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PRODUCTION OF ACTIVATED CARBONS FROM WASTE TYRES FOR LOW TEMPERATURE NO_X CONTROL

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Abstract

Waste tyres were pyrolysed in a bench scale reactor and the product chars were chemically activated with alkali chemical agents, KOH, K_2CO_3, NaOH and Na_2CO_3 to produce waste tyre derived activated carbons. The activated carbon products were then examined in terms of their ability to adsorb NOx (NO) at low temperature (25 °C) from a simulated industrial process flue gas. This study investigates the influence of surface area and porosity of the carbons produced with the different alkali chemical activating agents on NO capture from the simulated flue gas. The influence of varying the chemical activation conditions on the porous texture and corresponding NO removal from the flue gas was studied. The activated carbon sorbents were characterized in relation to BET surface area, micropore and mesopore volumes and chemical composition. The highest NO removal efficiency for the waste tyre derived activated carbons was ~75% which was obtained with the adsorbent treated with KOH which correlated with both the highest BET surface area and largest micropore volume. In contrast, the waste tyre derived activated carbons prepared using K_2CO_3, NaOH and Na_2CO_3 alkali activating agents showed much lower NO removal from the flue gases. The results suggest problematic waste tyres, have the potential to be converted to activated carbons with NOx removal efficiency comparable with conventionally produced carbons.

Keywords: Activated carbon; NOx; Tyre; Waste

1. Introduction

Activated carbons with developed porous texture and high surface area have been widely used as pollution control adsorbents to adsorb a range of pollutant gases from flue gas streams. An interesting environmental and sustainable concept is to convert waste materials to activated carbons which are then used in pollution control applications. Many researchers have reported on the production of activated carbons from various solid wastes materials such as lignocellulosic materials (Simitzis and Sfyrakis, 1994), corn cob (Tsai et al., 1998) Kraft lignin (Gonzalez-Serrano et al., 1997), scrap tyres (Sun et al., 1997), textile waste (Nahil and Williams, 2010), rice husk (Liou and Wu, 2009) and palm shell (Lim et al., 2010). However most of these studies aimed to only prepare activated carbons with textural properties similar to commercially available activated carbons and not to test their sorption abilities.

The presence of nitrogen oxides (NOx) in industrial flue gases is problematic since emissions of NOx produce acid rain and ozone formation. Conventional control of NOx involves addition of ammonia through the selective catalytic reduction process, but can result in slippage of ammonia (Klose and Rincon, 2007). Over 90% of fossil fuel derived NOx from power stations consists of NO (Neathery et al., 1997). There has been interest in producing adsorbents which can remove NOx through adsorption and reduction, without the use of a reducing agent (Klose and Rincon, 2007). Carbon based adsorbents have been investigated to remove NOx at lower temperatures, for example between 25 °C and 200 °C (Neathery et al., 1997). Such temperatures occur after an acid gas scrubber unit to remove SO_2 and HCl which are known to interfere with the selective catalytic reduction NOx removal process (Klose and Rincon, 2007).

Activated carbons can be prepared either by physical or chemical activation. Physical activation involves pyrolysis of the feedstock followed by the activation of the resultant char with steam or CO_2 as the activating agent (Wigmans, 1989; Kovacik et al., 1995; Hayashi et al., 2000). In chemical activation, the precursor is impregnated or mixed with chemical agents such as KOH, NaOH, H_3PO_4 and K_2CO_3 which promotes the formation of cross-links and the formation of a carbon with a rigid matrix (Hsu and Teng, 2000; Lozano-Castello et al., 2001; Oh and Park, 2002; Lim et al., 2010; Nowicki et al., 2010; Nahil and Williams, 2012;; Illingworth et al., 2012). In relation to chemical activation, both the activation preparation process parameters and the type of feedstock precursor have been shown to influence the properties and characteristics and consequently the end-use application of the product activated carbon (Lozano-Castello et al., 2002; Fierro et al., 2007; Armandi et al., 2011).

Waste tyres represent a major input to the European waste stream, with an estimated 3.3 million tonnes arising annually with an estimated stockpile in Europe of 5.7 million tonnes (Williams, 2013). Currently, waste tyre management in Europe includes, tyre retreading (~8%) fuel in cement kilns (~35%), materials recovery (~33%) civil engineering applications (~7%) and export (~10%). However, waste tyres have a high carbon content and have the potential to be processed to produce higher value activated carbons. For example, activated carbon production through physical activation (Cunliffe and Williams, 1999) or chemical activation (Teng et al., 2000) has been reported.

In this research, waste tyres have been processed to produce activated carbons which are then tested for their effectiveness in reducing NOx from a simulated flue gas representative of a typical industrial process. The work investigates the potential of a low cost waste derived feedstock resource to produce a valuable adsorbent material for control of a problematic industrial gaseous pollutant. The production of activated carbons from waste tyres was investigated via chemical activation with different alkali activating agents, KOH, K_2CO_3, NaOH and Na_2CO_3. The activated carbons were tested in terms of their ability to adsorb NOx (NO) at low temperature (25 °C) from a simulated flue gas in relation to the characteristics, particularly surface area and porosity, of the different product carbons.

2. Experimental

2.1 Waste tyre feedstock

Shredded passenger car tyres with an average particle size of 1.7 mm were used as the carbon precursor feedstock. The sample consisted of only the rubber component of the waste tyre, with the metal and textile reinforcement already removed. The characteristics of the feedstock waste tyre used was, volatile content, 62.2 wt.%, fixed carbon, 29.4 wt.%, ash content, 7.1 wt.% and moisture content 1.3 wt.%. The high fixed carbon content was due to the high content of carbon black present in the tyre which is used in tyre formulation to strengthen the rubber and improve abrasion resistance. Elemental analysis of the waste tyre gave a carbon content of 81.2 wt.%, hydrogen at 7.2 wt.%, nitrogen at 0.5 wt.% and sulphur content at 2.6 wt.%.

