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Influence of textural properties and iron content on the activated carbon performance for catalytic wet air oxidation of phenol

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Abstract

Catalytic Wet Oxidation is a promising treatment for wastewater containing refractory compounds, such as phenol. Activated carbon has demonstrated to perform as catalyst in wet oxidation, however it is not fully understood its role as catalyst. This study aims to clarify the effect of metal content, specifically iron and calcium, on the performance of a commercial activated carbon. Several modification of the activated carbon surface has been conducted and then calcium or iron has been supported on the modified materials. Then, the activated carbons were tested for the catalytic wet oxidation of phenol in a trickle bed system operating at 140ºC and 2 bar of oxygen partial pressure, with a space time of 0.12 hours. Activated carbons containing iron have given higher conversion, than the parent activated carbon, respectively 75 and 45%. However, a significant leaching was observed, which was limited for the iron containing activated carbon previously treated with nitric acid. In turn, no improvement was obtained from the activated carbons when calcium was added.

Keywords: activated carbon, catalyst, phenol oxidation, iron content, trickle bed

1. Introduction

Nowadays, increasingly stringent regulations about the disposal of hazardous chemical substances force the development of new low-cost and efficient alternatives for the treatment of effluents. Many of the available wastewater treatments are based on the oxidation of the substances at high temperature and pressure using oxidants. The use of dedicated catalysts allows to temper the operation conditions. In turn, AC has been used for years in water remediation (Dabrowski et al. 2005), typically in adsorption. AC can be made from almost any carbonaceous source such as wood and coal.; even great results have been obtained using sewage sludge as raw material (Rio et al. 2004). Different physico-chemical characteristics of AC, such as porosity and surface chemistry, can be obtained by controlling the media and conditions during the activation step. Also, post-manufactured treatments look like alternatives to improve the performance of AC in different applications. For instance, heat treatment under inert atmosphere has shown to be effective in reducing the surface oxygen content and increasing the adsorption capacity towards phenolic compounds, which are well-known pollutants because of their high toxicity and poor biodegradability (Ania et al., 2002; Tessmer et al., 1997). AC has also shown to possess catalytic activity for certain reactions. Pereira et al. (1999), and Stüber et al. (2001) have used AC carbon as catalyst in oxidative dehydrogenation (ODH) of ethyl benzene and CWAO of phenol, respectively. However, the specific physical and/or chemical characteristics that provided these catalytic activities are not yet well identified. Using heat treatment to partially remove surface oxygen, Pereira et al. (1999) found that surface quinones groups were responsible for the catalytic activity shown by AC in ODH. Nevertheless, the surface oxygen groups that could be partially responsible for the catalytic activity of AC in the CWAO of phenol have not been fully identified. In order to highlight which properties could influence the catalytic behaviour, a commercial AC with proven catalytic activity has been altered using several modification methods. It was found that a basic and stable to reoxidation AC surface, such as that obtained after a heat treatment under hydrogen, can increase the steady state phenol conversion up to 10%. Previous results obtained after acid treatment of the AC demonstrated that an increase in the surface oxygen content gave worse final phenol conversion (Santiago et al., 2005). Moreover, Fe content also seems to have some impact on the catalytic activity shown by AC, since previous studies made with demineralised samples showed a lower phenol conversion. However, the effect of textural properties has not been sufficiently studied, as all the treatments conducted until now have not practically changed either the surface area or the porosity. Therefore, the impact of porosity and Fe/Ca content on the CWAO of phenol was also investigated. A commercial AC was initially subjected to either Ca or Fe impregnation by ion exchange, and then heated under nitrogen up to 1000°C. An enhancement in the mesoporosity of the samples was observed due to carbon pore enlargement. Surface area and pore size distribution of carbons were characterised by nitrogen adsorption. The oxygen content was determined by elemental analysis while surface oxygen groups were characterised by Boehm method. The performance of these modified samples was evaluated by phenol adsorption and CWAO of phenol in a trickle bed reactor.

2. Experimental

Materials and analyses

A commercial activated carbon from Merck (ref. 2514) in form of 2.5 mm pellets was used. Prior to use, the activated carbon was crushed and sieved and the 25-50 mesh size particle range was separated. The above fraction was repeatedly washed to remove all fines and oven-dried overnight at 105ºC. This carbon was labeled as ME.

