Impact of the Carbonization Atmosphere on the Properties of Phosphoric Acid-activated Carbons from Fruit Stones[†]

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ABSTRACT: Activated carbons were obtained by phosphoric acid activation of a mixture of fruit stones (apricot and peach) in two different atmospheres (argon and air) at various temperatures in the 400–1000ºC range. The evolution of several characteristic parameters of the resulting carbons (bulk density, yield, BET surface area, ultramicropore, supermicropore and mesopore volumes and cation-exchange capacity) with activation temperature was examined. The above parameters were re-calculated on a volume basis (practical effectiveness) and a volume-yield basis (economic efficiency). It was concluded that carbons obtained in an argon atmosphere exhibit some practical advantages over those obtained in air regarding cation adsorption, although those obtained in air may represent an interesting alternative regarding porous structure.

1. INTRODUCTION

The utilization of activated carbons has increased consistently with the development of the industrial production of active carbon at the beginning of the last century. Nowadays, activated carbon is widely used in many fields of chemical technology. Indeed, the great success of modern adsorption techniques has been facilitated significantly by the continuously increasing quality of carbons generated by improvements in their production techniques.

Phosphoric acid activation is widely used for the production of activated carbons. The use of various precursors including wood, nutshells, viscose rayon and coal has been extensively investigated. It has been shown that the maximum surface area is obtained at carbonization temperatures of 350ºC for white oak wood (Jagtoyen and Derbyshire 1993), 450ºC for coconut shell and sub-bituminous coal (Laine *et al*. 1989) and 500ºC for bituminous coal (Jagtoyen and Derbyshire 1993). Recently, polymer precursors have also been investigated (Puziy *et al*. 2002a–e, 2003, 2007a; Sobiesiak *et al*. 2006; Suárez-García *et al*. 2004a,b).

Results on the influence of the atmosphere on the properties of carbons obtained by phosphoric acid activation of lignocellulosic materials have been reported (Molina-Sabio *et al*. 1995; Benaddi *et al*. 1998, 2000). For low impregnation ratios of a peach stone precursor, the yield was lower in air than in nitrogen (Molina-Sabio *et al*. 1995), with the reverse occurring at higher impregnation ratios. With wood as the precursor, the micropores and surface area were more developed using air

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or nitrogen than using steam (Benaddi *et al.* 1998). Indeed, use of the latter agent led to carbons with an almost neutral surface (Benaddi *et al.* 2000).

In previous papers (Puziy *et al.* 2005, 2007b), the surface chemistry, copper ion adsorption and porous structure of phosphoric acid-activated carbons from fruit stones were investigated. It was shown that phosphoric acid activation of a mixture of apricot and peach stones led to the one-step formation of mechanically stable porous carbons with acidic surface groups. The acidic character of the phosphoric acid-activated carbons thus obtained enabled them to adsorb heavy metal ions from aqueous solutions. In the present communication, studies of the impact of the activating atmosphere on the practical and economic effectiveness of fruit stone phosphoric acid-activated carbons are reported. Usually, parameters characterizing carbon are related to the mass of the adsorbent. However, in practice, the capacity of the adsorption device is measured in volume units and thus the bulk or packing density of the adsorbent can significantly influence the amount in mass units of the adsorbent that can be loaded into the adsorber (Jordá-Beneyto *et al.* 2008). Hence, the mass-based characteristics of a carbon adsorbent can be significantly different from the volume-based parameters. Thus, in the present study, volume-based parameters were chosen as a measure of the practical effectiveness of the adsorbent. From an economical point of view, carbon yield is one of the most important factors, as it determines the price of the adsorbent. Consequently, the economic efficiency of the adsorbent was estimated as the practical effectiveness (volume-based parameters) multiplied by the carbon yield. The evolution of various parameters characterizing the phosphoric acid-activated fruit stone carbons reported on these three bases (mass-based, volume-based and volume-yield-based) has been analyzed as a function of the carbonization temperature and atmosphere employed.

