Removal of detergents by activated petroleum coke from a clarified wastewater treated for reuse

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Abstract The removal of detergents from clarified wastewaters by activated petroleum coke (CAPA) was assessed. These substances, owing to their foamy properties, constitute a problem for ammonia removal by the air stripping process that could be installed in a wastewater treatment train to produce reclaimed water. CAPA was evaluated as a more economical alternative than a commercial activated carbon. Experimental work was divided in three stages: 1) production and characterisation of materials; 2) pretreatment of raw wastewater through the Fenton’s reagent or coagulation–flocculation process with Al₂(SO₄)₃; and 3) adsorption and bio-adsorption tests of clarified effluents. These tests were carried out in the laboratory in discontinuous and continuous reactors, the former by the “point-by-point” technique, with and without a previous fixing of bacteria, and the latter by the Rapid Small Scale Column Test. Detergents content, color, COD and UV₂₅₄nm were measured in raw and treated wastewaters. Results show that the best pretreatment for the adsorption process was coagulation–flocculation rather than Fenton’s method. Oxidation by this process decreased the adsorptive properties of detergents. Biomass fixed on the CAPA particles significantly increased the UV₂₅₄nm and COD removal efficiencies (20% and 170% respectively). The breakthrough curves showed that CAPA could attain the expected detergents removal efficiency (66%) for the alum effluent.

Keywords Adsorption; bio-adsorption; clarification; detergent; wastewater

Introduction

The feasibility of the artificial recharge of Mexico City’s aquifer with treated wastewater has been demonstrated (Sánchez Bribiesca et al., 1997; Ramírez Zamora et al., 1999). The aquifer recharge has been evaluated to palliate the increasing water deficit and the associated collateral problems, such as Mexico City’s soil sinking (between 5 and 30 cm/year). Ramírez Zamora et al. (1999) evaluated a physicochemical pretreatment comprising coagulation–flocculation, sedimentation and sand filtration to remove efficiently most of the organic and inorganic colloidal and suspended matter present in the raw wastewaters produced in Mexico City. These authors have also shown the effectiveness of the adsorption process to improve the quality of the clarified effluent, especially to remove detergents, in order to produce reclaimed water for aquifer recharge. These substances, owing to their foamy properties at concentrations of 1.3 mg/L, constitute a problem for ammonia removal by the air stripping process that could be installed in a wastewater treatment train to produce an effluent for recharging Mexico City’s aquifer.

However, the implementation of the adsorption process could be very expensive because of the cost of the carbon used for treating the high-rate flow that must be treated (10 m³/s) for the artificial recharge of Mexico City’s aquifer. To reduce costs, a substitution of classical products by efficient activated carbons obtained from cheap prime materials has been proposed. Activated carbon can not only be expensive, it can also be ineffective if it is not used properly. To ensure that activated carbon is used effectively, the design of full-scale Granular Activated Carbon (GAC) adsorption processes often requires
time-consuming and expensive pilot-plant studies. However, in the past ten years a rapid method to design large-scale fixed bed adsorbers from small-column tests has been used successfully. This method is known as Rapid Small-Scale Column Test (RSSCT) (AWWA, 1989). There are two main advantages of using RSSCT for design: 1) it can be conducted in a fraction of the time required to perform pilot studies and 2) the test requires only a small volume of water to be treated.

Significant efforts have been made in the production of activated carbons from agricultural wastes, wastewater sludges and old tires, among others (Ahmedna et al., 2000; Dastgheib and Rockstraw, 2001). In line with other studies that focus on the use of solid wastes as a raw material for the production of activated carbon, Ramírez Zamora et al. (2000) showed that an activated petroleum coke with a high sulphur content was able to remove heavy metals and phenol as efficiently as commercial adsorbents and that it is also 30% cheaper.

To evaluate the effectiveness of the aforementioned activated petroleum coke in removing detergents and to calculate the feasibility of the adsorption process with this material, this study assesses the removal efficiency and the costs associated with its use in fixed-bed adsorbers in comparison with the results obtained for a commercial activated carbon.

**Methods and materials**

**Adsorbents**

Petroleum coke activated with H₃PO₄ (CAPA) and a commercial activated carbon of mineral origin (LQ-1000, CARBOCHEM) were used as adsorbents. Raw petroleum coke (RC) is a solid waste produced during the refining process of petroleum in the PEMEX (Petróleos Mexicanos) Refinery of Cadereyta, Nuevo León.