2.2 Preparation of activated carbons

In some procedures for the preparation of chemically activated carbons, the activated carbon is produced by chemical addition or impregnation of the raw precursor followed by activation at temperatures above 400 °C (Lim et al., 2010; Lozano-Castello et al., 2001; Hsu and Teng, 2000; Nahil and Williams, 2012). In other cases the process involves the production of a char produced from the pyrolysis of the raw material, followed by impregnation of the char and subsequent activation at higher temperature (Nowicki et al., 2010; Oh and Park, 2002; Illingworth et al., 2012). In this work, the activated carbons produced from the waste materials were prepared by pyrolysis followed by chemical activation with alkali metals. Pyrolysis was carried out in a fixed bed, laboratory scale reactor, 250 mm long x 30 mm i.d. externally heated by an electrical furnace (Figure 1(a)). The reactor was fully instrumented in terms of gas flow control, furnace temperature control and temperature monitoring throughout. The waste tyre (10 g) was held in a sample crucible within the reactor and heated to a final temperature of 600 ºC at a heating rate of 10 ºC min^{-1} and held at this final temperature for one hour with a continuous inert N_2 purge (200 ml min.$^{-1}$). A condenser system of a water cooled condenser and two solid CO_2 cooled condensers was used to trap the condensable liquids. Non-condensable gases were trapped in a Tedlar™ gas sample bag for later off-line analysis. The chars recovered from the pyrolysis reactor were ground and sieved to 1.5 - 2 mm particle size and dried at a temperature of 105 ºC overnight. Typical characteristics of the derived pyrolysis char have been reported previously (Al-Rahbi et al., 2016), with the char consisting of 78.8 wt.% fixed carbon, 2.0 wt.% volatiles and a high ash content of 18.9 wt.%. Elemental analysis of the char was 70.1 wt.% carbon, 0.3 wt.% hydrogen, 0.83 wt.% nitrogen and 4.78 wt.% sulphur.

The char was then subjected to chemical activation with the use of KOH, K_2CO_3, NaOH and Na_2CO_3 as the activating agents. The char was physically mixed with the alkali chemical agent with a weight ratio of 1:3. The influence of the chemical impregnation ratio was also investigated using KOH, where the char was physically mixed with KOH with various weight ratios (0.5, 1, 3 and 4:1). All the activations took place at an activation temperature of 900 °C. However, additionally, the influence of varying the activation temperature on the porous texture of the final product was tested. Char was mixed with a 1:3 ratio of KOH and activated at 700, 800 and 900 ºC for 3 hours under nitrogen.

The activation process for the chemically impregnated char samples involved heating the char at a heating rate of 20 ºC min^{-1} to the final activation temperature under a nitrogen purge (200 ml min.$^{-1}$). After the activation, the carbons were cooled under N_2, and then washed first with 1 M HCl and later with distilled water until the pH of the washed solution was about 7. Finally, the washed samples were dried at 105 ºC overnight. The designation of the produced activated carbons are shown in Table 1.

2.3 NOx adsorption reactor

The nitrogen oxide adsorption tests on the prepared activated carbons were conducted using a stainless steel fixed bed reactor externally heated by an electrical furnace (Figure 1 (b)). The reactor system consisted of a gas mixing unit, the activated carbon-NOx adsorption reactor and on-line gas analysis system. The air, N_2 and NO/N_2 with an NO concentration of 1000 p.p.m was supplied by B.O.C Special Gases Ltd., UK. The gases were mixed together before entering the reactor in a gas mixing unit. The NOx adsorption reactor was of 20 cm height and 2.2 internal diameter, with 10 cm sample holder used to hold the activated carbon bed inside the reactor. The temperature of the carbon was monitored with a thermocouple. The adsorption tests were conducted with a fixed activated carbon mass of 2.8 g which was previously treated under nitrogen at 500 °C for 30 min in order to clean the surface oxides and desorb the adsorbed gases on the carbon surface. The bed depth was about 3 cm which gave ~1.7 s gas residence time through the carbon bed. A gas mixture (flow rate, 500 ml min^{-1}) flowed through the reactor the to the gas analyser system. The NO adsorption was carried out for two hours at a temperature of 25 °C and in the presence of 10% O_2 and 400 p.p.m NO. The gas composition was recorded every minute using a gas analyser unit supplied by Horiba Instruments UK Ltd., and consisted of a Horiba VA-3000 chemiluminesence analyser for NO/NOx and a separate Horiba VA-3000 paramagnetic analyser for oxygen.

2.4 Activated carbon characterization

The physical properties of the activated carbons including BET surface area and porosity of the activated carbons were determined by N_2 adsorption at 77K using a Micromeritics TriStar 3000 apparatus which measures the quantity of N_2 adsorbed/desorbed from the carbon at different equilibrium vapour pressures. Each carbon sample was degassed for 3 h at 300 °C under vacuum. The Dubinin Radushkevich (DR) method was used to calculate micropore volumes and Barret-Joyner-Halenda (BJH) calculation was used to determine mesopore volumes of the carbons. Density Functional Theory (DFT) calculation gave pore size distributions.

3. Results and discussion

3.1 Characterization of the porous carbons

The elemental analysis of the prepared adsorbents are shown in Table 2. The carbon content varied from 65 to 88 wt.%, increasing the char:activating agent for KOH increased the carbon content of the activated carbon products. Samples activated with KOH showed a greater content of carbon and a lower content of hydrogen and sulfur than those prepared with K_2CO_3, Na_2CO_3 and NaOH. Additionally, increasing the activation temperature led to higher carbon content and lower hydrogen and the sulfur contents. Similar results have been reported by Hofman and Pietrzak (2011). No correlation was found between the elemental compositions of the prepared samples and their NO capture capacity.

The textural properties of the activated carbon samples are shown in Table 3. The BET surface area, micropore volume and mesopore volume of the carbons were obtained from the adsorption/desorption isotherms of N_2 at 77K. The results clearly indicate the positive influence of the type of activating agent and the activation temperature on the porosity development. The modification of active carbons by KOH results in the formation of active carbons with high BET surface area and microporous structure as also reported by Hayashi et al. (2000).

The influence of the char:KOH impregnation ratio on the porosity of the product carbons was investigated at 900 °C activation temperature. As presented in Table 3, the specific surface area and the micropore volume increased in relation to increasing impregnation ratio (TA-KOH3), and then decreased (TA-KOH4). The BET surface area and micropore volume of TA-KOH3 was 621 $m^2\ g^{-1}$ and 0.437 $cm^3\ g^{-1}$ respectively. With the char to KOH ratio of 4 both the BET surface and pore volumes decreased. The higher KOH content producing increased activation, due to the fact that the potassium salt complexes which are formed in the carbons before carbonization act as sites for gasification (Ehrburger et al., 1986) :

$$K_2O + C \rightarrow 2K + CO \qquad (1)$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \qquad (2)$$

The decrease in surface area and micro and mesopore volume at the higher KOH ratio (TA-KOH4) has also been reported by Meng and Park (2012). They prepared various nano porous carbons using KOH chemical activation with KOH to carbon ratios between 0.5 and 4. The authors reported a decrease in the micropore volume when the KOH: carbon ratio was increased to 4. It could be suggested that at the higher levels of KOH addition, blockage of pores by potassium leads to a decrease in surface area and microporosity and mesoporosity of the activated carbons.