2. EXPERIMENTAL

Carbons activated with phosphoric acid were prepared according to a procedure described elsewhere (Puziy *et al.* 2005, 2007b). Briefly, crushed and sieved fruit stones (a mixture of apricot and peach stones, particle size 0.315–1.0 mm) were impregnated with 60% phosphoric acid to a 0.88–0.89 acid/precursor ratio (weight of H_3PO_4/weight of precursor, dry basis), dried in air and then carbonized in a quartz reactor at temperatures of 400–1000°C for 30 min. Carbonization was undertaken in a flow of argon (1 ℓ/min) or air (3 ℓ/min). To remove the excess phosphoric acid, the carbons were extensively washed with hot water in a Soxhlet extractor until the pH of the wash water was equal to 7. After such washing, the carbons were dried in air at 110°C.

The carbons were characterized by nitrogen adsorption isotherms measured at –196°C employing an ASAP 2010 apparatus (Micromeritics Corp., Norcross, GA, U.S.A.). Pore-size distributions were calculated from these isotherms using the DFT Plus software (Micromeritics Instrument Corporation), based on the non-local density functional theory (NLDFT).

The cation-exchange capacity (CEC) was determined using the Boehm method (Puziy *et al.* 2002b; Sobiesiak *et al.* 2006). Thus, a weighed amount of adsorbent (0.1 ± 0.0001 g) was placed in an Erlenmeyer flask, a 20 mℓ volume of 0.1 M NaOH solution added and the flask shaken for 24 h to attain equilibrium. After equilibration, the NaOH concentration was measured by titration with HCl. The quantity of NaOH consumed was converted into the CEC and expressed in mmol/g.

Volume-based parameters that reflect the practical effectiveness were calculated by multiplying the mass-based parameters by the bulk density of the carbon. In this way, the parameters can also be reported per unit volume of carbon bed. Parameters reflecting economic efficiency were obtained by

multiplying the mass-based parameters by both the bulk density and the carbon yield. Following McBain (1932), the bulk density is defined as the mass of unit volume of the tamped adsorbent bed. This value includes the adsorbent material (carbon), its pore space and the inter-particle voids.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the temperature dependence of the yield of carbon from fruit stones without phosphoric acid treatment as obtained in argon and for samples treated with phosphoric acid and carbonized in argon and in air. It will be seen from the figure that the yields of all the carbons progressively decreased with increasing carbonization temperature. The slight increase in yield at 800°C for phosphoric acid-activated carbons obtained in argon may be attributed to a higher amount of phosphorus incorporated into the carbon structure. The yields of carbon obtained in argon at temperatures in the range 400–700°C were the same as obtained for carbons in air. However, at the higher temperatures, the yield was lower for carbons obtained in air than for carbons obtained in an argon atmosphere. This is attributable to the strong anti-oxidant action of phosphoric acid at low temperatures which prevented oxidation at temperatures below 700°C. At higher temperatures, the extensive oxidation and gasification which occurred led to a decrease in the yield of carbon. At moderate temperatures within the range 400–800°C, the addition of phosphoric acid increased the yield of carbon obtained in both argon and air atmospheres. Carbons obtained by phosphoric acid activation in air at 900–1000°C exhibited the same yield as carbons heat-treated in argon without H_3PO_4.

The bulk density of fruit stone carbons obtained in both atmospheres (argon and air) increased as the carbonization temperature was increased up to 800°C and then diminished at higher temperatures [see Figure 1(b)]. This increase may be attributed to densification of the carbon and a progressive increase of incorporated phosphorus, while the decrease at high temperatures was due to evaporation of the phosphorus species and gasification of the carbon. The variations in yield and bulk density with carbonization temperature are expected to influence the practical and economical efficiency of the studied activated carbons.

