



Chemical modification of carbonized wheat and barley straw using HNO₃ and the adsorption of Cr(III)

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ABSTRACT

The effects of oxidation using HNO₃ on the properties of the carbonized wheat and barley straw were investigated by measuring different properties such as specific surface area, PZC, total surface acidic groups as well as FTIR and TG–DTA. A small decrease in the specific surface area due to pore blockage was observed after oxidation. After oxidation, the acidity was increased considerably and the point of zero charge shifted from approximately pH 9 to pH 2 in both types of carbon. By the oxidation of the carbon with nitric acid, carboxylic groups were produced as shown by absorption peaks at 1750 cm⁻¹ in the FTIR spectra. Boehm titration results showed that the number of carboxyl groups increased by approximately 11-fold after oxidation. The oxidized carbon samples were compared with the unoxidized original carbon samples for Cr(III) adsorption. It was observed that the oxidized carbons exhibit high adsorption efficiencies for Cr(III) ions compared to the original carbonized straws and this can be correlated to the decrease in PZC which is mainly due to the increase in carboxylic functional groups in the oxidized carbonized straws and these are responsible for their cation ion exchange phenomenon.

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1. Introduction

Activated carbons are versatile adsorbents due to their extended surface area, high adsorption capacity, microporous structure and special surface reactivity [1]. The most important application of activated carbon is its use in separation and purification technologies. The consumption of activated carbon is ever increasing due to increasing industrialization and pollution. Lignite coal, peat, wood and coconut shell have been used to prepare activated carbons [2]. Since such carbon sources are either limited or very expensive, production of carbon materials from agricultural wastes is required. Their advantages as carbon feedstocks include abundant availability and renewability, low cost and good quality carbon generation. It is a well established fact that the sorption properties of carbon materials are essentially influenced by their surface characteristics i.e. physical and chemical surface properties.

The adsorptive properties of carbons are controlled by their physical or porous structure [3], but they are strongly influenced by the chemical nature of the surface [4–6]. Surface functional groups like carboxyls, phenols, lactones, aldehydes, ketones, quinones, hydroquinones, have been postulated to exist on carbon surfaces [7]. Due to these functional groups the carbon will have an acidic or a basic character. The presence of various functional groups on

the carbon surface depends on the nature of the activation process and the surface post-treatments [8,9].

The ion exchange capacity of carbons depends on surface functionality [10]. The surface charge of a carbon in aqueous suspension is also conditioned by its surface functional groups. These two properties affect the adsorption capacity. The oxidation of carbon leads to the formation of various surface acidic functional groups and also decreases the PZC of carbon, which enhances the adsorption of cationic metal ions from solution [11].

Surface modification of carbons can be achieved by various physicochemical methods. The chemical oxidation of carbon materials is a frequently used method to introduce surface oxygen groups as ion exchanging sites. Various reagents like nitric acid, sulfuric acid, hydrogen peroxide, ammonium persulphate, and fluorine gas are used for this purpose [12–15]. Several types of surface functional groups can be produced by oxidation treatments. Carboxylic, phenolic, lactones and peroxides have been suggested as acidic surface groups produced by oxidation treatments. Among the oxidation treatments, nitric acid oxidation is the most extensively used method. A significant increase in the number of strong acidic groups like carboxylic groups was observed during oxidation by nitric acid [16]. The surface modified carbon has numerous applications as adsorbents and catalysts [17,18].

The aim of the present study was to investigate the influence of nitric acid oxidation on the surface properties of low cost wheat and barley straw carbons. The effects of surface modifications on the properties of the carbons were studied in terms of the specific sur-

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face area, FTIR, total number of acidic groups, PZC and TG–DTA. The adsorptive properties of the carbons before and after modification were also studied for the adsorption of Cr(III) ions.