In contrast to KOH, activation with other alkali metals led to the formation of samples with less developed porosity (Table 3). Using the K_2CO_3, NaOH and Na_2CO_3 as activating agents resulted in the formation of active carbons with BET surface areas of 133 m^2 g^{-1}, 128 m^2 g^{-1} and 92 m^2 g^{-1} respectively. The increase in microporosity appears to depend more on the nature of the cation used (Na$^+$ or K$^+$).

Besides the type of activating agent, the activation temperature also has an influence on the BET surface area and on the porosity development. The influence of the activation temperature was investigated for the sample with a 3:1 KOH to Char ratio and activated at various temperatures of 700, 800 and 900 °C under nitrogen. The sample obtained at the activation temperature of 900 °C had a more developed porous structure with BET surface area and micropore volume about five times greater than the sample activated at 700 °C. In the study by Hsu et al. (2000), the maximum porosity of the activated carbons produced from bituminous coal treated with KOH was produced at a temperature 800 °C but at higher temperature the porosity was found to decrease due to the breakdown of cross-links in the carbon matrix.

From Table 3, the activated carbons exhibited a high mesoporous volume which confirms the mesoporous properties of the prepared carbons. For the series of samples prepared with different KOH ratio, the higher BET surface area of around 600 m^2 g^{-1} was reported for the sample prepared with a KOH-char ratio of 3. This sample also shows a high micropore and mesopore volume.

The porosity development of the prepared samples was investigated by N_2 adsorption at 77K, The mesoporous character of the prepared samples was confirmed by the typical adsorption desorption isotherms of carbons shown in Figure 2 (a), (b) and (c). The IUPAC designation system for such isotherms classifies them as Type IV which shows a hysteresis loop at relative pressures above 0.4 suggesting a mesoporous carbon (Pevida et al., 2008). The isotherms show a widening of the microporosity and higher mesoporosity as the activation temperature was raised (Figure 2-a).

The pore size distribution is one of main factors to consider while developing a carbon adsorbent with high NO capture. The DFT pore size distribution plots of the produced adsorbents are shown in Figure 3. The micropore structure was predominantly enhanced with the use of KOH as an activating agent. Most of the micropores of waste tyre were enhanced by chemical activation with KOH at a temperature of 900 °C and with KOH: char ratio of 3:1 (TA-KOH3). Additionally, mesopore development is suggested around the pore width of 4 nm. With increasing KOH to char ratio, the high intensity of gasification reactions results in the breakthrough of micropore walls leading to an increase in the mesopore volume. As reported in the literature, the porous structure of carbons activated with KOH is highly dependent on the KOH:char ratio (Diez et al., 2015). It can be observed that the change in activation temperature influenced the pore size distribution with the proportion of micropore and mesopore volumes increasing with increasing temperature.

It can be concluded that KOH is more effective in developing the porosity of the activated carbons than K_2CO_3, NaOH and Na_2CO_3. During carbonization, these reagents play different roles which can significantly affect the porosity. Potassium hydroxide is a strong base and has the ability to interact with the carbon atoms, catalyzing the dehydrogenation reaction leading to a carbon with developed porous structure (Ehrburger et al., 1986).

The widening of pore distribution at higher activation temperature > 800 °C is due to the following redox reactions. Potassium is formed through a series of redox reactions (equations, 3-6) (Nowicki et al., 2010);

$$6KOH + 2C \rightarrow 2K + 2K_2CO_3 + 3H_2 \quad (3)$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \quad (4)$$

$$K_2O + H_2 \rightarrow 2K + H_2O \quad (5)$$

$$K_2O + C \rightarrow 2K + CO \quad (6)$$

The generally accepted mechanism of KOH activation involves a series of redox reactions. During the activation, K_2CO_3 is decomposed to K_2O which is then reduced to form potassium. The intercalation of potassium resulting in the opening of carbon pores.

3.2 Nitrogen Oxide adsorption

The NO adsorption efficiency of the prepared activated carbon adsorbents was investigated at a temperature of 25 °C and with inlet NO concentration of 400 p.p.m and in the presence of 10% oxygen. The addition of O_2 was essential, since it increases the adsorption of nitric oxide via the catalytic oxidation of NO to NO_2, producing in an increase of the NO adsorption because of the higher adsorption potential of NO_2 (Yang et al., 2000; Klose and Rincon, 2007). In the absence of oxygen the NO removal efficiency was only about 5%, similar findings have been reported in the literature (DeGroot et al., 1991; Teng and Suuberg, 1993). Prior to any test, the samples were dried under an inert N_2 atmosphere. The NO breakthrough curves and the NO removal efficiency curves of the prepared activated carbons in relation to char:KOH activating agent ratio are shown in Figure 4. The NO breakthrough curve for the lowest concentration of activating agent impregnation (char:KOH ratio of 1:0.5) showed an immediate breakthrough of NO through the activated carbon bed of 75 p.p.m. in relation to the inlet NO concentration of 400 p.p.m. and reached at NO outlet concentration of 250 p.p.m. after 120 minutes. For the activated carbons produced at higher char:KOH impregnation ratios, the NO breakthrough occurred after about 1 minute and the carbons were much more effective in removing NO. The NO removal efficiencies after 120 minutes was highest for the char:KOH impregnation ratio of 1:3 at 75% (Figure 4). A comparison of the NO removal efficiency with the porous texture data for the activated carbon products (Table 3) and the pore size distribution (Figure 3) indicates that the TA-KOH3 carbon produced at the char:KOH ratio of 1:3 had the highest NO removal efficiency which correlated with the highest micropore volume of 0.437 $cm^3 g^{-1}$ and highest surface area of 621 $m^2 g^{-1}$. Both TA-KOH1 and TA-KOH4 showed almost the same micropore and mesopore volumes. However, the NO conversion with TA-KOH4 was higher than that with TA-KOH1.