Crystallized phenol was purchased from Panreac (ref. 144852.1211, 99.9 % purity). HCl and NaOH solutions used for the Boehm method were standard tritation solutions, whereas Na_2CO_3, $NaHCO_3$ have 99.9% purity and were supplied by Sigma Aldrich. Sulphuric and nitric acid, sodium acetate and iron chloride were also supplied by Sigma Aldrich. Deionized water (DI) from a millipore system was used to prepare all the solutions and for measuring pH. Air and nitrogen was supplied by Carburos Metálicos, S.A. with a purity over 99.995%

Phenol concentration in samples from CWAO and adsorption experiments was measured by High Liquid Pressure Chromatography (HPLC). The HPLC was performed in an Agilent Technologies 1100 Series chromatograph, with a C18 reverse phase column (Hypersil ODS, 5 µm, 25 x 0.4 cm). The mobile phase was a 35/65 v/v mixture of methanol and deionised water, acidified at 1.41 with H_2SO_4, at a flow rate of 1 ml/min. The detection of phenol was made by UV absorbance at a wavelength of 254 nm. The Total Organic Carbon (TOC) was measured in a TC Multi Analyser 2100 N/C equipment from Analytic Jena with a non-diffractive IR detector.

Modification of AC

Nitric acid wash was conducted in a rotavapor at 80ºC. The HNO_3 concentration was 65% and 170 ml were used with 35 g of ME. AC was in contact with acid for 3 hours. Then, it was washed with distillated water until neutral pH and dried overnight at 105ºC. This thus treated AC is labeled as ME-N.

For sulfuric acid wash, a carbon sample was boiled for 1 hour in 96% H_2SO_4. The weight to weight ratio of acid to dried AC was 9:1. Then, it was washed with distillated water until neutral pH and dried overnight at 105ºC. The obtained AC is named ME-S.

Iron impregnation was performed by the ion-exchange method. AC samples were immersed for 2 days in $FeCl_2$ solution at 2% wt Fe concentration in an orbital shaker. This impregnation was conducted on ME, ME-N and ME-S. The iron impregnated AC's are termed correspondingly as ME-Fe, ME-N-Fe and ME-S-Fe.

Calcium impregnation was performed by the same method using a calcium acetate, $Ca(CH_3COO)_2$, solution at 0.4 % wt Ca concentration. This impregnation was conducted on ME, ME-N and ME-S. The calcium impregnated carbons are labeled correspondingly as ME-Ca, ME-N-Ca and ME-S-Ca.

At the end of these treatments, all samples were recovered and washed with distillated water until neutral pH and dried overnight at 105ºC. All iron impregnated AC's were subsequently carbonized in an horizontal furnace under nitrogen atmosphere at a heating rate of 20ºC min^{-1} up to 1000ºC and then let to cool until room temperature.

Characterization of activated carbon

Surface area and porosity of the AC's were obtained from nitrogen isotherm at 77 K using a Micromeritics 2010ASAP instrument. Samples were outgassed at 250ºC for 24 hours before the analysis. Surface area was determined from BET equation, total pore volume from the near saturation uptake (at the relative pressure of 0.98), mesopore and micropore volume was estimated according to BJH (Barret et al., 1951) and Horwath and Kawazoe theories (Horwart et al., 1983), respectively.

Mass titration method was used to determine the point of zero charge of each sample. 5% wt carbon slurries in deionized water were prepared, then shaken for 24 h and the final pH of the slurry was measured and taken as the pH_{pzc}.

For measuring the iron and calcium load, samples were digested in concentrated nitric acid by a microwave digestion equipment. Dilute solutions were analyzed by atomic absorption spectrophotometry.

Boehm titration was applied to determine the acidic surface functional group content of the samples. Solutions of $NaHCO_3$, Na_2CO_3 and NaOH (0.05 N) were used. The number and type of acidic sites were calculated by considering that NaOH neutralizes carboxylic, lactonic and phenolic groups, Na_2CO_3 neutralizes carboxylic and lactonic groups, and that $NaHCO_3$ neutralizes only carboxylic groups. Carboxylic groups were therefore quantified by direct titration with $NaHCO_3$. The difference between the groups titrated with Na_2CO_3 and those titrated with $NaHCO_3$ was assumed to be lactones and the difference between the groups titrated with NaOH and those titrated with Na_2CO_3 was assumed to be phenols. Each determination was performed by triplicate.

