one step, carbonization/activation and urea modification using PET and cork as precursors.

Methods

The experimental procedure for the activated carbon production, from waste cork or waste PET, was detailed in previous paper [3]. The activated carbon sample was

produced by chemical activation with potassium hydroxide (KOH>87.5%) from a waste cork or from a waste granulated recycled PET, kindly provided by Selenis, Portugal. The urea was applied as reagent (N-reagents) introducing nitrogen functions in the AC. During the chemical activation and nitrogen enrichment, the raw materials were dry impregnated with KOH and urea. After that mixing step, with a mass ratio of urea/precursor of 1, all the mixture was submitted to pyrolysis, for 30 min at a final temperature of 973 K, achieved using a heating rate of 10 K min^{-1}, in a horizontal tubular furnace in a flow of dry nitrogen of 85 cm^3/min.

All the AC were characterised via nitrogen adsorption at 77 K, the corresponding isotherms being measured on an AutosorbiQgas adsorption manometric equipment from Quantachrome. Prior to that, the samples were outgassed up to 573K over a period of 5 h using a heating rate of 2K/min. Chemical characterisation was achieved by elemental analysis using a Eurovector EuroEA elemental analyser. The point of zero charge was determined using a modified version of a simple method proposed by Noh and Schwarz[3, 4].

Results and Discussion

This work presents a new method based on the introduction of nitrogen functional groups during the carbonisation/activation step. A comparison was made with preliminaries results obtained with analogous AC just activated chemically with KOH, using the same procedure, but submitted to a post treatment with urea [3]. In order to obtain the textural properties, the AC were characterised by N_2 adsorption at 77 K. The AC submitted to a post treatment with urea, exhibit a slight change in the textural properties when compared with the untreated one. The AC directly enriched with

nitrogen during the activation step present a very high micropore volume, reaching 0.99cm^3/g.

The elemental analysis and point of zero charge also reflect differences between the AC produced in different ways, namely regarding the carbon and nitrogen content. As presented before, the post treatment modification with urea promoted a slightly increase in its nitrogen content, resulting in 0.6% [3], which is in agreement with Bashkova [2]. The direct nitrogen incorporation promoted as lightly increase in the carbon content, but a more significant increase in the nitrogen content.

Using cork or PET as a precursor, the nitrogen incorporation reached 2.5 or 3.8% respectively. It is expected that, the AC containing higher nitrogen content will present higher adsorption capacities for acidic pollutants.

References

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