The results obtained for the waste tyre activated carbon products may be compared with results from the literature, for example Lee et al., (2001) studied NO_2 adsorption at a temperature of 130 °C using KOH impregnated commercial activated carbon produced from coconut shells. The removal efficiency was found to decrease with increasing NO_2 concentration, with NO_2 concentration of 400 p.p.m, the removal efficiency was ~20 %. The influence of varying the amount of added KOH, over the range 0-2.0 wt%, to chars produced from coal on NO removal efficiency has been studied by Zhong and Zhang (2003). Increasing the KOH content to 1.0 wt. % led to an increase on NO reduction. However, when the KOH content in char was increased to 2.0 wt.%, the NO reduction capacity remained almost the same. The authors concluded that with increasing KOH content to 1.0 wt.%, the activation energy decreased and the collision frequency factor for the carbon and nitrogen oxide increased. Consequently, the NO reduction capacity of the studied carbons increased. However, a further increase of KOH content to about 2.0 wt.% had no major influence on the collision frequency factor. Therefore, the NO reduction remained unaffected. Cha et al. (2010) produced chemically activated carbons using rice straw char and sewage sludge char and investigated NO removal at a temperature of 50 °C using a fixed bed reactor. The chemically activated carbons treated with KOH exhibited a higher NO removal efficiency compared to the physically activated carbons. This was attributed to the differences in the number of oxygen functional groups, pore volumes and BET surface areas which were dependent on the activation process. The maximum NO removal efficiency was observed with the rice straw activated carbon at 85%, while the sewage sludge activated carbon showed a NO removal efficiency of 45%.

Materials with different pore width are expected to exhibit different behavior during the gas adsorption. The results presented in Table 3 suggested the high dependence of NO conversion with the pore diameter of the carbon. Considering the kinetic diameter of NO is 0.3 nm, so carbonaceous materials with pore diameter similar to this should have higher adsorption efficiency than others with higher pore diameter. Carbons with pore diameters of 1.1 nm have been found to have a much higher capacity for NOx adsorption than those with pore diameters larger than 1.1 nm (Neathery et al., 1997). In this study a maximum conversion was observed with on carbon with an average pore diameter of 0.9 nm. In the Zhang et al. (2008) study, carbon with an average micropore size of 0.7 nm was found to produce the highest NO adsorption at about 52%. These results suggest the dependence of NO adsorption on the average pore diameter along with the BET surface area of the activated carbon products.

In order to further ascertain if the porosity and BET surface area affect the NO capture, the sample treated with KOH at a char:KOH weight ratio of 1:3 was activated to 700 and 800 °C. The results shown in Figure 5 indicate that activation temperature had a significant role in influencing the surface area and porosity of the activated carbon products and in turn influencing the NO capture capacity. The surface area of the carbons increased from 170 m^2 g^{-1} at 700 °C activation temperature, to 243 m^2 g^{-1} at 800 °C and to 621 m^2 g^{-1} at

900 °C activation temperature (Table 3). There was a similar increase in microporosity from 0.184 cm^3 g^{-1} at 700 °C to 0.437 cm^3 g^{-1} at 900 °C. Both increasing surface area and increasing microporosity of the activated carbons correlating directly with increased NO breakthrough and NO removal efficiency. The results found in this study were in good agreement with the results reported by Illan- Gomez et al. (1993) where they reported a direct correlation between NO adsorption capacity and BET surface area of the samples used.

To determine the influence of the type of alkali activating agent on the characteristics and NO removal efficiency of the activated carbon products different types of activating agents (K_2CO_3, NaOH and Na_2CO_3) were physically mixed with the tyre char and compared to the results with KOH. All the carbons were prepared at an activating agent impregnation ratio of 1:3, char:activating agent and a final activation temperature of 900 °C. According to the results shown in Figure 6, the type of activating agent used during the chemical activation significantly influenced the NO adsorption ability, KOH was the most effective in providing the best NO removal efficiency with around 75% after 120 minutes, followed by K_2CO_3, NaOH and Na_2CO_3 with 37, 30 and 19% respectively. Based on the textural properties shown in Table 3, the chemical activation of waste tyre with KOH produced a sample with much more developed structure than those activated with other alkali metals, which were found to markedly enhance the NO sorption capacity. As mentioned before, the activation with KOH and at higher temperature (900°C) resulted in the formation of active carbon with a high BET surface area and well developed porous structure. As a consequence, the NO removal efficiency was higher with this sample than those activated with other alkali metals. Potassium has been shown to have high catalytic activity in the NO_X carbon reaction (Bueno-López et al., 2007). The NO_X reduction capacity by coal char samples has been found to increase from 3% to 63% when the char was loaded with 4 wt.% potassium

According to studies by Lee et al. (2002) and Nowicki et al. (2010), the high NO capture by carbons treated with KOH is due to the basic nature of hydroxides provided on the carbon surface. In the presence of oxygen, NO could oxidize to NO_2 and then react with KOH, which provides selective adsorption sites for NOx, according to the following reactions (Lee at al., 2002):

$$2KOH_{(aq)} + 2NO_{2\,(g)} \rightarrow KNO_{2(aq)} + KNO_{3(aq)} + H_2O_{\,(l)} \qquad (7)$$

$$KNO_{2(aq)} + NO_{2\,(g)} \rightarrow KNO_{3(aq)} + NO_{\,(g)} \qquad (8)$$

KNO_3 was found to be present in high amounts on the carbon surface after the NO adsorption (Lee et al., 2001). However, in this study, KNO_3 could not be detected and this is may be because of the nature of the precursor used.

The NO removal efficiency of the waste tyre derived activated carbons produced in this work may be compared with NO removal efficiencies reported for other more conventionally produced activated carbons. For example, Guo et al. (2001) prepared pitch based activated carbons with a BET surface area of 1000 $m^2\ g^{-1}$ and investigated NO adsorption at a temperature of 30 °C in the presence of oxygen. The NO removal efficiency of the investigated activated carbons was found to be in the range of 44-75%. In another study carried out by Zhang et al. (2008) used commercial activated carbons for NO conversion at a low temperature. In the presence of ~10% oxygen, the NO conversion of the activated carbons was found to be 50%. The results suggest that waste tyres, which represent a waste disposal problem, have the potential to be processed through pyrolysis and chemical activation to produce activated carbons which are effective in NOx removal and are comparable with conventionally produced carbons. However, a full techno-economic assessment would be required to determine whether the proposed process would be comparable to currently produced activated carbons using conventional feedstocks.