**Chemical reagents for the activation of CAPA and characterisation of adsorbents**

The activating agent (H₃PO₄) was industrial grade (85% purity). All reagents used for the physicochemical characterization of adsorbents were analytical grade. For the determination of the iodine index two 0.10 N solutions (iodine and sodium thiosulphate) and a 5% HCl solution were used. Methylene blue (MB) index and specific surface were determined using a 6 x 10⁻⁴ M MB solution. All reagents used in the characterisation and adsorption tests were reagent grade.

**Raw wastewater**

The influent used in this work (M₁) was a mixture 1:1 (v/v) of industrial and municipal samples collected in two points of the final discharge of the Mexico City sewerage system; the first sampling point is called Gran Canal (GC) and the second Rio Churubusco (RCh). Some physicochemical characteristics of M₁ were as follows: pH = 7.7, turbidity = 118 NTU, color = 566 U Pt-Co.

**Chemical reagents for Fenton and coagulation–flocculation**

Fenton’s reagent tests were performed with ferrous sulphate and hydrogen peroxide solutions prepared at 30% and 40% (w/w) respectively, from products of analytical grade (Merck). Coagulation–flocculation experiments were carried out with Al₂(SO₄)₃ solutions at 30% (w/w) also prepared from an analytical-grade solid salt (Merck).

**Experimental set up and techniques**

*Activation of petroleum coke.* Raw petroleum coke (RC) was chemically activated as follows: one hundred grams of the petroleum coke sample (W₁) was crushed to obtain particles of 60 x 80 mesh, then it was mixed with the same quantity of concentrated
H₃PO₄. The activation and carbonisation of this mixture was carried out as described by Ramírez Zamora et al. (2000). Finally, the activated coke was characterised and stored until it was used in the adsorption tests.

Coagulation–flocculation and Fenton’s reagent. Raw wastewater was pretreated by the coagulation–flocculation process or Fenton’s reagent. The optimum experimental conditions were as previously reported by Ramírez Zamora et al. (1999): 20 mg Al³⁺/L, pH = 6.5 for the alum clarification process and 20 mg of Fe²⁺/L, 30 mg H₂O₂/L and pH = 3.7 for the Fenton Method.

Adsorption and bio-adsorption processes. The clarified effluent was used in adsorption tests in 1) discontinuous and 2) continuous reactors. In the first case, after a previous fixing of bacteria onto activated carbon particles, the point-by-point technique was used for the bio-adsorption tests, and in the second case the RSSCT was used. The techniques applied in each case were as follows.

a) Discontinuous reactor: adsorption isotherms
For each of the two clarified wastewaters (coagulation–flocculation and Fenton’s reagent) 200 mL was placed in each of seven flasks. One reactor was used as a blank, and increasing amounts (from 0.2 to 1.5 mg/mL) of adsorbent (CAPA or LQ 1000) were applied to the other six reactors. Four different combinations of effluent-adsorbent were then obtained. All combinations (solution-adsorbent) were mixed with a magnetic stirrer, during 24 h at 100 rpm and 18°C. At the end of this time, all mixtures were filtered through a GF/A paper filter and the liquid phase was used for a physicochemical characterisation. Besides detergents content, several physicochemical characteristics (color, COD, UV₂₅₄nm) were measured in raw and treated wastewaters as global indicators of organic compounds. All experiments were performed in duplicate.

For the bio-adsorption process, the techniques proposed by Durán Moreno (1997) were applied for the bacteria acclimatisation and for their subsequent fixing onto the CAPA particles. Once the bacteria were fixed, the adsorption isotherm protocol described above was applied. To reduce the standard error, the contribution of humidity was taken into account in weighing the adsorbent.

b) Continuous reactor: RSSCT
All tests were conducted at 18°C (room temperature) with Pyrex mini-columns 1.1 cm in diameter and 50 cm in height. Channelling and wall effects were avoided since the ratio of column diameter to particle diameter was above 50 (AWWA, 1989). Teflon end caps were sealed with Teflon-wrapped rubber o-rings on each end of the column to ensure a proper seal. The carbon bed was supported on a 100-mesh stainless screen. The sleeves were sized to fit tightly in the column to prevent any fluid flow between the sleeves and column wall. Influent was fed into the column, in up-flow mode, by a peristaltic pump from a 50 L container, at a flow rate of 13 mL/min to simulate two EBCTs (Empty Bed Contact Times), 5 and 15 min. The bed height of adsorbents was respectively 6 and 18 cm for LQ1000 and 7 and 21 cm for CAPA. Samples were taken at intervals of 60 min, until the breakthrough was reached (\( C_F = 1.3 \text{ mg/L of detergents or } C_F/C_O = 0.3 \)). The same parameters measured in the discontinuous reactor were also quantified in all the discontinuous reactor effluents.