Figure 2(a) shows the temperature dependence of the BET surface area of the fruit stone phosphoric acid-activated carbons obtained in argon and in air. The mass-based surface area of the
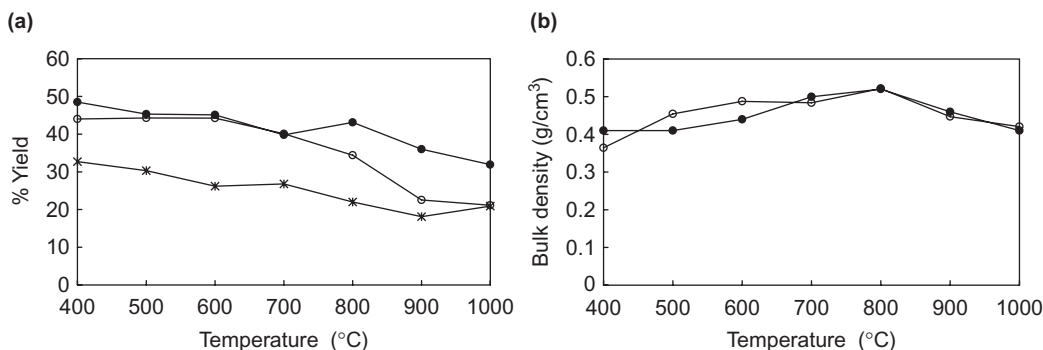

Figure 1. Temperature dependence of (a) the yield and (b) the bulk density of the fruit stone phosphoric acid-activated carbons obtained in argon and air. The data points in the two parts relate to the following: (a✳, argon without H_3PO_4; ●, argon with H_3PO_4; ○, air with H_3PO_4; (b) ●, argon; ○, air.
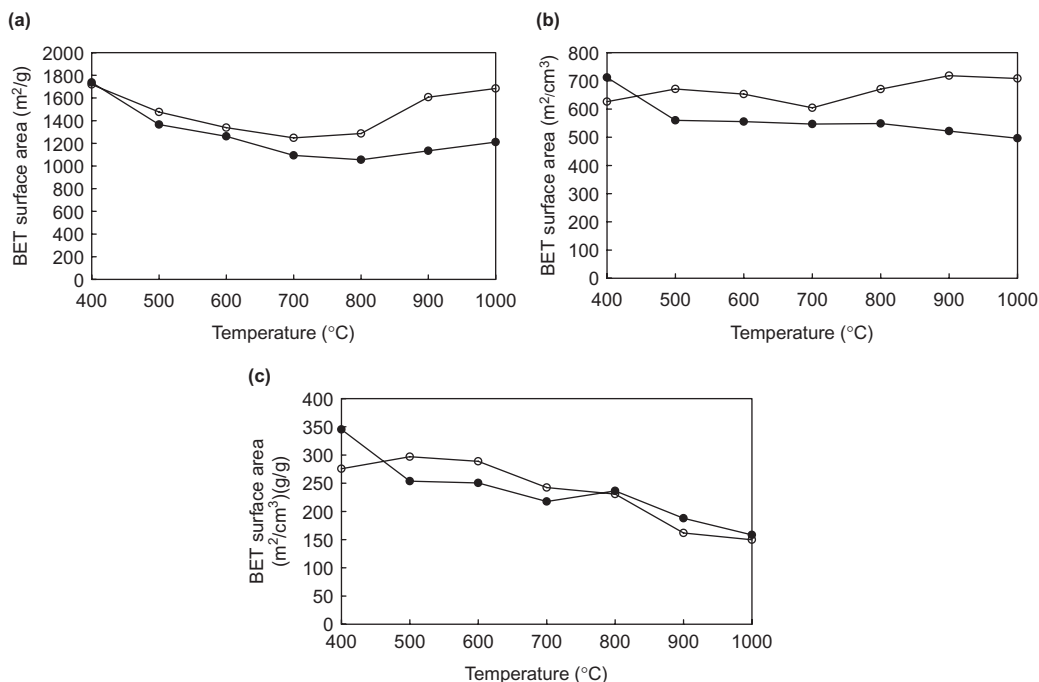
Figure 2. Temperature dependence of the BET surface area of the fruit stone phosphoric acid-activated carbons obtained in (●) argon and (○) air as plotted (a) on a mass basis, (b) a volume basis and (c) a volume-yield basis.