Experimental procedures

Phenol adsorption isotherms were obtained at 20ºC (± 2ºC) in oxic conditions. Solutions with phenol concentrations ranging from 0.5 to 7 g/l were used to evaluate the adsorption capacity at high concentrations. 0.25 g of AC was allowed to equilibrate with 50 ml of phenol solution at different concentrations. They were stirred for approximately 2 hours, and left 0.5 hour to let the AC to settle. The final concentration of samples was measured by HPLC.

CWAO experiments were carried out in a trickle bed reactor in downflow co-current. The reactor containing the AC packed bed consists of a titanium tube (20 cm long and 1.1 cm i.d.), which is placed in a controlled temperature oven (±1ºC). Typically, 7.0 g of AC was loaded into the reactor. The air flow rate was held constant at 2.4 STP ml/s. The liquid space velocity was set to 8.2 h^{-1} which is equivalent to a space time of 0.12 h, according to the weight of the catalytic bed. Phenol feed concentration was always 5 g/l. The experimental conditions were fixed at a temperature of 140ºC and 2 bar of oxygen partial pressure, giving a total working pressure of 13.1 bar. The experiments were run for 55 hours. Liquid samples were periodically withdrawn and then analyzed to determine phenol conversion (X) and TOC abatement (X_{TOC}). Also pH was measured in all the samples.

For calculations of X and X_{TOC} the following general expression was used:

$$X(\%) = \frac{C_o - C_e}{C_o} x100$$

where C_o is the inlet concentration and C_e the concentration in the exited effluent.

3. Results

Values in Table 1 indicates that all the modification treatments did not change significantly the surface area of the parent activated carbon ME, since it was reduced by 10% practically in all treated samples. The mesopore volume increased in ME-S-Ca nearly up to 3 times the original value. However, the total porosity volume is around the same value for all samples, only in the case of ME-S-Ca total porosity was 10% higher than that of ME. Several researchers have reported the same behaviour. For instance, Rio et al. (2005) have made activated carbon from activated sludges, and by adding lime, the final value of mesopore volume was 4 times higher than the mesopore volume of AC obtained without any additive.

Sample	A_{BET} (m^2/g)	$V_{micropore}$ (cm^3/g)	$V_{mesopore}$ (cm^3/g)	V_{total} (cm^3/g)
ME	1206	0.483	0.029	0.569
ME-Fe	1119	0.448	0.072	0.567
ME-N-Fe	1085	0.431	0.082	0.562
ME-S-Fe	1147	0.453	0.087	0.599
ME-Ca	1111	0.444	0.074	0.566
ME-N-Ca	1117	0.442	0.075	0.573
ME-S-Ca	1175	0.461	0.108	0.631

Table 1. Properties of parent and modified AC

After carbonisation the content of oxygen in AC surface decrease in most of the cases (see Table 2). The decrease of content of carboxylic type groups altogether with the pH_{pzc} value increased in all modified carbons, showing that elimination of acidic groups was achieved successfully. The increase of total oxygen surface content in case of ME-S-Ca can be attributed to the later condensation of phenolics and carboxylics groups producing a higher content of lactones type.

Sample	Phenolics (meq/g)	Lactones (meq/g)	Carboxylics (meq/g)	Total (meq/g)	pH_{pzc}
ME	0.097	0.123	0.031	0.251	7.36
ME-Fe	0.033	0.075	0.000	0.108	8.55
ME-N-Fe	0.119	0.202	0.049	0.370	7.99
ME-S-Fe	0.021	0.074	0.048	0.143	8.27
ME-Ca	0.000	0.128	0.000	0.128	8.84
ME-N-Ca	0.002	0.142	0.035	0.179	9.36
ME-S-Ca	0.000	0.531	0.011	0.542	10.77

Table 2. Chemical characteristics of activated carbons.

Table 3 shows the iron and calcium content in all modified samples. The iron content in samples ME-N-Fe and ME-S-Fe is 4 and 5 times higher, respectively, than in ME. Regarding the calcium content, the increase was considerable, achieving a Ca content in sample ME-S-Ca 6 times the value in ME. In all cases acid wash pretreatment shows to be effective in the creation of groups that later are responsible for the anchoring of metals like iron and calcium.

Sample	Fe content (wt%)	Ca content (wt%)
ME	0.40	0.15
ME-Fe	0.51	--
ME-N-Fe	1.43	--
ME-S-Fe	2.08	--
ME-Ca	--	0.40
ME-N-Ca	--	0.79
ME-S-Ca	--	0.90

Table 3. Iron and Calcium content of activated carbons.