Analytical methods
The RC, the CAPA and the LQ1000 were characterised by use of the following norms: ASTM D 3037 (specific area), ASTM D 4607-86 (iodine number), CEFIC or Conseil R.M. Ramírez Zamora et al. 93
Physicochemical characterisations of liquid effluents were obtained by applying the techniques proposed by the Standard Methods for the Examination of Water and Wastewater (APHA et al., 1998) and a Hach 4000 spectrophotometer. SEM observations were done by using a JEOL model JSM-5900LV electronic microscope.

**Results and discussion**

**Physicochemical characterisation of adsorbents**

The evaluated physicochemical characteristics of the materials (Table 1) revealed that: 1) crushing and activation of raw petroleum coke significantly increases its adsorption properties, since specific area, iodine and methylene blue numbers increase respectively 300, 22 and six times; and 2) these values are similar to those obtained for the commercial activated carbon “LQ 1000”. It appears that CAPA could be as efficient as LQ1000 to remove detergents in wastewater. However, this hypothesis has to be verified or rejected through complementary adsorption tests, as is shown in the next section.

**Adsorption and bio-adsorption processes**

*a) Discontinuous reactor: adsorption isotherms.* In this stage, the effectiveness of CAPA was evaluated in terms of two global indicators of organic compounds (COD and UV$_{254}$nm (ABS)). Figure 1 shows the ratio of the residual/initial concentration ($C_F/C_O$ ratios) of these two parameters as a function of the applied dose of CAPA or LQ1000.

A rapid examination of these curves shows that the hypothesis proposed above is apparently not verified since the COD and ABS ratios are, for all the doses evaluated, smaller for LQ1000 than for CAPA. Nevertheless, a more accurate analysis must be done to verify this and other statements suggested by these curves. Since COD and ABS represent many compounds, the data obtained in this work were not properly described by any of the classical isotherm models. Therefore, a statistical study based on a multiple comparison test or Least Significance Difference (LSD) test was performed.

**Table 1** Physicochemical characteristics of materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific area (m$^2$/g AC)</th>
<th>Iodine number (mg I$_2$/g AC.)</th>
<th>Methylene blue number (mg MB/g AC)</th>
</tr>
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<tbody>
<tr>
<td>Activated carbon LQ 1000</td>
<td>380</td>
<td>513</td>
<td>252.2</td>
</tr>
<tr>
<td>Raw petroleum coke</td>
<td>0.30</td>
<td>4</td>
<td>52.7</td>
</tr>
<tr>
<td>Activated petroleum coke</td>
<td>245.3</td>
<td>90.5</td>
<td>300</td>
</tr>
</tbody>
</table>

**Figure 1** Removal of COD and UV$_{254}$ nm (ABS) in two clarified wastewaters (with alum and Fenton’s reagent) treated by the adsorption process with CAPA and LQ1000 as a function of the applied dose of adsorbent with or without fixed bacteria.
The average and the standard deviation from the residual values of COD (Figure 2) show CAPA to be slightly less efficient than LQ1000 since their values are similar, with or without bacteria fixed on the adsorbent particles. The presence of biomass on the adsorbent particles increases the global removal efficiency of both adsorbents.

The ABS results (Figure 3) show that this influence is less important and it seems to be even contrary for Fenton’s reagent, in comparison with the COD results. However, the oxidation of aromatic compounds can result in the production of smaller and less adsorptive molecules. Thus, considering that detergents are aromatic compounds, the best pretreatment is coagulation–flocculation with alum. This pre-treatment was then applied to produce the influent for adsorption tests in the continuous reactor.

b) Continuous reactor: RSSCT. The final concentration/initial concentration ($C_F/C_O$) ratios
of ABS, detergents and dissolved oxygen (OD) for the four combinations of adsorbent and EBCTs, as a function of litres of influent treated by coagulation–flocculation per gram of adsorbent (V/M) are shown in Figure 4.

Before discussion of the adsorption and bio-adsorption results, it is important to note that the $C_F/C_O$ ratio is similar for detergents and ABS, over the entire V/M interval evaluated. This could mean that the breakthrough curve of detergents can be predicted by the ABS measurements. This is important since ABS measurements are faster and easier to do than the ones for detergents.

