Production of activated carbon from petroleum coke and its application in water treatment for the removal of metals and phenol

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Abstract: The feasibility of the reuse of petroleum coke, with high sulphur content, produced as waste in a Mexican petroleum refinery, its properties for use in water treatment were assessed. Several classical activation methods were used and the physicochemical characteristics of the treated material were measured using normal ASTM standards. Use of scanning electron microscopy and microprobe analysis permitted most of the effects of the activation processes on the structure and properties of the coke. Adsorption capacities of mercury and silver and the physicochemical characteristics determined for these activated carbons as well as scanning electron microscopy show that the H3PO4 is the best activating agent. It is shown that the process is highly promising for the production of an activated carbon aimed at the removal of heavy metals from wastewater.

Keywords: Activated carbon; metal removal; petroleum coke; SEM; wastewater treatment

Introduction

In 2000, the largest petroleum refinery in Mexico goes into operation at Cadereyta, Nuevo León. The most important solid waste product expected to originate from this plant will be petroleum coke (3,000 tonnes/day). Taking into account the high production rates of this residual it is interesting to promote research to find alternative applications for this product. Processes that can be considered for the reuse of petroleum coke are gasification, energy production by combustion and the recuperation of metals from contaminated waters (Di Panfilo and Egiebor, 1995). Nevertheless, the first two options confront severe technological limitations due to the high sulphur contents (6 wt.%) of the coke under consideration. In this context, the production of activated carbon for wastewater treatment remains as an interesting option.

The adsorption capacity of activated carbons and its applications depend on the base material involved and the processing parameters. By fine-tuned physicochemical processes it is possible to influence the its pore structure, surface area, density and surface chemistry. Factors to be considered are the temperatures of the process, time at temperature, activating agent and oxidant flow rate. Activated carbon can be produced from materials consisting mainly of carbon by applying physical or chemical methods, which have as an objective the generation of a high specific area due to a strongly developed microporosity. This goal is reached by removing or modifying aromatic and non-aromatic chain molecules from the carbon in favour of the aromatic sheets, which are present in carburized materials. The resulting loss of material (usually between 20 and 50%) provokes the formation of a microporosity between the original aromatic sheets, which is responsible for the high
specific surface of the final product. Those micropores, which have a typical width of less than 20 nm, can act as molecular sieves when macromolecules are concerned.

Besides the effect of the porosity on the adsorbing properties of an activated carbon, also the functional groups on the sheet edges play an important role in the reactivity of the carbon. This is most strikingly illustrated by the pH of the material, dividing carbons in acid and base, as a function of their origin and processing. While acid and base character appears to be based on the presence of C–O and O–H functional groups, other properties can be related to the presence of other elements in the carbon structure. Interesting is the sulphurisation of carbons, in which the O– containing groups are substituted for S by treatment with SO₂, H₂S or elemental sulphur. It was shown that the presence of sulphide groups at the sheet edges of the activated material enhanced the absorption of heavy metals suspended in contaminated air (Bansal et al., 1988). The study also suggested that the sulphur contained in the aromatic structure of the C– sheets did not have an influence on activity and cannot be removed as easily or added during chemical modification processes.


Based on those factors, the aim of this work was to evaluate different processes proposed in the literature for the production of activated carbon from petroleum coke to remove metals and phenol from water. Three production methods (chemical) are considered: activation by means of zinc chloride, phosphoric acid and sodium hydroxide. It is important to mention that the success of a particular method is strongly dependent on the characteristics of the base material. The high sulphur content of the coke used for the present study may classify it as a particular variant of the aforementioned cases. This led us to the decision to treat this material by chemical processes, using zinc chloride, phosphoric acid and sodium hydroxide.

Experimental
The influence of the type of activating agent is discussed for the different methods in terms of the physicochemical characteristics and adsorptive capacity of metals, phenol and methylene blue. The relation between process parameters, physicochemical characteristics, adsorptive capacity of contaminants and surface morphology observed by means of scanning electron microscopy has been studied in detail. Physicochemical characterisation and adsorptive properties of activated carbons produced were compared with a commercial activated carbon (LQ 1000).