In Figure 1 the adsorption isotherms of phenol of each sample is represented. The increase of metal content did not modify the phenol uptake capacity since all samples show approximately the same behaviour. Only sample ME-S-Ca show an increase of about 30% at high concentrations. This can be attributed to the high micro and mesopoure volume value, allowing more phenol molecules to be adsorbed on the phenol internal porosity structure. Also, the decrease of acidic oxygen surface groups contributes to improve the interaction between phenol and aromatic rings of phenol, by reducing the hydrophilicity of AC surface.

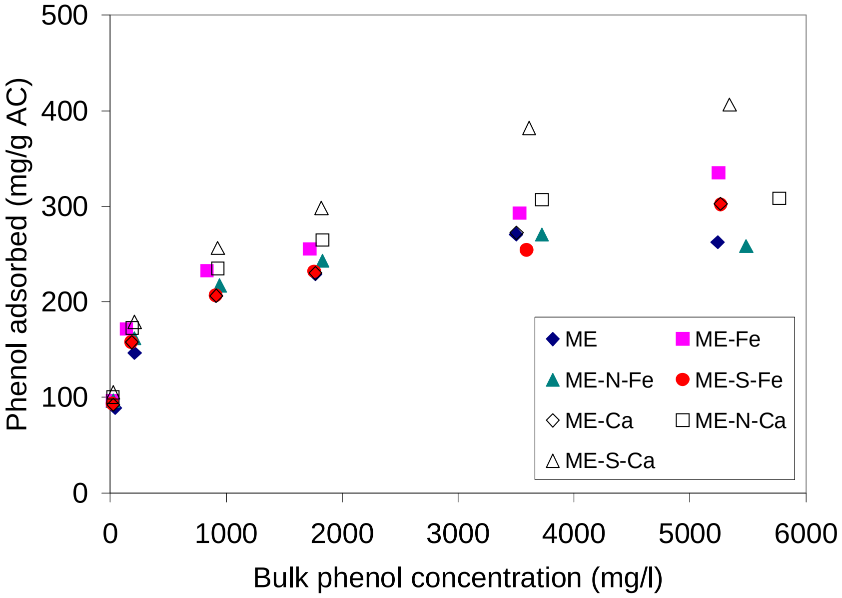

Figure 1. Adsorption isotherms of phenol over activated carbons at 20ºC.

Figure 2 shows the phenol elimination for the TBR tests during the time on stream using AC as catalyst. Samples with a high content of iron showed a better conversion in steady state than the original ME and all calcium treated samples. Even ME-Fe that was not pretreated with acid performed better as catalyst than ME. It is worth to notice that there is no difference between the final conversion value obtained with ME-N-Fe and ME-S-Fe, despite the iron content of the latter is higher. A modification in calcium content did not modify the catalytic activity of ME. In case of sample ME-S-Ca a slight decrease of activity with time is observed. This could be attributed to the formation of polymers by oxidative coupling reactions that take place in AC surface, and that in this case are promoted by the high surface oxygen content and the high value of mesopore volume, affecting the surface area available for phenol oxidation reactions.

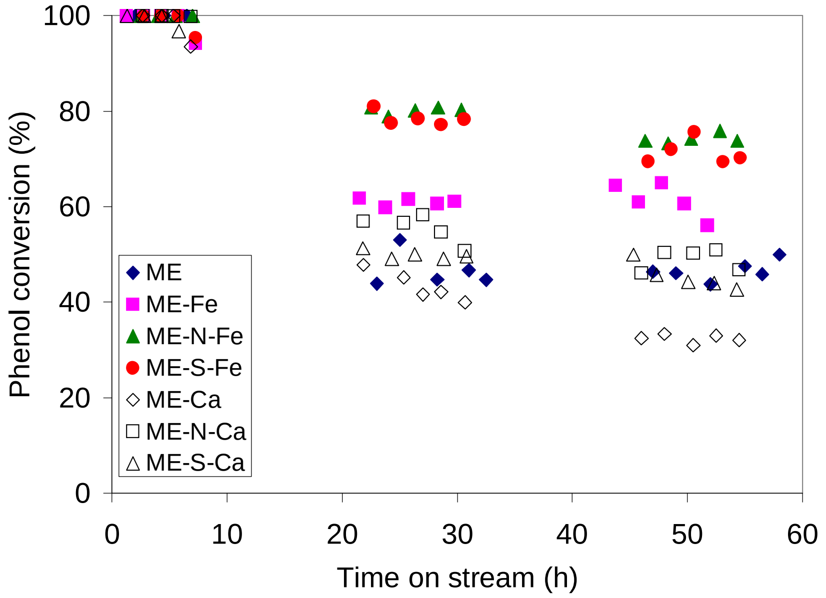

Figure 2. Phenol conversion by different activated carbons in the TBR at 140ºC, 2 bar of oxygen partial pressure and 0.12 h of space time.