2. Experimental

2.1. Carbonization of straw

Carbonization of carbon containing raw materials is the prerequisite step for the preparation of carbon, but carbonization is followed by physical and chemical activation process for the production of highly porous carbon. Consequently, the production of highly porous carbon becomes expensive. In this research work very simple and comparatively low cost method of carbonization was employed. Wheat and barley straw obtained in Saga prefecture, Japan, was cut into small pieces. The samples were put in an alumina crucible with an alumina cover. This crucible was put in a larger alumina crucible and covered with graphite powder. The outer crucible had an alumina cover in order to avoid the combustion of the graphite powder in air. The crucible set was heated at 800 °C for 1 h at a heating rate of 5 °C/min to carbonize the straw. The carbon thus obtained was ground, washed with distilled water and dried in a convection oven at 50 °C for 24 h and was used in the experimental work under the following names: carbonized barley straw (CBS) and carbonized wheat straw (CWS). The graphite powder used in the experiments can be reused. The only thing that cost in this carbonization process is low cost agrowaste and electricity. Thus this carbon making process is comparatively very simple and cheaper.

2.2. Oxidation of carbon

The CWS and CBS were oxidized at 90 °C using 50% nitric acid. The reaction mixture was heated to 90 °C and the reaction was allowed to continue for 6 h with continuous stirring. The used reaction solution was discharged and a fresh reaction mixture of 50% nitric acid was added. The reaction was allowed to continue for a further 3 h under the same reaction conditions. The oxidized carbons were then filtered and washed with distilled water till neutral pH. The samples were then dried in convection oven at 50 °C for 24 h and used in the experimental work under the following names: oxidized carbonized barley straw (OCBS) and oxidized carbonized wheat straw (OCWS).

2.3. Characterization of carbon

Physical gas adsorption is an extensively used technique in the characterization of porous materials which accurately determines the surface area, pore volume and pore size distribution. The adsorption of such gases as N₂, Ar and CO₂ is frequently used for this purpose. In this case N₂ adsorption at 77 K was carried out using a Belsorp 18PLUS-SP (Bel. Japan. Inc.). Before measuring the adsorption of N₂, the sample was subjected to degassing for 3 h at 300 °C to a final pressure of 0.1 Pa. The N₂ adsorption–desorption isotherms were analyzed to characterize the nature of the pores. BET-Plots and *t*-Plots were analyzed to calculate the specific surface area and average pore diameter. The classical pore size model developed by Barret, Joyner and Halande (BJH) was used for the pore size distribution calculation.

2.4. Thermogravimetric–differential thermal (TG–DTA) analysis

Simultaneous thermogravimetric–differential thermal analysis was performed on the oxidized and unoxidized carbon materials using a TG/DTA 6300 (Seiko Instruments Inc.). About 5 mg of

each sample were heated from 10 to 1000 °C at a heating rate of 10 °C/min. The results provided both TG and DTA plots.

2.5. PZC

The pH value required to give zero net surface charge, designated the point of zero charge (PZC), was measured by a mass titration method [19]. Three solutions with different initial pH values were prepared using HNO₃ and NaOH, while NaNO₃ was used as the background electrolyte. For each initial pH value, six conical flasks were filled with 25 mL of the solution and different amounts of carbon were added so as to make the solid fraction 0.05%, 0.1%, 0.5%, 1%, 5% and 10%. The mixture was shaken for 24 h and the equilibrium pH was measured. The change in pH values as a function of the mass fraction of carbonized material in the solution (w/v %) was plotted. The plot exhibits a plateau and the PZC was evaluated as the average of three asymptotic pH values. The carbon surface is positively charged below this pH and negatively charged above this pH.

2.6. Determination of the acidic surface functional group

The Boehm titration method [20] was used for the determination of the acidic surface functional groups on the carbon materials. A carbon sample, 100 mg, was placed in 25 mL of the following 0.05 M solutions: sodium hydroxide, sodium carbonate and sodium bicarbonate. The solutions were shaken for 24 h and then 5 mL of each filtrate was pipetted and excess of base was titrated with standard HCl. The number of various types of acidic sites was calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na₂CO₃, carboxylic and lactonic groups; and NaHCO₃, only carboxylic groups.