Adsorbent materials tested
To show the viability of using coke as a raw material for the production of adsorbent materials, several adsorption tests were performed with raw coke, obtained from the Cadereyta refinery of PEMEX (Petróleos Mexicanos), and with activated coke obtained by three different chemical activation methods (H₃PO₄, NaOH and ZnCl₂). Results of coke and activated cokes (size of particle 0.7–0.9 mm) were compared with those obtained with a commercial activated carbon, Carbochem LQ1000 (size of particle 0.9–1.1 mm). The petroleum coke sample was washed with distilled water and then dried at 110°C. Finally, it was stored in closed glass bottles before its application in activated carbon production methods.

Production of activated carbon from coke
One hundred grams of the petroleum coke sample (W₁) was mixed with the same quantity
of H₃PO₄, NaOH or ZnCl₂ predissolved in 0.1 litre of distilled water. The mix of petroleum coke and activating agent was boiled at 110°C for 2 hours. The dried mass in each case was then carbonised in a quartz vessel at 700°C for 2 hours in a nitrogen atmosphere (1 L/min) and then weighed (W₂). The solids were then filtered and washed with distilled water to eliminate the acid, the hydroxide and the chloride ions. The solids were finally dried to a constant weight (W₃).

Physicochemical characterisation of adsorbents
The raw coke (RC), the coke activated with H₃PO₄ (CAPA), the coke activated with NaOH (CASH), the coke activated with ZnCl₂ (CAZC) and the commercial activated carbon (LQ1000) used in this work were characterised using the following norms: ASTM D 3037 (superficial area), ASTM D 4607-86 (iodine number), CEFIC * (Methylene blue number), ASTM D 3838-80 (pH). (*CEFIC, Conseil Européen des Fédérations de l’Industrie Chimique-Test Methods for Activated Carbon).

Finally, the original coke and the different samples of treated product were examined by scanning electron microscopy (SEM, PHILIPS XL20SEM). The conductivity of all samples was sufficient to permit observation of the carbon powders without special sample preparation. Observations were made using an accelerating voltage of 25 to 30 kV, at magnifications from 20 to 12000×, the latter with a resolution of about 8 nm, still too big to reveal micropores which are defined to be smaller than 2 nm.

Observations by means of secondary electrons were completed with local chemical analysis using energy dispersive X-ray spectroscopy (EDS, EDSPHILIPS), which for the case of light elements and in absence of extensive calibration efforts gives a qualitative impression of the presence of the different constituents of the coke. Composition maps were made to reveal the relative concentrations of C and S in the coke. Those maps can be compared with the original secondary electron images which, apart from topographical information, contain data about the local density of the material.

Adsorption process
In this part of the study, the adsorptive capacity of the adsorbents was evaluated using four different adsorbates: two metals (mercury and silver) and two organic compounds (phenol and methylene blue). These substances were chosen because they are important from an environmental point of view because of their toxicity. On the other hand, they are difficult to eliminate from water using conventional methodology, but efficiently removed with activated carbon. Adsorption isotherms for Hg, Ag, phenol and methylene blue were obtained using a similar technique described below.

The pH of a water solution of HgCl₂ (0.5 mg/L) was adjusted to 4 with HCl. The pH of the AgNO₃ (100 mg/L) solution was 5, the phenol (100 mg/L) solution had a pH of 7 (adjusted with NaOH) and, the pH of the methylene blue (600 mg/L) solution was adjusted to 2.5 with acetic acid. These pH values correspond to the optimal value reported in literature (Adams, 1991, 1992; Huang and Blankenship, 1984). 200 mL of the previously made solutions were placed in six bottles of 500 mL (batch reactor). Increasing amounts of the adsorbent were added to five reactors (0.1–0.5 g for Hg, 0.3–3 g for silver, 1–5 g for methylene blue and 0.25–5 for phenol). The sixth reactor was used as a blank without adsorbent. The reactors were sealed to avoid evaporation and mixed during 24 hours. After this time (equilibrium), mixing was stopped and the phases were separated through filtration with a polycarbonate membrane (0.45 µm Millipore).