4. Conclusions

This study focused on the production of activated carbon from waste tyre to be used for NO capture using a chemical activation method. The influence of treating the carbon with various alkali chemical agents on the porous texture was studied. The chemical activation of waste tyre with KOH has been shown to effectively enhance the NO reduction at room temperature to about 75% removal in direct relation to the increase in BET surface area and micropore volume. The textural properties seem to be the dominant factor affecting the NO adsorption. Treating the waste tyre with other alkali agents (K_2CO_3, NaOH, Na_2CO_3) produced much lower NO removal efficiencies. The textural properties of the product activated carbon adsorbents were determined mainly by the type of chemical agent and the temperature of activation. Adsorbents prepared by KOH activation had a well developed porous texture than those treated with K_2CO_3, NaOH and Na_2CO_3 which enhanced the NO capture. The NO capture activity of the activated carbons produced from waste tyre decreased in the order of alkali impregnation as KOH > K_2CO_3 > NaOH >Na_2CO_3 .

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FIGURE CAPTIONS

Fig. 1. Schematic diagrams of (a) the waste tyre pyrolysis reactor and (b) the NOx adsorption reactor

Fig. 2. Adsorption and desorption isotherms of the waste tyre derived activated carbons in relation to (a) char:KOH impregnation ratio (b) activation temperature with KOH char impregnation (c) type of alkali activating agent

Fig. 3. Pore size distribution (DFT) of the waste derived activated carbons

Fig. 4. (a) NO breakthrough curves and (b) removal efficiency of the waste tyre derived activated carbons in relation to char:KOH ratio.

Fig. 5. (a) NO breakthrough curves and (b) removal efficiency of the waste tyre derived activated carbons in relation to activation temperature.

Fig. 6. (a) NO breakthrough curves and (b) removal efficiency of the waste tyre derived activated carbons in relation to char:activating agent.

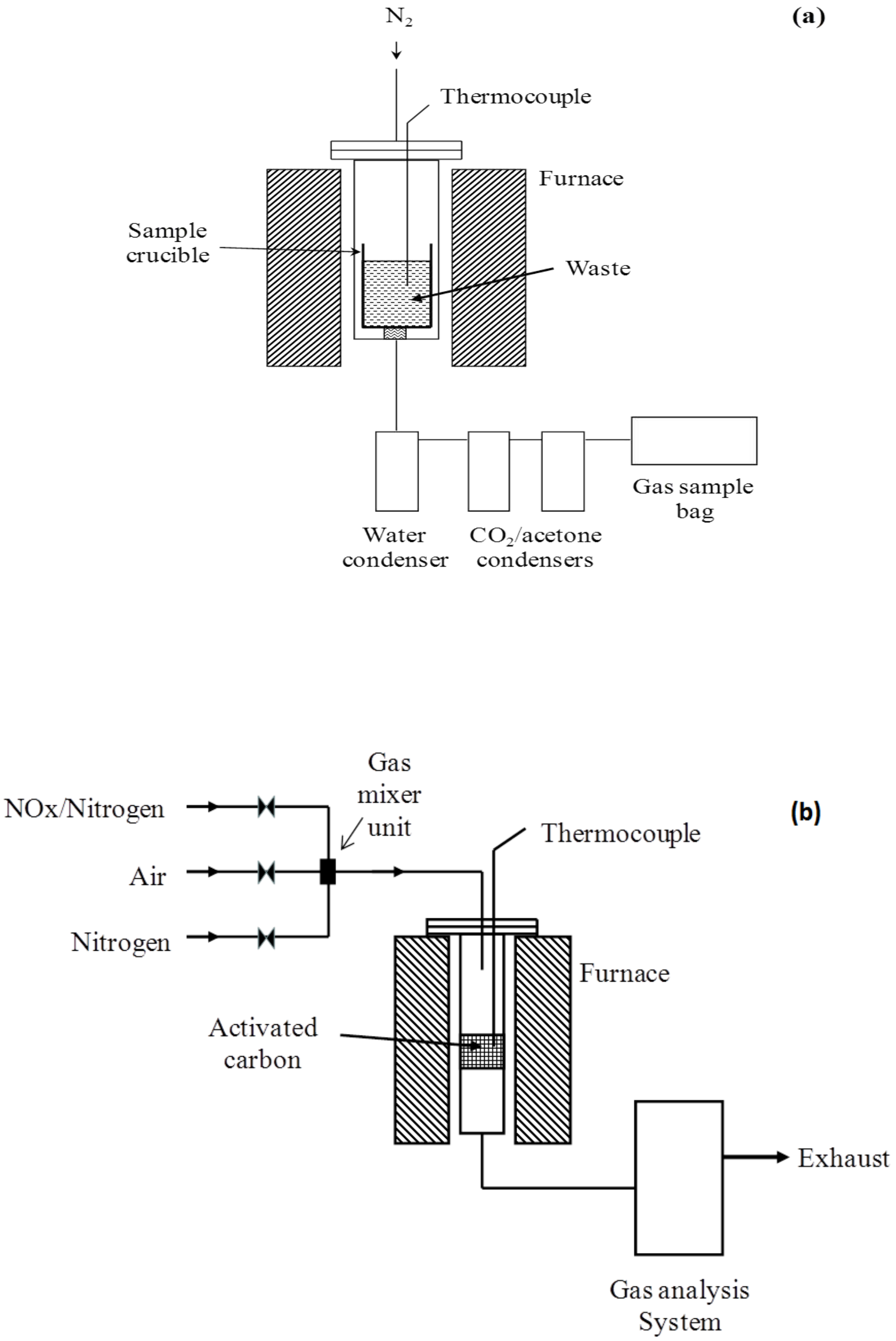

Figure 1. Schematic diagrams of (a) the waste tyre pyrolysis reactor and (b) the NOx adsorption reactor

