Facile Synthesis of Carboxylated Activated Carbon Using Green Approach for Water Treatment

L Mahardiani¹*, S Saputro¹, F Baskoro²,³, N M Zinki¹, and M Taufiq¹
¹ Department of Chemistry Education, Faculty of Teacher Training and Education, Universitas Sebelas Maret, Jl. Ir. Sutami 36A, Kentingan, Surakarta, Indonesia
² Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan (ROC)
³ Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan (ROC)

E-mail: lina80_ssa@yahoo.com

Abstract. A chemical treatment by using oxidizing agents is the most common methodology to modify or create functional groups on activated carbon. The modified activated carbon obtained from chemical oxidation needs further treatment and produced waste, therefore a new approach is needed. A facile green approach is reported. In this approach the activated carbon was oxidized using air without additional chemical treatment to increase the content of acidic surface functional groups, especially carboxyl groups. The formation of carboxyl groups was confirmed by Temperature Programmed Decomposition, Boehm titration, and Infra-red spectroscopy results. The Boehm titration result showed higher contents of carboxyl groups by three-fold. The carboxylated activated carbon synthesized by green approach showed excellent performance for water treatment.

1. Introduction
Activated carbon (AC) is a common term used to describe carbon-based materials produced from various carbonaceous rich materials, such as wood, coal, lignite and coconut shell [1]. Activated Carbon is inexpensive and have been applied for many purposes, and as an adsorbent is one of it. It has been proven that AC is an excellent adsorbent for organic and inorganic pollutant removal for both in aqueous or gaseous environment [2,3]. However, it is believed that it is important to enhance the effectiveness of AC as adsorbent for specific usage. Therefore, the modification of surface of AC is necessary to develop affinity for certain contaminant [4]. One of the methods to modify is by chemical activation since it able to create acidic functional groups onto the surface of activated carbon [5, 6]. Regardless of the advantage of chemical activation, the waste that produced after its activation can not be avoided. Recently the synthesize and modification of materials is based on the green chemistry principles. Green chemistry offers an alternative to the traditional environment protection agenda, such as preventing waste production and minimizing the use of reagents and solvents [7].

Air oxidation is one alternative to alter the surface [6,8]. This method is facile since AC was oxidized only by using the air to create the acidic functional groups such as carboxylic, phenolic, and lactone [9]. In addition, there was no waste produced and use no reagents or solvents during the oxidizing process. There are some experimental techniques that able to identify the formation of functional groups crafted onto the surface of AC. Infra-red spectroscopic methods also applicable to distinguished different functional groups based on the bands observed at different wavenumbers.
Generally, carbon will absorb almost all the radiation in the visible spectrum, since carbons are black. Therefore, it is not easy to get good spectra of functional groups on carbon material using FTIR. There are some techniques that able to conveniently identify the functional groups on the carbon materials.

The surface oxides on a carbon can have both acidic and basic properties. The Boehm titration are widely used to determine the number of the total acidic functional groups based on the volume of titrant consumed by the functional groups \[10,11\] and similar with basic functional groups. The temperature-programmed method is a recent analysis to determine the surface oxygen groups on the AC based on the CO and CO\(_2\) released at different temperature \[4,12\]. It is assumed that each type of surface group decomposes to defined product, namely carbonyl and hydroxyl groups and ether-type oxygen will generate CO, while carboxyl groups will generate CO\(_2\).

In this present work, we perform the study of the air oxidation on AC to modify its surface using green approach via air oxidation method and compare with AC treated with chemical activation, HNO\(_3\). In addition, various techniques were conducted to confirm the formation of functional groups resulted from air oxidation. Further, we applied the modified AC for water treatment.

2. Experimental
2.1 Chemicals and materials
Activated carbon (BA) was supplied by Ajinomoto Fine-Techno. Sodium bicarbonate (> 99.5%), sodium hydroxide (> 97%), nitric acid (>70%), potassium bromide (FTIR grade, crystal block), standard solution 0.05 mol/L HCl and 0.05 mol/L NaOH used for Boehm’s titration, metil orange was purchased from Wako Pure Chemical Industries, Ltd.

2.2 Methods
2.2.1 Synthesis of functional carbon sample
Treatment 1. Air oxidation: dried carbon (BA) about 4.0 g was spread into petri dish and heated under air flow in calcination apparatus. The calcination temperature was 425 °C with temperature rate 10 °C/min and kept the temperature for 3 h.