Analytical methods
The concentrations of adsorbates tested in water were quantified following the technique
described in the *Standard Methods* (APHA, 1994). The solutions of mercury and silver were quantified using a mass spectrophotometer analyser equipment with Inductive Coupling Plasma (ICP-MS) Thermo Jarrell Ash (DUO-ICP), model IRIS/ICAP. The phenol and the methylene blue were quantified at a wavelength of 270 nm and 650 nm, respectively in a PERKIN ELMER Vis/UV spectrophotometer.

**Results and discussion**

**Physicochemical characterisation of adsorbents**

Table 1 shows the determined parameters for the activated and non-activated petroleum coke and the commercial activated carbon. Two determinations of the two produced batches (100 g) of activated carbon were done; therefore, the values presented in Table 1 are the average of four measures.

Considering the methylene blue index, it can be showed that the activation with NaOH produced an adsorbent (CASH) with similar characteristics to those presented by the commercial activated carbon LQ1000 (20% of difference). These results indicate a comparable adsorptive capacity for CASH and LQ1000 when molecules of significant size are adsorbed.

The iodine index and superficial area show a significant increase after the coke activation but not enough to be compared to those values presented by the LQ1000. Based on this result it can be expected that the microporosity of the activated coke will not be significant compared to that of the commercial product. This can be explained by the fact that the small molecules involved are capable of entering the micropores, resulting in a higher adsorption surface available.

The observations in SEM are presented in Figures 1 and 2. It must be mentioned that the images presented are a selection made to illustrate the findings of the microscopical observations rather than to give a statistical representation of what can be found, as it would be impossible to represent a complete overview of the study. Moreover, images at rather modest amplifications are shown because they were found to represent a better view of the phenomena involved.

A first observation represents single grains of coke treated by the three activants. In Figure 1a, two grains treated by ZnCl\(_2\) are shown. The image illustrates the important fact that different grains respond differently to the process, as one of the grains is non-affected and the other one shows an clear attack of its surface. The non-affected grain shows a pattern of white and grey patches, the white ones emerging slightly from the surface. It is seen in Figure 1a,b how the attack by ZnCl\(_2\) is basically concentrated in the dark zones. This also holds to a certain extent for the NaOH (Figure 1c), but deeper general cracks appear on in this grain.

The H\(_3\)PO\(_4\) causes a deep and general fissuration of the whole specimen (Figure 1d). The pictures presented exemplify a general trend, in which the darker zones are firstly attacked and a fissuration pattern is generated. Next, fissures start to extend more profoundly, while the pre-existing concentric layers of the coke “peel off”. The effect of the latter is shown in

<table>
<thead>
<tr>
<th>Code</th>
<th>Material</th>
<th>pH</th>
<th>Iodine index (mg/g)</th>
<th>Methylene blue index (mg/g)</th>
<th>Specific area (m(^2)/g)</th>
<th>Yield (%)</th>
<th>Total ash content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LQ1000</td>
<td>LQ 1000 (commercial carbon)</td>
<td>6.5</td>
<td>513</td>
<td>252.2</td>
<td>380</td>
<td>-</td>
<td>11.7</td>
</tr>
<tr>
<td>RC</td>
<td>Raw coke</td>
<td>3.9</td>
<td>4</td>
<td>52.7</td>
<td>0.3</td>
<td>-</td>
<td>13.4</td>
</tr>
<tr>
<td>CAZC</td>
<td>Coke + ZnCl(_2)</td>
<td>3.5</td>
<td>73</td>
<td>146.3</td>
<td>16.3</td>
<td>84.7</td>
<td>10.9</td>
</tr>
<tr>
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<td>Coke + NaOH</td>
<td>9.4</td>
<td>42</td>
<td>203</td>
<td>35.4</td>
<td>83.9</td>
<td>12.3</td>
</tr>
<tr>
<td>CAPA</td>
<td>Coke + H(_3)PO(_4)</td>
<td>2.7</td>
<td>57</td>
<td>160</td>
<td>31.6</td>
<td>80.9</td>
<td>6.6</td>
</tr>
</tbody>
</table>
figure (Figure 2a) for H₃PO₄. It is important to notice that the images (1b) to (1d) present typical situations for each product, as similar grains like Figure 1b can be found for NaOH and H₃PO₄, as well as grains like Figure 1c are present in the product treated by H₃PO₄. This indicates that the process is very similar for each of the three activants used, but that the degree of physicochemical alteration is significantly different for the three products, H₃PO₄ being the strongest, followed by NaOH and finally ZnCl₂.