2.7. FTIR spectra analysis

The CWS, CBS and their oxidized forms before and after adsorption of Cr(III) were examined using a JASCO FT/IR-460 Fourier transform infrared (FTIR) spectrometer. The discs were prepared by mixing 1 mg of powdered carbon with 100 mg of KBr. The spectra were recorded between 4000 and 400 cm⁻¹.

2.8. Adsorption studies

The Cr(III) solution was prepared by dissolving analytical grade Cr(NO₃)₃·9H₂O (Wako Pure Chemical Industries, Ltd.) in distilled water. The pH of the solution was adjusted using 0.1 M HEPES buffer. Adsorption tests were performed by adding 25 mg of the

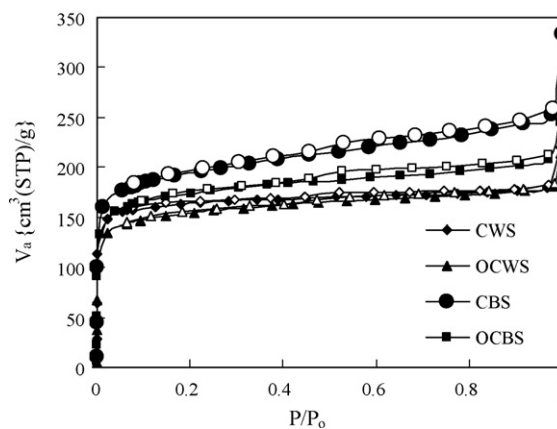


Fig. 1. Nitrogen adsorption (closed symbol) and desorption (open symbol) isotherms for carbons.

Table 1
Variation in characteristics of carbonized straw after oxidation.

Carbon	Specific surface area (m ² /g)	Average pore diameter (nm)	Carboxylic functional group (mmol/g)	Phenolic functional group (mmol/g)	Lactonic functional group (mmol/g)	Total acidic group (mmol/g)	PZC
CWS	700	2.03	0.24	0.02	0.02	0.29	9.00
OCWS	636	2.13	2.84	0.66	0.64	4.14	2.45
CBS	792	2.52	0.12	0.07	0.07	0.27	9.20
OCBS	721	2.24	1.38	1.49	1.08	3.95	2.58

adsorbent to 15 mL of the Cr (III) solution. The mixture was shaken in a thermostated shaker at 30 °C. The suspended mixture was filtered through a filter paper and the equilibrium pH of the filtrate was measured using an ORION model 720A pH meter. The chromium concentration was measured using a Shimadzu Model ICPS-8100 ICP/AES spectrometer. The adsorption experiments were performed at different pH values, at different concentrations and at different contact time. All the experiments were conducted in triplicate and mean values are reported in this paper. The maximum standard deviation observed was less than 5%.

3. Results and discussion

3.1. Physical properties

The N₂ adsorption–desorption isotherms are shown in Fig. 1. The adsorption isotherms for all samples investigated were primarily of Type I, a characteristic of microporous materials. However, the small hysteresis loop in the adsorption–desorption isotherms indicates the existence of mesopores. When a solid contains very fine micropores, the potential force field from the neighboring walls of the pores will overlap causing an increase in the interaction energy between the solid surface and the gas molecules [7]. This will result in an increase in adsorption, especially at low relative pressures causing complete filling of the pores at quite a low relative pressure, giving rise to a Type I isotherm. These isotherms are thus characterized by a plateau exhibiting a small amount of adsorption at higher relative pressures. The pores are too narrow to accommodate more than a single molecular layer, and so the Type I isotherms do not increase continuously.

In the presence of mesopores, capillary condensation will occur during adsorption and is preceded by a metastable fluid state (“cylindrical meniscus”), while capillary evaporation during desorption occurs via a hemispherical meniscus, separating the vapor and the capillary condensed phase, which will result in hysteresis, since mesopores are filled at higher pressure and emptied at lower pressure [21].