In all cases and all V/M intervals evaluated, CAPA did not achieve the $C_F/C_O$ ratio of 0.3 needed to avoid problems in the removal of ammonium by the air stripping process. Nevertheless, if the trend of the breakthrough curves for CAPA is considered, at V/M ratios higher than 3.0, the required detergents removal could be attained for an EBCT of 15 min. The decreasing trend of the residual detergent content is probably due to the coupled action of the adsorption and biodegradation processes. In the first 0–0.8 (V/M), the $C_F/C_O$ ratio of detergents and OD increases constantly (as far as the functional reducing groups of adsorbents are consumed by the reaction with oxygen), as can be seen in most of the breakthrough curves. For higher V/M values, the slope of each curve changes and the ratio slightly decreases. In the case of OD curves, the biological activity developed on the adsorbent particles seems to be bigger for CAPA than for LQ1000, since the OD depletion is higher and faster in the first case. This is because more bacteria are fixed onto the CAPA particles, as it is illustrated in the next SEM photos.

In photo 1a some bacteria have been fixed onto a LQ1000 particle sampled from the mini-column operating at a simulated EBC of 15 min. Photo 1b shows more details of these bacteria. In both photographs these microorganisms are represented by a few long, flat and black spots fixed over the adsorbent surface.

As a contrast, for CAPA at the same EBCT (photo 1.c), the bacteria are present in much higher amounts than for LQ1000 and they are long, round and white (Photo 1.d). The difference in the morphology of bacteria fixed on both materials is probably due to the fact that the presence of cracked zones on CAPAs surface protects bacteria from the dewatering

![Figure 4](https://iwaponline.com/wst/article-pdf/50/2/91/421559/91.pdf)

**Figure 4** Breakthrough curves of ABS, detergents and OD for mini-columns packed with CAPA and LQ1000 at simulated EBCTs of 5 and 15 min

By guest
effect produced by the vacuum of the electronic microscope. These cracked and rugose zones also allow the bacteria to be better fixed over the CAPAs surface.

The dimensions of the bed adsorbers and the associated costs (Table 2) were calculated based on a flow rate of 150 m$^3$/d and on the best EBCT obtained in the RSSC tests (15 min).

As it can be seen, higher amounts of CAPA are needed for the calculated adsorber, therefore costs are also higher (2.6 times) than the LQ000 costs. Nevertheless, this material could be a better adsorbent to remove other types of contaminants such as heavy metals, so the costs associated with its use could be similar to those obtained for commercial activated carbons.

Conclusions

The tests carried out in the discontinuous and continuous reactors have shown that CAPA is less efficient and more expensive to remove detergents by adsorption than the commercial activated carbon which was taken as a comparison baseline. Nevertheless, the rugosity and cracked zones, help bacteria to be better fixed on the particle surface. Biological activity on the CAPA surface significantly increased the global COD removal efficiency of CAPA to the extent that its value is similar to that obtained for a commercial activated carbon.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LQ-1000</th>
<th>CAPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total flow</td>
<td>150 m$^3$/d</td>
<td>150 m$^3$/d</td>
</tr>
<tr>
<td>Number of adsorbers</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Flow rate per adsorber</td>
<td>75 m$^3$/d</td>
<td>75 m$^3$/d</td>
</tr>
<tr>
<td>Type of flow</td>
<td>Up-flow</td>
<td>upflow</td>
</tr>
<tr>
<td>GAC mesh</td>
<td>12 × 40</td>
<td>12 × 40</td>
</tr>
<tr>
<td>Adsorber height</td>
<td>1.65 m</td>
<td>1.75 m</td>
</tr>
<tr>
<td>Adsorber bed height</td>
<td>1.3 m</td>
<td>1.52 m</td>
</tr>
<tr>
<td>Adsorber diameter</td>
<td>0.87 m</td>
<td>1.015 m</td>
</tr>
<tr>
<td>Total mass of GAC</td>
<td>564 kg</td>
<td>1,280 kg</td>
</tr>
<tr>
<td>Capital costs (US dollar)</td>
<td>17,525.4</td>
<td>17,723.8</td>
</tr>
<tr>
<td>Operating costs (US dollar)</td>
<td>28,262.1</td>
<td>74,161.1</td>
</tr>
<tr>
<td>Total cost (US dollar/m$^3$)</td>
<td>0.52</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Considering this, adsorbers could be packed with both materials for efficiency and economy. In addition, this material could be used as a good adsorbent or biological support to remove other organic compounds besides detergents to produce reclaimed water.

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References