In Figure 2b, an example of the formation of mesoporosity is shown. This kind of attack is only seen when H₃PO₄ is used, supporting the latter hypothesis. Generally, the observations can be resumed as the formation of small cracks in the darker zones of the original grain. Small flakes “peel off” at the surface around the cracks in a next phase. For coke activated by NaOH, the cracks observed are longer, and the peeling effect is stronger. Underneath the first layer, a second becomes visible, which upon further processing will show the same evolution as the outer layer. Coke activated by H₃PO₄ shows a severe cracking, which is typical for the treatment by this reagent.

An interesting aspect of the observations is the fact that the darker zones of the coke are attacked first. When analysing this, the reasons for the formation of contrast in scanning electron microscopy, using secondary electrons should be remembered. While secondary electrons are principally influenced by surface topography, they also feel the influence of material density. The topography of the darker regions indicates they are less elevated than the white patches, but the difference is insufficient to completely explain the difference in contrast.

As the material contains mainly carbon and sulphur, an inhomogeneous distribution of both products must be responsible for this difference in brightness. To explain the effect, two complementary techniques were used. The first one consisted of accurate EDS measurement in two neighbouring points on the grain surface (in both types of zones), eliminating as strongly as possible influences of surface inclination and topographical effects which could affect the detection of the X-rays. The second method consists of the complete mapping of a grain of coke, scanning its surface for the presence of S and C. The results are presented in Figures 3a to 3d.

In Figure 3b only some rough topographical features are reproduced, indicating the sul-
phur is homogeneously distributed over dark and bright zones. Figure 3c shows that the lighter zones are areas of higher density of carbon, which can be explained by assuming a different chemical configuration of the carbon molecules in both zones. Figure 3d compares two different spectra obtained using constant specimen current in zones which are topographically similar. The vertical axis represents counts per second, the horizontal are eV. No additional data treatment was applied, making the coincidence of the S peaks in both spectra rather striking.

The results of both techniques indicate the same trends. Point measurements of composition indicate that, while the sulphur peaks of the dark and bright zones coincide perfectly, their carbon peaks differ significantly. The X-ray mapping of both signals shows that the C-image reproduces the secondary electron contrasts fairly well, while the S-map only reproduces the most significant topographical features. This proves that the differences in brightness are due to differences in density of the carbon component, while sulphur is homogeneously distributed over all of the material. Similar measurements also indicate that, whatever the chemical used for activation, it is difficult to get rid of it afterwards, as is shown by the Cl peak in the EDS spectrum presented.
Adsorption process

The results of the adsorption process for phenol and methylene blue with the activated coke were very similar to those presented by the commercial product. However, the adsorption process for metals was more efficient with the treated cookes than with the commercial product. The analysis of the data obtained for the removal of mercury and silver is presented in Figures 4a and b. The adsorption isotherms according to the Langmuir model (Eq. 1) are presented by the equation

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_{mb}} \cdot \frac{1}{C_e}
\]

where, \(q_e\) = adsorption capacity at equilibrium (mg/g AC), \(C_e\) = Concentration of the adsorbant in water at equilibrium (mg/L), \(q_m\) = maximal adsorption capacity (mg/g AC), \(b\) = constant of the Langmuir model.