The structural characterization results are shown in Table 1. The specific surface area was measured by means of a BET-Plot and a *t*-Plot. The mean of these two specific surface areas is given in Table 1. It can be seen that although no activation process was employed for preparation of carbon, yet the specific surface area of carbon is high enough to that of activated carbon. The specific surface area

decreased after oxidation in both types of carbonized materials. The average pore diameter evaluated by the BET-Plot is also given in the same table.

Fig. 2 shows the pore size distribution of oxidized and unoxidized carbon materials, which suggests that carbon oxidation brings about a decrease in pore volume. This is attributable to the blockage of the pore entrances by the formation of humic substances during HNO₃ treatment [22]. The specific surface area of the oxidized materials has decreased for the same reason. The pore blockage occurs mainly in the microporous region but the mesoporosity structure remained mostly unchanged. In both types of oxidized and unoxidized carbonized wheat and barley straw samples, the narrow distribution of pores averaged around 1.22 nm as shown in Fig. 2, indicating that the nature of the porosity has not been altered by the oxidation. This is in good agreement with the average pore diameter of approximately 2 nm evaluated from the BET-Plot for all four types of carbon.

3.2. TG–DTA

Fig. 3 shows the TG and DTA plots for oxidized and unoxidized carbon samples. In both types of oxidized carbonized straw, weight loss commences quite early as shown by the peak in the DTA plot close to 70 °C, indicating a higher affinity for water. In the case of the oxidized carbons, successive weight loss and decomposition commences quite early and their weight gradually decreased. In the case of the unoxidized carbon samples, weight loss in the lower temperature range is not marked but a sharp weight loss occurs near 500 °C.

From the TG–DTA results, it can be deduced that wet oxidation of CWS and CBS with HNO₃ leads to the formation of an appreciable degree of functionality on the carbon surface. These functionalities become attached to such a high degree that their removal, primarily as CO₂ requires high energy. CWS and CBS showed a rapid weight loss near 500 °C while OCWS and OCBS showed a more gradual weight loss that extended up to 600 °C even though the weight loss commenced at low temperature, which reflects the relative thermal stability of the oxidized sample compared to the unoxidized samples. It can be concluded from the TG analysis that the different nature of weight changes monitored up to 1000 °C reflects the successful functionalization of CWS and CBS using 50% HNO₃.

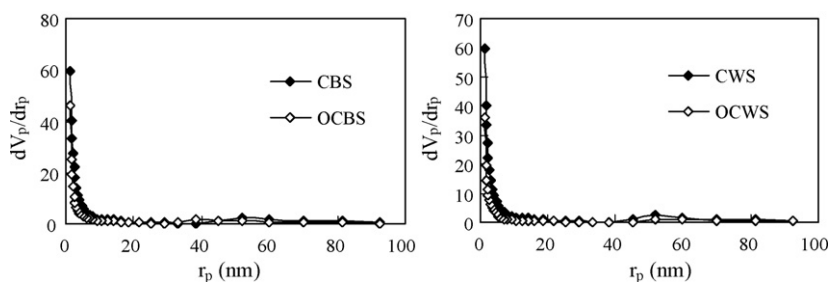


Fig. 2. Pore size distribution of the carbons.

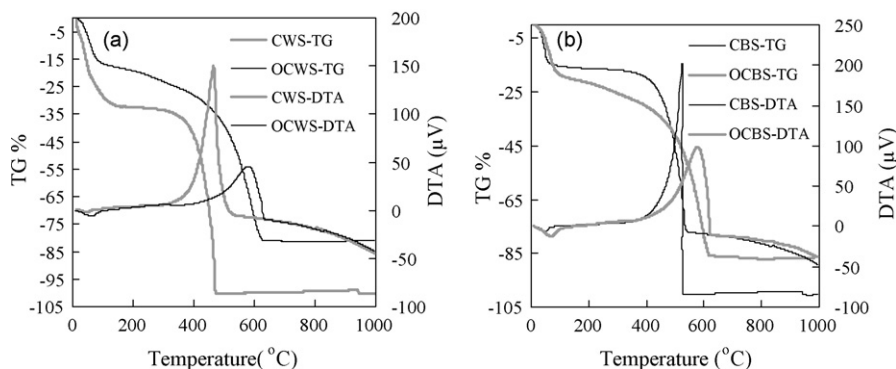


Fig. 3. TG-DTA curves.