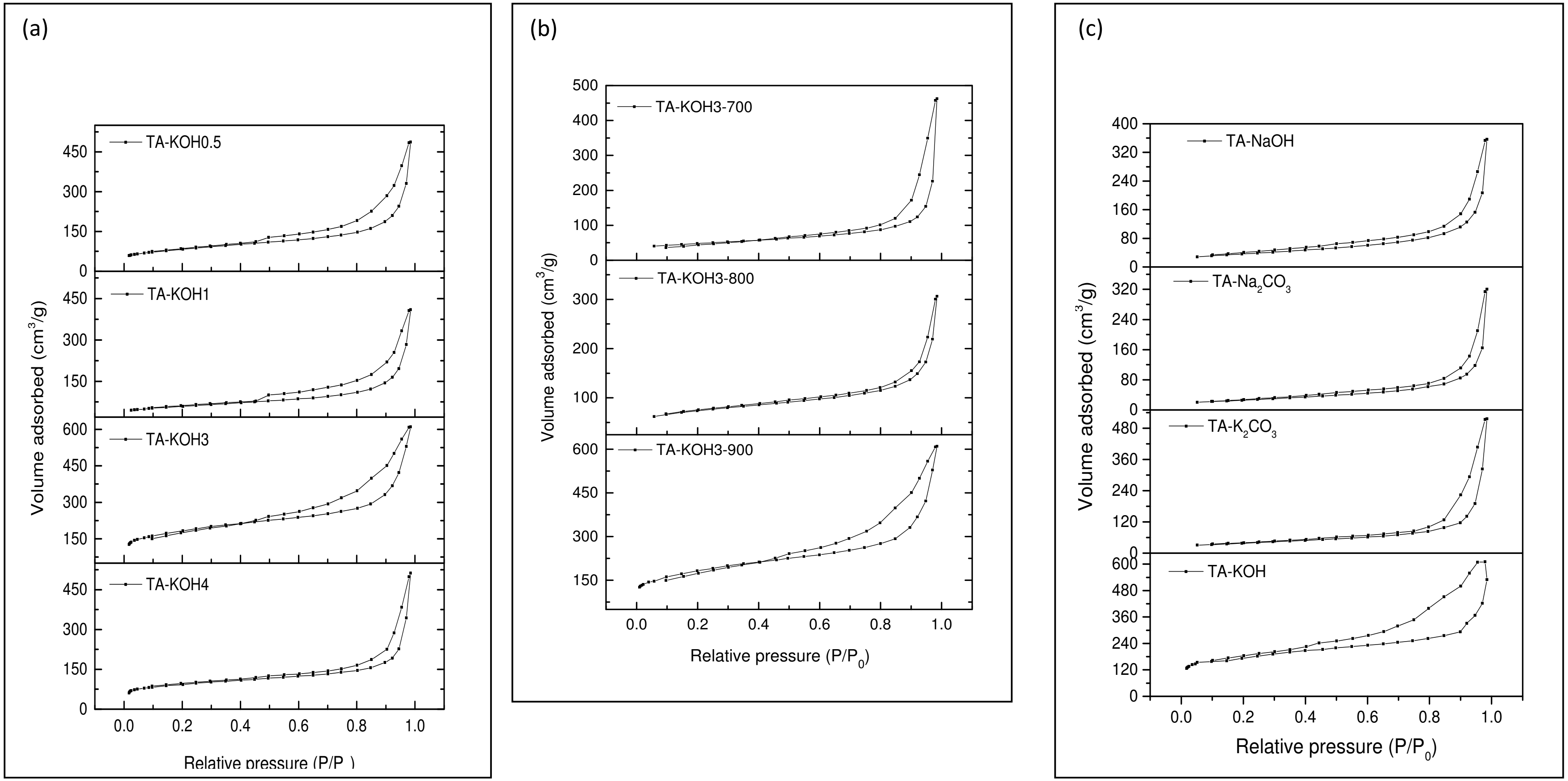

Figure 2. Adsorption and desorption isotherms of the waste tyre derived activated carbons in relation to (a) char:KOH impregnation ratio (b) activation temperature with KOH char impregnation (c) type of alkali activating agent

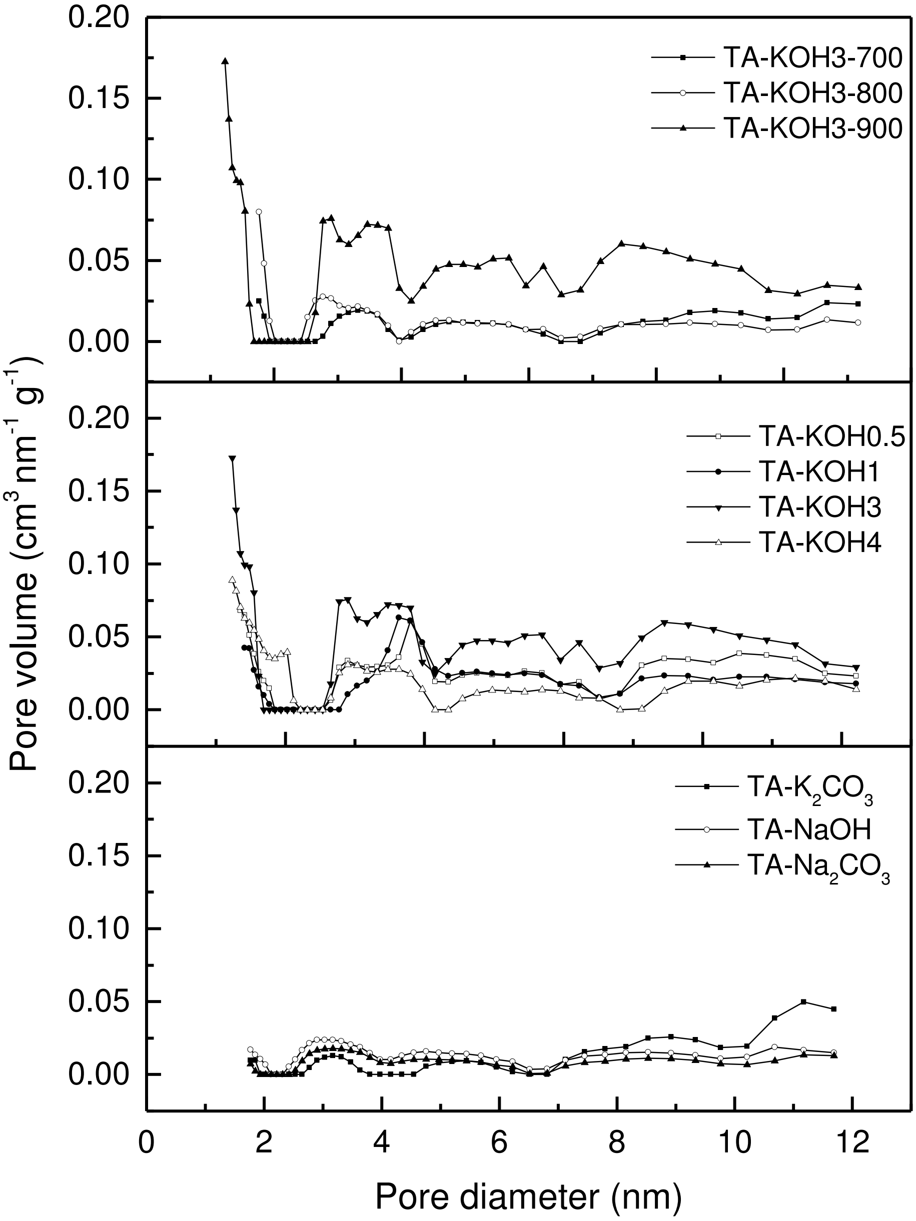

Figure 3. Pore size distribution (DFT) of the waste derived activated carbons in relation to (a) char:KOH impregnation ratio (b) activation temperature with KOH char impregnation (c) type of alkali activating agent