synthetic carbons obtained in air was larger at carbonization temperatures higher than 400ºC, probably due to additional activation with oxygen. The difference in the BET surface area increased with increasing carbonization temperature. The same trend was observed for the volume-based surface area [Figure 2(b)], except for carbons obtained at 400ºC. For this temperature, the volume-based BET surface area was higher for the carbon obtained in argon. The volume-based surface area roughly corresponds to the practical effectiveness of synthetic carbons in applications connected with the adsorption of organics from the gaseous phase or from solutions. The economic effectiveness of surface-area development [Figure 2(c)] for the fruit stone phosphoric acid-activated carbons obtained in argon gradually decreased up to 700ºC, slightly increased at 800ºC and then again decreased at higher carbonization temperatures. However, for carbons obtained in air, a slight increase in practical effectiveness was observed for carbonization at 500ºC, with a progressive decrease occurring at higher carbonization temperatures. From an economic point of view, carbonization in argon at 400ºC and in air at 500–600ºC would be preferable for applications where molecular adsorption is of great importance.

Figures 3–5 show the evolution of different pore-volume parameters (ultramicropore volume, V_{umi}, supermicropore volume, V_{smi}, and mesopore volume, V_{me}) as a function of activation temperature in the two studied atmospheres. These pore volumes were calculated from the NLDFT-calculated pore-size distributions. Here, ultramicropores are those pores with a width < 1 nm, supermicropores are those with a width between 1 and 2 nm, and mesopores are those with a width > 2 nm.
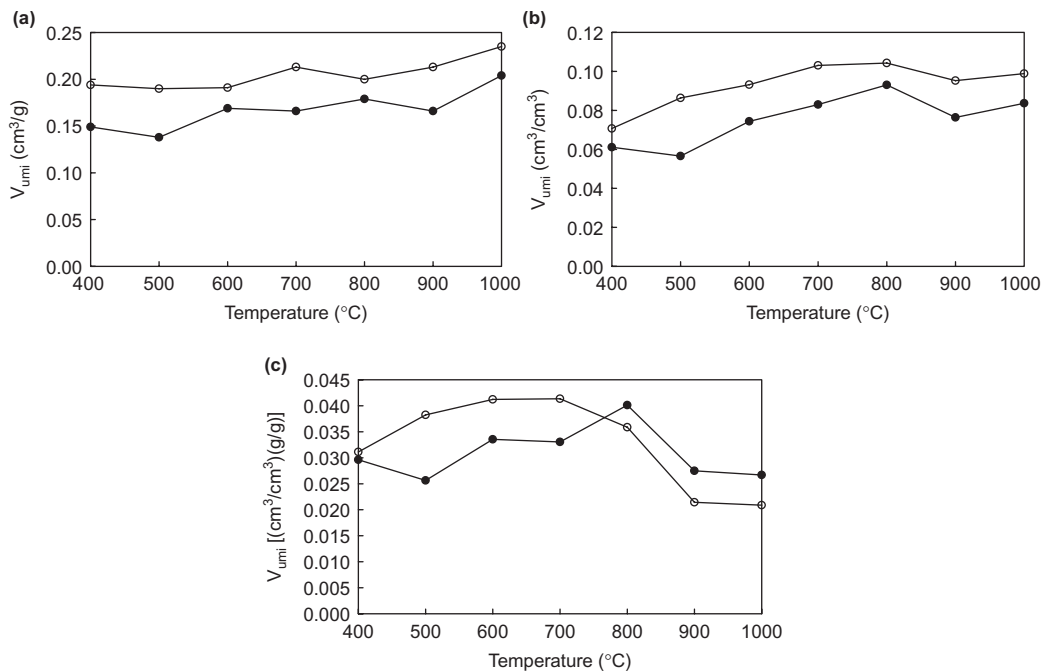
Figure 3. Temperature dependence of the ultramicropore volume (V_{umi}) of the fruit stone phosphoric acid-activated carbons obtained in (●) argon and (○) air as plotted (a) on a mass basis, (b) a volume basis and (c) a volume-yield basis.