In Figures 3 and 4, the Fe and Ca content before and after being used in the TBR are represented.

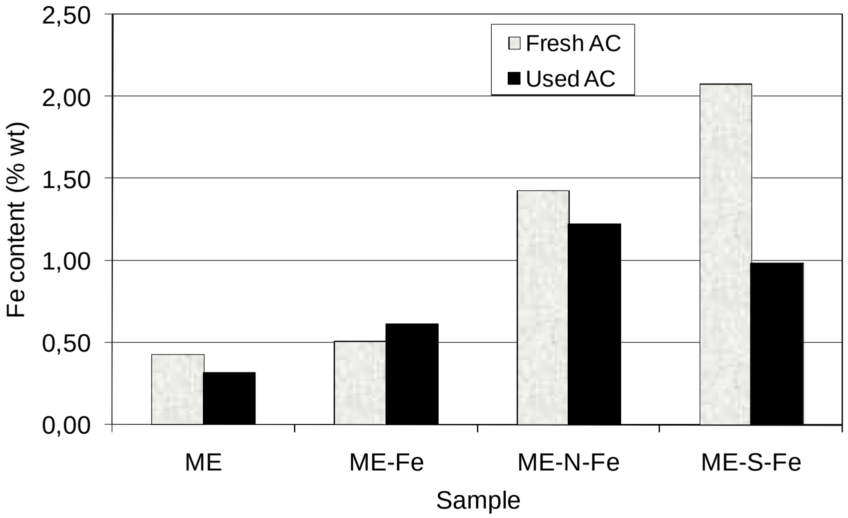

Figure 3. Iron content (%wt) of fresh and used in CWAO activated carbons.

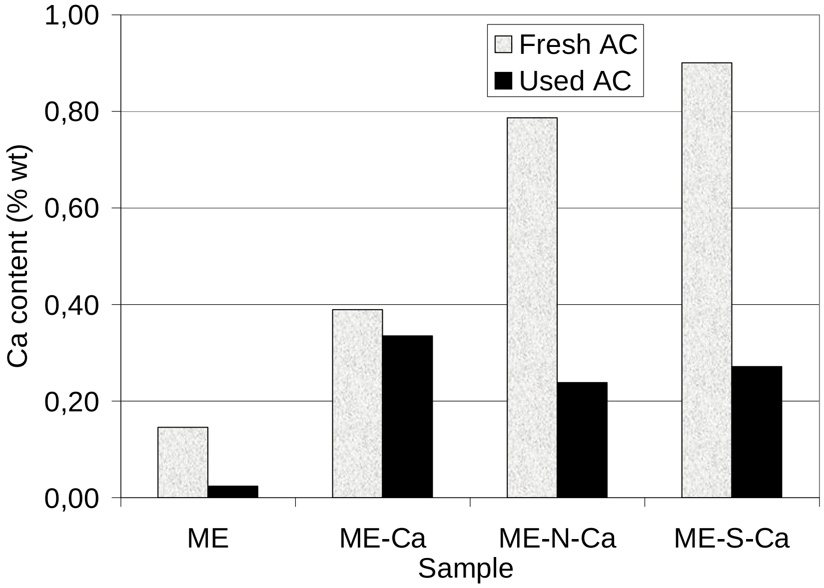

Figure 4. Calcium content (%wt) of fresh and used in CWAO activated carbons.

In case of samples treated with Fe, a significant leaching was observed. In ME-S-Fe practically half of the iron content was lost after 55 hours of operation in the TBR. However, the final value was very close to that of ME-N-Fe and still 2 times higher than the content of the parent ME. This could be the reason why they showed the same catalytic activity in steady state. The calcium that was introduced in ME was strongly lowered during the TBR operation, despite the calcium content obtained in samples after being used in the reactor is considerably higher than in original ME.