Treatment 2. HNO\(_3\) activation: a 2.0 g of BA was placed into round bottom flask and mixed with 20 mL of HNO\(_3\) for 3 h at 90 °C. The mixture was filtered and washed to neutral the pH using distilled water and further dried at 110 °C overnight and BA-HNO\(_3\) was obtained.

2.2.2 Characterization
The surface functional groups of catalyst were detected by a Fourier transformed infrared (FTIR) spectrometer (Perkin Elmer Spectrum 100 S). The samples (0.1 wt %) were mixed with KBr and analyzed in the 4000 – 400 cm\(^{-1}\) wavenumber range, with resolution of 4 cm\(^{-1}\), by averaging 64 scans.

Temperature Program Decomposition (TPD) spectra was obtained from BelCat II instrument (MicrotracBEL). This analysis was to determine the numbers of functional groups existed in the catalyst. For each run, 50 mg of catalyst was pretreated at 150 °C for 1 h before heated up to 1000 °C with ramp of 10 °C/min for 10 min under He flow. The concentration of CO and CO\(_2\) were determined by the intensities of m/z at 28 and 44, respectively.

Boehm’s titration was also conducted to determine the numbers of acidic functional groups were on the catalyst. For each analysis, 100 mg of catalyst was pretreated in 20 mL NaHCO\(_3\) and NaOH solution for 24 h at room temperature. Filtrate obtained from filtration of pretreated sample were used for back titration. The quantity of acidity of various type were determined from the assumption that NaHCO\(_3\) reacts with carboxylic groups and NaOH reacts with carboxylic, lactonic and phenolic groups.

2.2.3 Adsorption activity of modified AC
The adsorption activity of modified AC was conducted by contacting 0.1 g of AC with 20 mL Pb(NO\(_3\)\(_2\)) 10 ppm and Cu(NO\(_3\)\(_2\)) 10 ppm. Samples were collected at certain interval times then filtered before filtrate then was analyzed using Atomic Absorption Spectroscopy (AAS).
3. Results and Discussion

3.1 Temperature Program Decomposition

Thermal decomposition of activated carbon is useful to identify its surface chemical properties. Surface oxide of carbon are formed from various functional groups [11]. Carboxylic, lactone, phenol, carbonyl, anhydride, ether and quinone functional groups have been identified on carbon surface. The decomposition of those functional groups can release CO and CO$_2$ at different temperature by heating under inert conditions [4, 12]. Peaks of CO and CO$_2$ from TPD result can be distinctive accordingly with certain functional groups, namely CO peak was resulted from carboxylic anhydride, hydroxyl, ether or carbonyl, carbonyl, and pyrone-type structure decomposition, while CO$_2$ peak was resulted from carboxyl, carboxylic anhydride, peroxide, and lactone decompositions [13].

Untreated carbon (BA) showed a little functional group on its surface, which were 0.88 and 0.32 mmol g$^{-1}$, for CO and CO$_2$ respectively. The functional groups that existed on the surface of BA are hydroxyl, carbonyl and small amount of carbonyl. The functional groups existed on carbon were significantly increased after air oxidized and HNO$_3$ treatment (Table 1). The TPD spectra obtained showing a gradual increase both in CO and CO$_2$ released. However, the CO peak increased much more than the CO$_2$. This can be explained in terms of the mechanism for carbon gasification proposed by Zhuang et al. [14]. The reaction of free active site on the AC with oxygen into carbonyls, ethers and CO and further oxidized to CO$_2$ + CO or carbonyls, ethers are much more important compared with the reaction between free active site on the AC with oxygen into lactones and anhydrides. The amount of CO released was higher than that of CO$_2$ indicating that there are much more carbonyl, ether and phenol groups than lactones and anhydrides. The amount of CO was also obtained from the decomposition of carboxylic anhydrides into one CO and CO$_2$ molecule [15] in addition to the contribution of phenolic and quinones [16].

3.2 Boehm titration

The surface oxides on carbon can have both acidic and basic properties which coexist usually, but the concentration of basic site decreases with increasing of acidic property on the carbon surface. The acidic surface properties are caused by the presence of carboxyl groups (also for anhydride), lactone, and hydroxyl group of phenolic property [11]. The total acidity, which consists of lactone, hydroxyl and carboxylic functional groups, can be determined with titration of NaOH. In addition, carboxylic functional group alone can be determined with titration of NaHCO$_3$.