Figure 3(a) shows that the ultramicropore volume of both series of carbons tended to increase as the carbonization temperature increased. The mass-based ultramicropore volumes of carbons prepared in air were systematically higher than those of carbons prepared in argon, indicating that an oxygen-containing atmosphere favoured the development of small micropores. The volume-based ultramicropore volumes passed through a maximum as the carbonization temperature increased, indicating that the optimal practical effectiveness towards small molecules was achieved at 700–800ºC for both series of carbons [Figure 3(b)]. The volume-based ultramicropore volumes of carbons prepared in air were also steadily higher than those of carbons prepared in argon. The volume-yield-based ultramicropore volume also passed through a maximum at 800ºC for carbons prepared in argon and at 600–700ºC for carbons prepared in air, showing that the economic effectiveness for small molecules was achieved at different temperatures depending on the atmosphere used [Figure 3(c)].

The mass-based supermicropore volume was independent of the atmosphere employed for carbonization and diminished as the carbonization temperature increased up to 700ºC [Figure 4(a)]. At higher temperatures, the mass-based supermicropore volumes of the carbons prepared in an argon atmosphere continued to decrease with a tendency towards saturation, while those of carbons obtained in air increased. A similar tendency was observed for the volume-based supermicropore volume [Figure 4(b)], the difference being in a higher value for the carbon obtained in argon at 400ºC. The volume-yield-based supermicropore volume progressively decreased as the carbonization temperature increased [Figure 4(c)]. The maximum economic effectiveness was observed for the carbon obtained at 400ºC in an argon atmosphere.
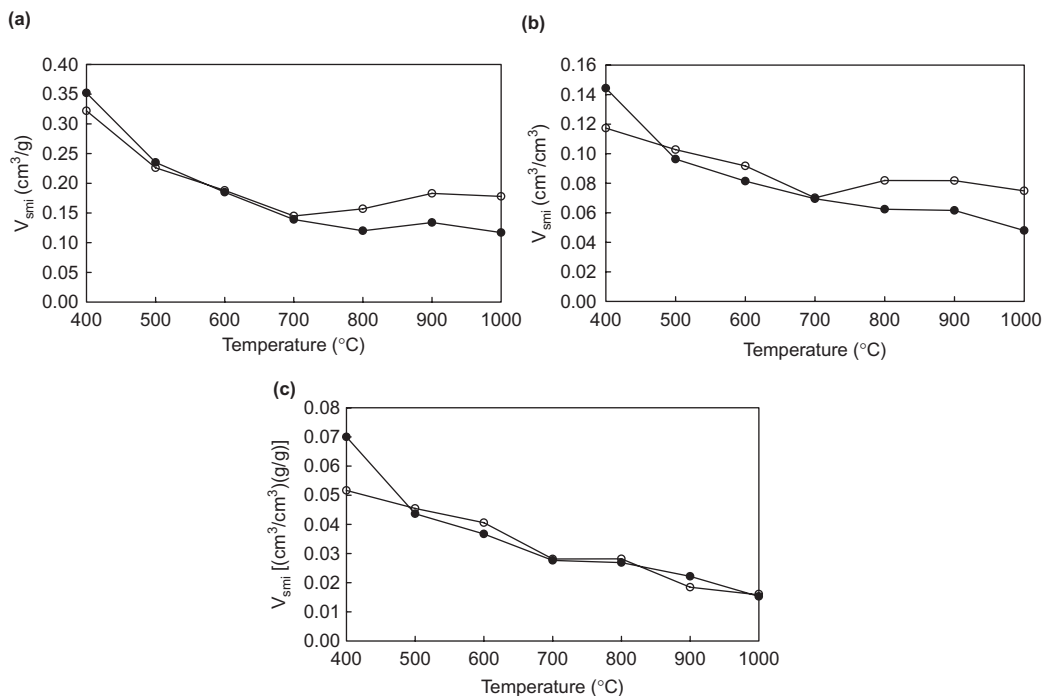
Figure 4. Temperature dependence of the supermicropore volume (V_{smi}) of the fruit stone phosphoric acid-activated carbons obtained in (●) argon and (○) air as plotted (a) on a mass basis, (b) a volume basis and (c) a volume-yield basis.