The data in represented in Figures 4a, b show an excellent fit between the model and the data. The evaluation of the maximal adsorption capacity (\(q_m\)) has been made using the same model. Results are presented in Table 2.

The results presented in Figures 4a,b and the data of Table 2 show a clear increase in the adsorption capacity for Hg, Ag and methylene blue of the activated coke, especially when phosphoric acid is used. Given the low specific area of the activated product, the increase in adsorption capacity must be explained by the generation of active functional groups on the surface of the material. The fissuration observed in the scanning electron microscope can explain this phenomenon, as it generates a higher surface area than in the non-treated coke. The fact that phosphoric acid is capable of cracking the zones of higher density might explain the higher efficiency of this product. Indeed, it is logical to assume that those zones consist mainly of aromatic sheets, and the cracking must expose new functional groups on their edges.

Comparing the data for the activated coke with results for the commercial product, the adsorption of metals is especially efficient for the former. This is in agreement with studies showing the role of sulphur in activated carbon, although in this present investigation the sulphur is inherently present in the base material while in the other studies it was artificially added to improve removal of metals.

Conclusions

The study clearly shows that petroleum coke can be valorised as an adsorbent material for wastewater treatment. The product, consisting of carbon and sulphur, can be activated by \(\text{ZnCl}_2\), \(\text{NaOH}\) and \(\text{H}_3\text{PO}_4\). While the activation with \(\text{NaOH}\) generates the highest surface area observed, this one remains small compared to the value obtained for a commercial coke. However, comparing methylene blue indexes for coke activated by \(\text{NaOH}\) and the

<table>
<thead>
<tr>
<th>Material</th>
<th>(q_m) for phenol (mg/g)</th>
<th>(q_m) for methylene blue (mg/g)</th>
<th>(q_m) for mercury (mg/g)</th>
<th>(q_m) for silver (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LQ 1000</td>
<td>169.5</td>
<td>291.7</td>
<td>8.4</td>
<td>-</td>
</tr>
<tr>
<td>RC</td>
<td>47.7</td>
<td>0.23</td>
<td>4.9</td>
<td>1.8</td>
</tr>
<tr>
<td>CAZC</td>
<td>53.1</td>
<td>17.8</td>
<td>7.6</td>
<td>5.8</td>
</tr>
<tr>
<td>CASH</td>
<td>62.9</td>
<td>29.6</td>
<td>7.9</td>
<td>13.3</td>
</tr>
<tr>
<td>CAPA</td>
<td>67.8</td>
<td>26.0</td>
<td>10.8</td>
<td>43.9</td>
</tr>
</tbody>
</table>
commercial product, similar values were found but values for coke activated by the other chemicals are lower. The iodine indexes and adsorption capacity of phenol of all products were significantly lower than the ones determined for the commercial product, suggesting that the activated cokes are suited more for the adsorption of large molecules. In the adsorption of metals, the best results were obtained by the activation with phosphoric acid, which generates a product, whose adsorption capacity for silver and mercury is significantly higher than that observed for the commercial product.

Scanning electron microscopy showed that the activation process consists of a fissuration of the grains, generating new surfaces capable of adsorption. EDS showed that cracking principally occurs in zones of lower density, compared with highly aromatic zones. Only phosphoric acid was capable of cracking the denser zones. It can be supposed that the newly exposed functional groups on crack sides and interlaminar surfaces play an important role in the adsorption process. The fact that the activated coke has a high sulphur content may be important to explain its high adsorption capacity for metals compared with commercial coke with a significantly higher surface area.

The general conclusion of the study is that the waste material considered has the potential of being transformed into a valuable product for applications in wastewater treatment. While its properties for the removal of silver and mercury are satisfactory, it is obvious that the chemical process of activation still has to be optimised to commercialise the product.

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