The number of acidic functional groups calculated by Boehm titration are shown in Table 1. The total acidic functional groups of BA was 0.35 mmol g$^{-1}$ and 0.09 mmol g$^{-1}$ of it was carboxylic functional group. Total functional groups were increased after the chemical treatment by using various oxidants or by using air (Table 1). The air oxidation result showed increased of total acidic functional groups, about seven-folds of total acidic functional groups and eleven-folds for carboxylic group. Functionalization by using HNO$_3$ was showed that total acidity of carbon greatly increased up to 3.38 mmol g$^{-1}$. This is because HNO$_3$ is really strong acid, therefore HNO$_3$ could made defects on surface of carbon that allow formation of phenolic, hydroxyl, carboxylic and anhydride in large amount. The differences on the value of surface oxygen functional groups on carbon between TPD and titration results may be due to the inaccessibility of some functional groups within the pores. In general, these results suggested that chemical activation were able to make carbon structure altered and they showed acidic character.
Table 1. Summary of chemical and physical properties of activated carbon as adsorbent

| Sample              | TPD CO (mmol g\(^{-1}\)) | TPD CO\(_2\) (mmol g\(^{-1}\)) | Boehm titration Total acidic amounts (mmol g\(^{-1}\)) | Boehm titration –COOH (mmol g\(^{-1}\)) | S\(_{BET}\) (m\(^2\) g\(^{-1}\)) | Pore vol. (cm\(^3\) g\(^{-1}\)) |
|---------------------|---------------------------|----------------------------------|------------------------------------------------------|---------------------------------------|---------------------------------|-------------------------------|
| BA                  | 0.88                       | 0.32                             | 0.35                                                 | 0.09                                  | 1163                            | 0.61                          |
| Air oxidized BA     | 5.29                       | 2.16                             | 2.64                                                 | 1.00                                  | 1065                            | 0.62                          |
| BA-HNO\(_3\)        | 3.42                       | 2.34                             | 3.38                                                 | 2.03                                  | 990                             | 0.51                          |

3.3 Infra-red spectroscopy

In order to examine the types of functional groups formed in BA before and after functionalization with various oxidants, FT – IR spectroscopy was used (Figure 1). The FT – IR spectra for all samples show band around 1566 – 1582 cm\(^{-1}\) due to the presence of C–C stretching of aromatic C=C. In addition, there was peak around 1200 cm\(^{-1}\) assigned for physically adsorbed oxygen or aromatic–OH stretching. There was also strong peak observed at 1781 cm\(^{-1}\) which is attributed to the anhydride group resulting from C=O asymmetrical stretching mode and peak at 3500 cm\(^{-1}\) assigned for C–OH [17-19].

Figure 1. The infrared spectra of (a) BA, (b) BA – HNO\(_3\), and (c) Air oxidized – BA

3.4 Adsorption activity of modified AC

As shown in figure 2, the adsorption of Pb(II) and Cu(II) using various AC adsorbents were evaluated. The modification of the AC surface influence the adsorption activity towards Pb(II) and Cu(II). The BA adsorbent showed lowest adsorption activity for Pb(II) and Cu(II), 20 and 35%, respectively. Meanwhile, the BA-HNO\(_3\) showed the highest adsorption activity for Pb(II) solution (68%) but showed moderate adsorption activity towards Cu(II) about 40%. In other hand, the adsorption activity of air oxidized BA was not changed for Pb(II) and Cu(II), which are 60 and 68%, respectively. Thus, the AC with air oxidation or chemical activation shows higher activity [20, 21]. This is expected because the total of acidic amounts plays important role for this process. The more the acidic functional groups exist on the surface of AC, the more the Pb(II) and Cu(II) were adsorbed. However, the chemical activation method of AC becomes more selective towards certain species, but loses...
adsorption capacity to others [22]. This trend shows on the adsorption activity of BA-HNO₃ for Pb(II) and Cu(II). Meanwhile, air oxidized AC shows no difference of its adsorption activity for Pb(II) and Cu(II).

![Figure 2](image)

**Figure 2.** The adsorption activity of various AC adsorbent toward Pb(II) and Cu(II). Adsorption conditions: Pb(II) and Cu(II), 10 ppm, m<sub>adsorbent</sub>, 0.1 g

4. Conclusion

The air oxidation is one of the methods to modify the surface of AC without producing waste and using the reagents or solvents. The modification results of air oxidation are comparable with that of chemical activation method. The modification results were confirmed by some techniques such as temperature programmed decomposition (TPD), Boehm titration, infra-red spectroscopy. TPD showed that evolution of CO and CO₂ of modified AC was increased significantly compared to untreated AC. TPD results was in accordance with Boehm titration where total acidic amounts of modified AC were increased almost ten-folds compared to untreated AC. Furthermore, the modified AC showed high adsorption activity toward Pb(II) and Cu(II).

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