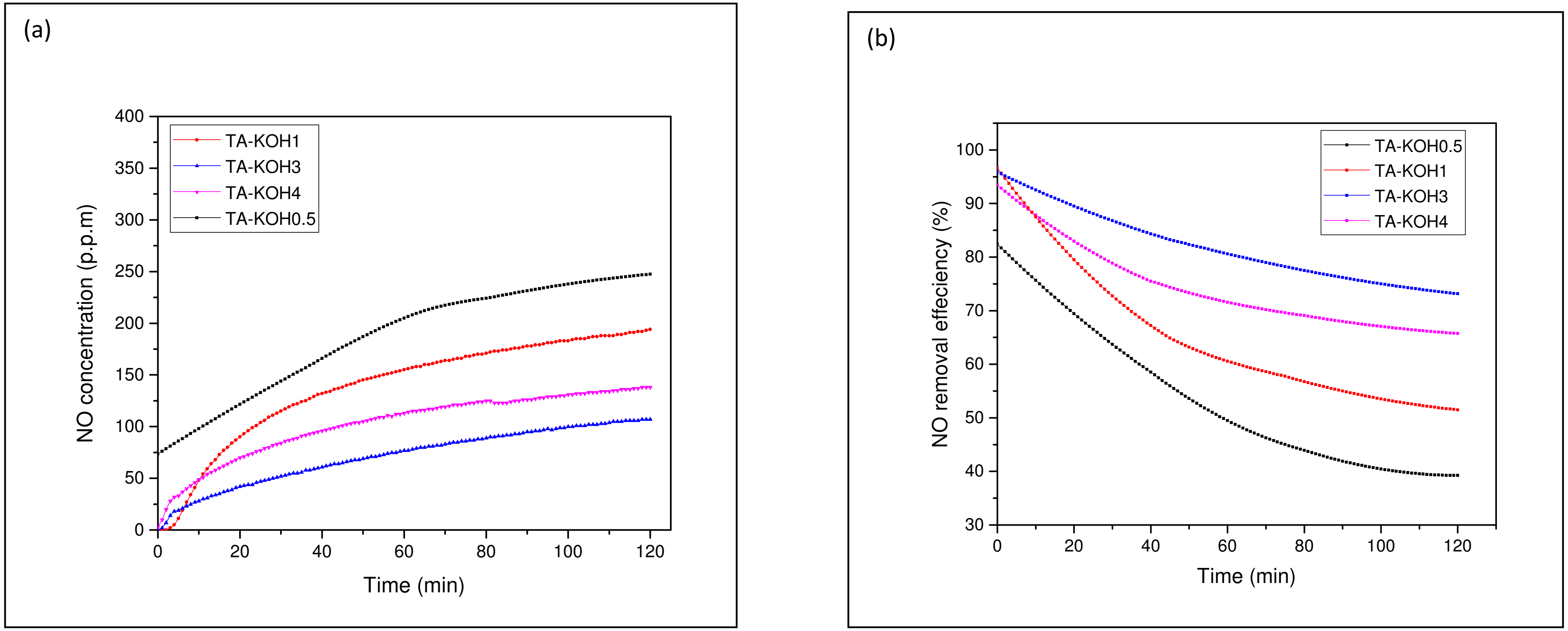

Figure 4. (a) NO breakthrough curves and (b) removal efficiency of the waste tyre derived activated carbons in relation to char:KOH ratio

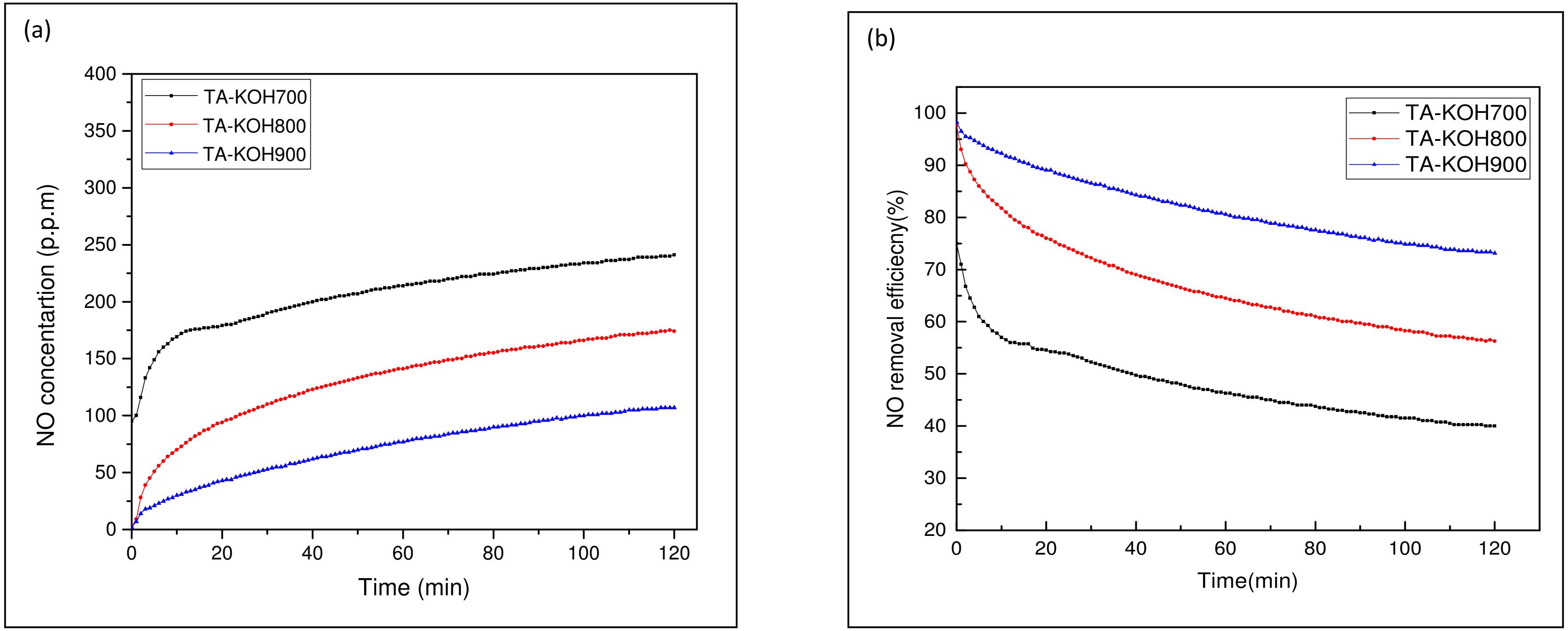

Figure 5. (a) NO breakthrough curves and (b) removal efficiency of the waste tyre derived activated carbons in relation to activation temperature