The evolution of the mass-based mesopore volume [Figure 5(a)] was somewhat similar to the progress of the supermicropore volume. Despite increasing the carbonization temperature up to 700°C, the mesopore volume was independent of the carbonization atmosphere and constantly decreased. At higher temperatures, the mesopore volume showed a more pronounced increase for the carbons prepared in air. The same tendency was observed for the volume-based mesopore volume [Figure 5(b)], showing that the optimal practical effectiveness for large molecules was achieved for carbons obtained at 900–1000°C in air. The volume-yield-based mesopore volume for both series of fruit stone carbons showed a tendency to decrease with increasing carbonization temperature up to 700°C, but remained virtually unchanged on carbonization at higher temperatures [Figure 5(c)]. This latter observation indicates that, from an economic point of view, the most effective material for the adsorption of relatively large molecules would be the carbon obtained at the lowest temperature (400°C) in an argon atmosphere.

Fruit stone phosphoric acid-activated carbons exhibit a significant adsorption capacity towards metal ions from aqueous solutions due to the presence of acidic surface groups (Puziy *et al.* 2005, 2007b), with the amount of metal ion adsorbed being roughly proportional to the cation-exchange capacity (CEC) as measured by Boehm's method. Figure 6(a) shows the temperature dependence of the mass-based CEC value. The value of the CEC increased as the carbonization temperature employed increased, passing through a maximum for carbons obtained in argon at 800°C and at 700°C for those obtained in air. For lower carbonization temperatures (400–700°C), the CEC
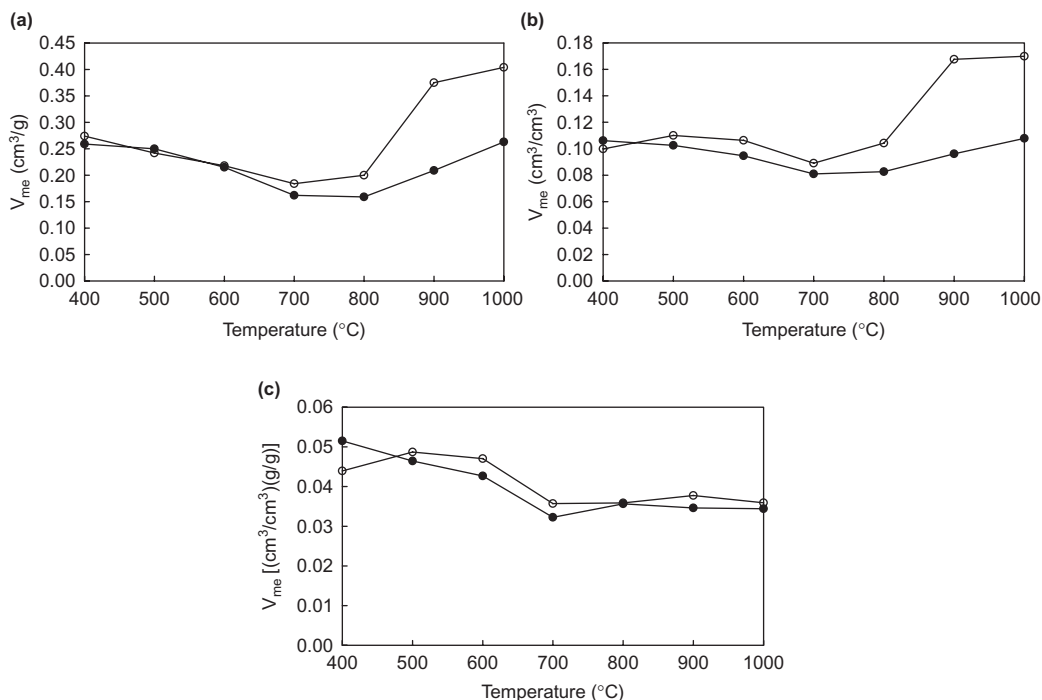
Figure 5. Temperature dependence of the mesopore volume (V_{me}) of the fruit stone phosphoric acid-activated carbons obtained in (●) argon and (○) air as plotted (a) on a mass basis, (b) a volume basis and (c) a volume-yield basis.