Regarding the TOC conversion, as it can be seen in Figure 5, a clear difference between the values obtained with ME-N-Fe and ME-S-Fe can be observed. In this case, the high iron leaching observed in ME-S-Fe could be making iron to act as catalyst in the homogenous phase, promoting the higher elimination of TOC, which was not so evident when using ME-N-Fe in the TBR. In turn, calcium does not seem to have any effect in TOC elimination, since conversion obtained with calcium treated sample is practically the same than that obtained with original ME.

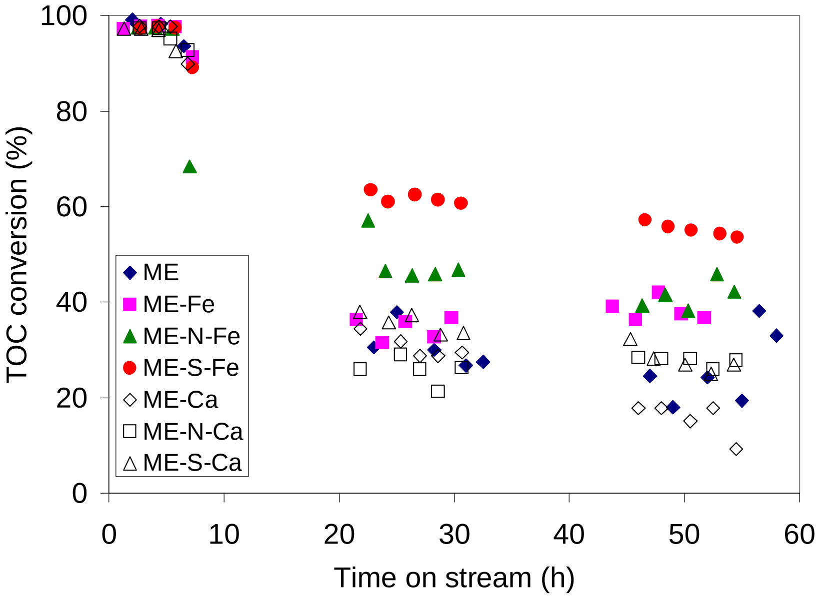

Figure 5. TOC conversion by different activated carbons in the TBR at 140ºC, 2 bar of oxygen partial pressure and 0.12 h of space time.

4. Conclusions

Activated carbons can be successfully modified to improve their performance as catalysts in the wet oxidation of phenol. A commercial activated carbon was subjected to acid wash and subsequently calcium or iron was supported over them.

Acid wash, either with sulphuric or nitric acid, does not modify the textural properties of the parent activated carbon. Iron and calcium were effectively supported over these pre-treated carbons. All the activated carbons showed similar adsorption capacity of phenol.

CWAO tests in the trickle bed reactor showed that iron containing activated carbons were able to give higher conversion than the parent activated carbon, 75% and 45% respectively. However, some leaching was found. In turn, addition of calcium did not improve the performance of the original activated carbon.

Thus, an activated carbon can be successfully modified to give higher catalytic activity for CWAO applications. In any case, the leaching should be avoided for a wide implementation of this method.

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References

Ania, C.O., J.B. Parra, and J.J. Pis, (2002) *Fuel Process. Technol.,* 79, 265-271.

Dabrowski, A., P. Podkoscielny, Z. Hubicki and M. Barczak, (2005) *Chemosphere*, 58**,** 1049-1070.

Pereira, M.F.R., J.J.M. Orfao, and J.L. Figueiredo, (1999) *Appl. Catal., A*., 184, 153-160.

Rio, S., Faur-Brasquet, C., Le Coq, L., Lecomte, D., and P. Le Cloirec, (2004) *Water Sci. Technol.,*49, 139-146.

Rio, S., Faur-Brasquet, C., Le Coq, and P. Le Cloirec, (2005) *Environ. Sci. Technol.*,39, 4249-4257.

Santiago, M., F. Stuber, A. Fortuny, A. Fabregat and J. Font, (2005) *Carbon*, 43, 2134-2145.

Stüber, F., I. Polaert, H. Delmas, J. Font, A. Fortuny, and A. Fabregat, (2001) *J. Chem. Technol. Biotech.,* 76, 743-751.

Tessmer, C.H., R.D. Vidic, and L.J. Uranowski, (1997) *Env. Sci. Technol.*, 31, 1872-1878.