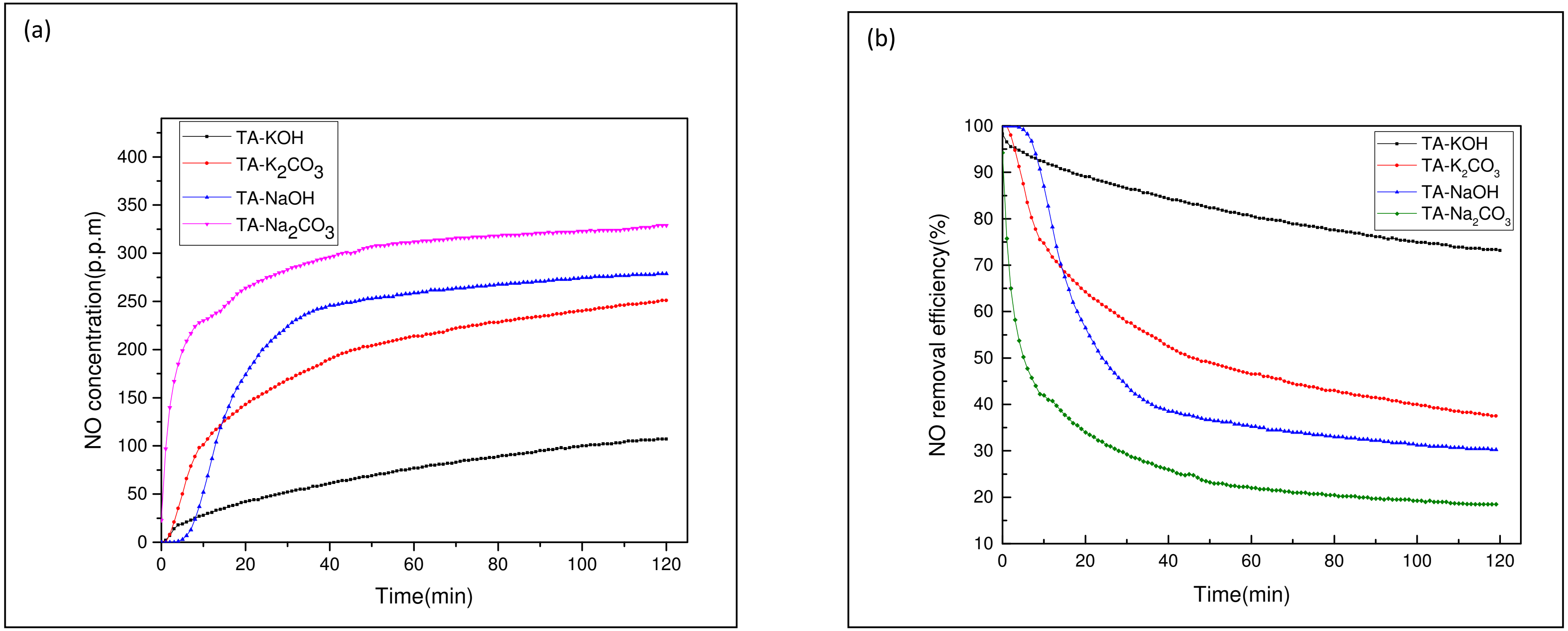

Figure 6. (a) NO breakthrough curves and (b) removal efficiency of the waste tyre derived activated carbons in relation to char:activating agent

Table 1.

Preparation conditions of the activated carbons

Sample Designation	Activating agent	Wt. ratio (Char: Chemical agent)	Activation Temperature (°C)
TA-KOH0.5	KOH	1:0.5	900°C
TA-KOH1	KOH	1:1	900°C
TA-KOH3	KOH	1:3	900°C
TA-KOH4	KOH	1:4	900°C
TA-KOH3-700	KOH	1:3	700°C
TA-KOH3-800	KOH	1:3	800°C
TA-K_2CO_3	K_2CO_3	1:3	900°C
TA-NaOH	NaOH	1:3	900°C
TA-Na_2CO_3	Na_2CO_3	1:3	900°C

Table 2.

Elemental analysis of the waste derived activated carbons

Activated Carbon Sample	C	H	N	S
TA-KOH0.5	65.00	3.19	1.6	0
TA-KOH1	64.51	2.35	1.4	0
TA-KOH3	88.26	2.44	1.5	0
TA-KOH4	88.02	2.78	0.62	0
TA-KOH3-700	69.67	5.37	2.25	0.53
TA-KOH3-800	83.97	4.58	1.76	0.55
TA-K_2CO_3	87.02	3.61	1.52	0.39
TA-NaOH	80.01	3.04	1.52	0.38
TA-Na_2CO_3	76.20	3.37	1.25	0.27

Table 3.

Porous properties of the waste derived activated carbons.

Sample	Total surface area[a] [m^2/g]	Micropore volume[b] [cm^3/g]	Mesopore volume[c] [cm^3/g]	Pore diameter[d] (nm)
TA-KOH0.5	202	0.185	0.611	1.038
TA-KOH1	287	0.240	0.728	1.098
TA-KOH3	621	0.437	0.884	0.962
TA-KOH4	315	0.269	0.775	0.905
TA-KOH3-700	170	0.184	0.690	1.675
TA-KOH3-800	243	0.192	0.427	1.443
TA-K_2CO_3	133	0.201	0.788	2.450
TA-NaOH	128	0.173	0.543	2.426
TA-Na_2CO_3	92	0.132	0.490	2.446

[a] Multi-Point Brunauer, Emmett & Teller (BET) Method.
[b] Dubinin-Radushkevich (DR) Method.
[c] Barrett, Joyner & Halenda (BJH) Method.
[d] Density Functional Theory (DFT) Method.