RE-UTILIZATION OF SEWAGE SLUDGES AS A PRECURSOR FOR ACTIVATED CARBON PRODUCTION

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ABSTRACT

The possibility of re-utilization of sewage sludges from wastewater treatment plants as raw-material for activated carbon production was investigated. Activated carbons were prepared from secondary sludges by physical activation with carbon dioxide. Pyrolysis was carried out in nitrogen atmosphere at 873 K during 3 h. Physical activation was performed in pure CO_2 flow, for 1h, at temperatures between 1123 and 1223 K. Global yields of the process range from 30 to 40 wt %. Activated carbons have surface areas from 60 to 100 m^2/g and micropore volumes up to 0,020 cm^3/g. Porous structure presents about 50% microporosity. A chemically activated sample (H_2SO_4, 973 K, 15 min, N_2 flow) was also prepared for comparative purposes. Results show that activated carbons produced have potential to be used as pollutant adsorbent, but further optimization studies will be needed in order to improve its porous structure.

INTRODUCTION

Sewage sludges are important by-products of the activity of wastewater treatment plants. It is a well known fact that the number and capacity of these infrastructures is increasing fast, producing large amounts of these residues.

Usual methods for sewage sludge disposal are landfilling, farmland applications and incineration. Landfill deposition faces the problem of decreasing availability of land and increasing deposition costs. Sewage sludge utilisations as a fertilizer also presents odour problems and risk of soil contamination with heavy metals and pathogens. Incineration, although being an effective way to reduce sludge volume and to produce energy, has the disadvantage of requiring expensive flue gas cleaning systems. It is therefore necessary to search for new alternatives for sewage sludge disposal and valorisation. Carbonization of these residues to produce activated carbon is a process recently studied by some authors (Khalili at al., 2000, Martin et al., 1996; Rio et al., 2005). Optimization of activated carbon production from sewage sludges may provide an innovative, environmentally safe and economically feasible solution to sludge management problems in wastewater treatment plants.

Activated carbon is an adsorbent material widely used in industry, as well as in effluent purification, due to its good adsorption properties, especially porous structure and surface chemistry. It is also used as a catalyst or catalyst support in a variety of other industrial and environmental applications. Commercially available activated carbons are produced from coal or lignocellulosic materials (e.g. wood, peat, vegetable wastes as nutshells, fruit stones and coconut) and the production cost is relatively high. Search for cheaper raw-materials is also a concern. Sewage sludge, as a carbon containing material, is an attractive precursor for activated carbon production, lowering production costs and also helping to solve sludge disposal problems.

Activated carbon production processes include chemical and physical activation. Chemical activation involves impregnation of raw-materials with chemical agents as phosphoric acid (Zhang et. al., 2005), zinc chloride (Khalili at al., 2000) and sulphuric acid (Lu et al,1996), followed by carbonization in inert atmosphere (773-973 K). Physical activation is usually a two-step procedure: carbonization in nitrogen atmosphere (773-873 K) and an activation step at higher temperatures (1073-1273 K) with an oxidant gas (air, water vapour or carbon dioxide) (Alaya et al, 2000, Zhang et al, 2005). Activated carbons obtained by different processes have distinct characteristics, specially concerning its porous structure. Chemical activation is more widely used than physical activation, but presents some environmental problems and also higher production costs.

The objective of the present work is to study the production of activated carbons from sewage sludges by physical activation with carbon dioxide as an activating agent and to characterize its textural properties, in order to assess its potential as an adsorbent.

WORK DESCRIPTION

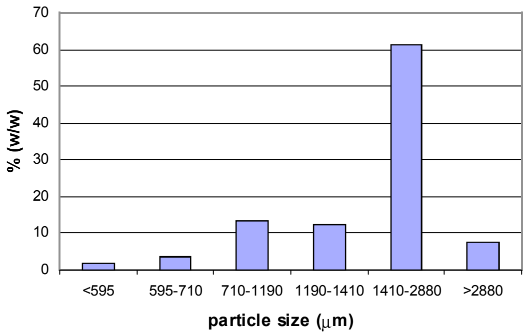
Sewage sludge characterization

Sludges used in the study are produced in an urban wastewater treatment plant. They have been anaerobically digested and mechanically dewatered, and are collected with a low solid content.

Solid and ash content of the samples were determined and a granulometric analysis was also performed on the dried material. Sludges present a solid content of 15,5% (w/w) and an ash content of 35,0% (w/w dried sample). Figure 1 represents the granulometric distribution of the sample.

Particle size distribution of dried sludges indicates that about 60 wt% of the material has a particle size between 1,41 and 2,88 mm. The material has high ash content, compared with conventional activated carbon precursors.

Figure1 Granulometric distribution of sewage sludge dried sample.



Activated carbon preparation

Experimental set-up for activated carbon production is represented in figure 2. It consists in a vertical alumina tubular reactor (0,029 m i.d.) with controlled flow atmosphere, heated by an electric furnace (max. temp. 1200 °C). Samples are placed in stainless steel perforated baskets.

In physical activation experiments raw dried sludges were pyrolysed at 873 K (heating rate = 0,5 K/s), for 3h, in a 0,007 m^3/s nitrogen flow. Carbonized materials were then activated at temperatures between 1123 and 1223 K, for 1h (heating rate = 0,5 K/s) under carbon dioxide flow (0,007 m^3/s). A chemical activation experiment was also performed, for comparative purposes, with sulphuric acid as activating agent. Dried sludges were mixed with sulphuric acid ($0,5 \times 10^{-6}$ m^3 H_2SO_4/g solid) and then dried at room temperature for 12 h. Activation was performed at 973 K (heating rate = 0,25 K/s) for 15 min and 0,007 m^3/s nitrogen flow. Activated materials were then washed.