values of carbons obtained in air were higher than those for carbons obtained in argon, obviously due to the more extensive formation of oxygen-containing surface groups in an air atmosphere. With increasing carbonization temperature, the volume-based CEC passed through a maximum at 800°C for both series of carbons, indicating that the optimal practical effectiveness for metal-ion adsorption was achieved by carbonization at 800°C for carbons obtained in argon and at 700–800°C for carbons obtained in air [Figure 6(b)]. However, the volume-yield-based CEC values show that, from an economic point of view, the most effective carbon would be that obtained after carbonization at 800°C in an argon atmosphere [Figure 6(c)].

4. CONCLUSIONS

Volume-based parameters are important for the evaluation of the practical effectiveness of the studied carbon adsorbents, being significant from an economic point of view. On the basis of this criterion, fruit stone phosphoric acid-activated carbons obtained in an argon atmosphere have been found to exhibit some practical advantages for cation adsorption from aqueous media over those obtained in air. However, the carbons obtained in air offered some alternative advantages in pore structure, although the lower yields obtained in this atmosphere tended to obscure such differences when examined from an economic point of view.
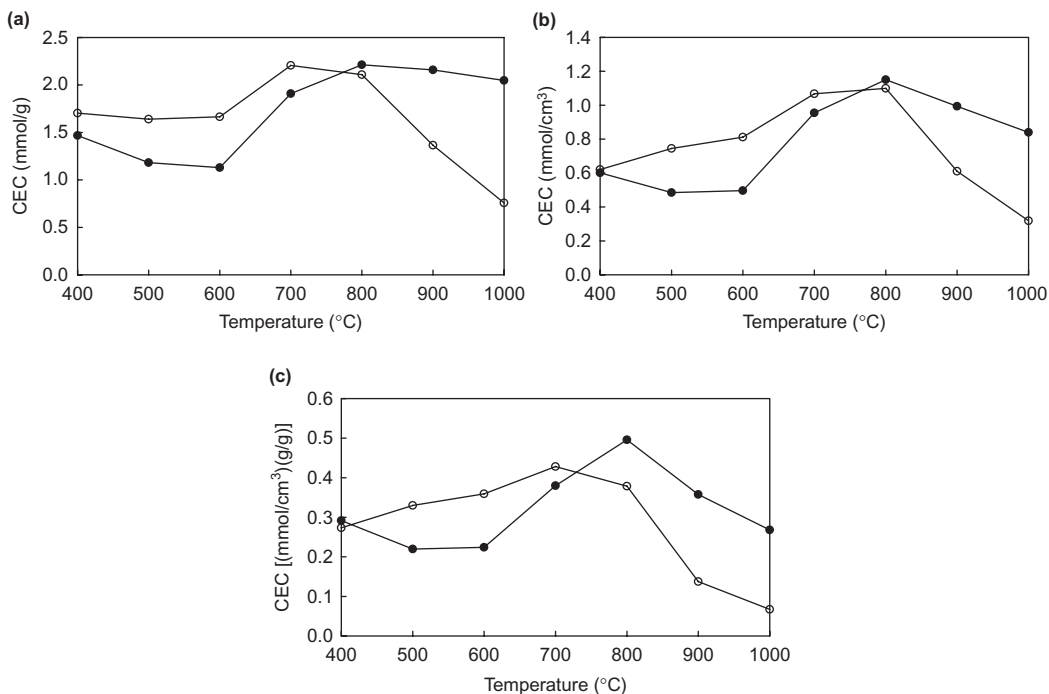
Figure 6. Temperature dependence of the cation-exchange capacity (CEC) of the fruit stone phosphoric acid-activated carbons obtained in (●) argon and (○) air as plotted (a) on a mass basis, (b) a volume basis and (c) a volume-yield basis.

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