Yields of the process were determined and are presented in table 1. Pyrolysis yields are averaged values of sets of experiments.

For physically activated samples results are consistent with those obtained with other carbon precursors except for the AC950 sample, where "burn-off" is too low. It is expected that "burn-off" increases with activation temperature, as a result of partial oxidation of the material by carbon dioxide. In the chemically activated sample (ACCH) global yield is similar to values obtained elsewhere in similar conditions (Martin et.al., 1996, Martin et.al., 2002).

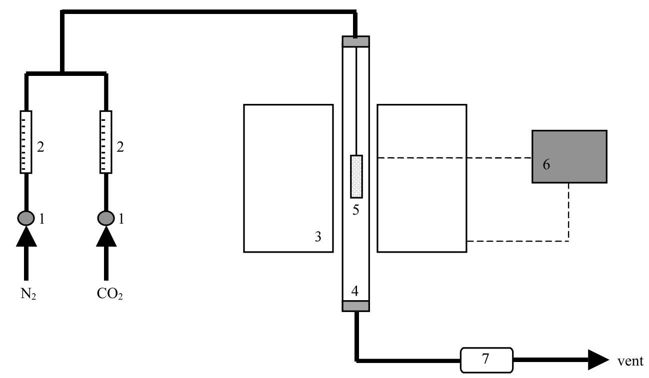


Figure 2
Experimental set-up: 1- needle valves; 2- flow meters; 3- electric furnace; 4- tubular reactor, 5- sample basket; 6-furnace control unit; 7- "trap".

Table 1
Experimental results.

Sample	Activation	Temperature (K)	Pyrolysis yield (weight %)	Activation "burn-off" (weight %)	Global yield (weight %))
AC850	Physical	1123	44,2	14,7	37,7
AC900		1173	44,2	26,5	32,5
AC950		1223	46,6	11,4	41,3
ACCH	Chemical	973	---	---	52,2

Activated carbon characterization

Textural characterization of activated carbons was performed by nitrogen adsorption at 77 K. Specific surface areas (S_{BET}) were determined from adsorption isotherms using B.E.T. equation. Micropore volume (V_{micro}) and surface area corresponding to meso and macropores (S_{meso}) were computed by t-plot method, using a standard isotherm for carbon material (Rodríguez-Reinoso et. al, 1987)

Nitrogen adsorption isotherms of the samples are plotted in figure 3 and textural parameters are presented in table 2.

These activated carbons present low values of surface area, compared with commercial carbons, but similar to those obtained from this kind of residue in different production conditions (Martin et al., 1996; Méndez et al., 2005). As it can be seen from the shape of the N_2 isotherms, porous structure shows some degree of microporosity, which is confirmed by textural parameters. This kind of porous structure can indicate a good performance in heavy metal adsorption (Rio et al., 2005; Méndez et al., 2005). Results from the chemical activated sample anticipate a better quality material, but the use of a chemical agent in the process presents both environmental and economical disadvantages.

The re-use of sewage sludges as activated carbon precursors through a physical activation production process is feasible. The materials produced have relatively low surface areas, but its porous structure seems to be promising towards pollutant adsorption. Microporous activated carbons usually display good adsorption capacities towards heavy metals in liquid effluents. Further studies will be needed, in order to evaluate adsorption capacities of the carbons.

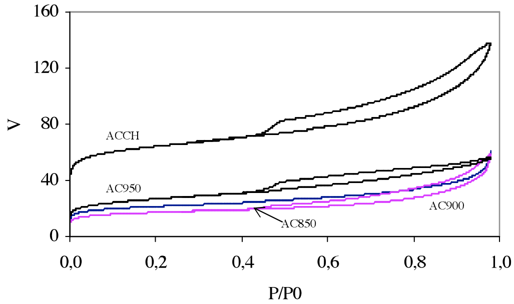


Figure 3. N2 adsorption isotherms at 77 K of the samples: adsorbed volume, V, in cm3(PTN)/g vs. relative pressure, P/Po.

Table 2 Textural properties.

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	S_{meso} (m^2/g)	Microporosity (%)
AC850	78	0,016	38	51
AC900	62	0,015	27	56
AC950	95	0,019	52	45
ACCH	238	0,064	80	66

CONCLUSION

Activated carbons were produced by physical activation of sewage sludges from wastewater treatment plants, using carbon dioxide as activating agent.

Results of textural characterization of the carbons showed that surface areas and micropore volumes are low compared to usual carbon adsorbents. This behaviour is most probably related to the high ash content of the precursor. Both nitrogen adsorption isotherms shape and textural parameters indicate that porous structure is already developed, with microporosity accounting for approximately 50% of total pore volume. These characteristics anticipate a good behaviour of the material as a cheap adsorbent for liquid phase pollutants.

Comparing the activation methods studied, the sample obtained by sulphuric acid activation presents better textural properties, but introduction of a chemical agent in the production process presents both environmental and economical disadvantages.

As a final conclusion, it can be said that sewage sludges valorisation as activated carbon precursor by physical activation with CO_2 is feasible. However, further studies will be required, in order to improve textural properties of the materials, and also to evaluate adsorption capacities of the carbons.

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