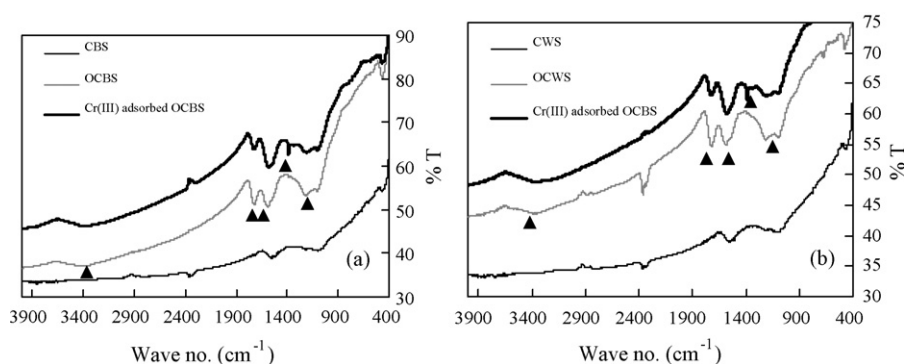


Fig. 4. Fourier transform infrared spectrogram (FTIR).

3.3. PZC

The PZC values of the samples are shown in Table 1. The PZC values of unoxidized carbons are basic, whereas after oxidation using HNO_3 , they become acidic. It is known that oxidation of carbon with HNO_3 induces a significant amount of carboxylic, lactonic and phenolic groups on the carbon surface [16] due to which causes the PZC values to shift from pH 9.00 and 9.20 down to pH 2.45 and 2.58 after the oxidation for CWS and CBS, respectively.

3.4. Boehm titration

The results of the Boehm titrations are listed in Table 1. The titration results suggest that all the carbon samples possess oxygen functionalities in the form of carboxylic, lactonic and phenolic groups. The content of strongly acidic carboxylic groups is substantially increased by oxidation. Modification by oxidation increased the total acidity by 13.9- and 14.2-fold in the case of CWS and CBS, respectively. The results show that the carboxylic surface group content, which is very low in the unoxidized carbon samples, has been increased by 11.5- and 11.3-fold by the oxidation in CWS and CBS, respectively.

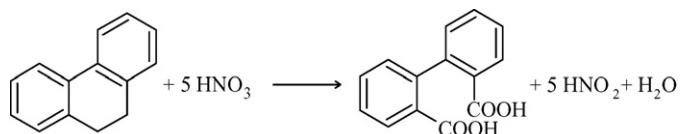
3.5. Fourier transform infrared spectroscopy

Fig. 4 shows the FTIR spectrum of CWS, CBS and their oxidized forms before and after adsorption of Cr(III). Observation of the absorption bands shows that the changes between the oxidized and unoxidized carbons are mainly due to the formation of oxygen functionalities. The most characteristic changes are observed in the 1800–1000 cm^{-1} range. The band centered at 1750 cm^{-1} is usually ascribed to the stretching vibration of C=O in ketones, aldehydes, lactones, and carboxyl groups. The band around 1600 cm^{-1} is attributed to COO^- asymmetric stretching. The appearance of

these peaks after oxidation indicates the formation of new oxygen functionalities or an increase in the already existing oxygen functionalities. The broad adsorption band in the 1300–1000 cm^{-1} range can be assigned to various C-bonds, such as those in ethers, phenols and hydroxyl groups. These results indicate that HNO_3 treatment give rise to a large increase in carboxylic and lactone group C=O bonds, resulting in the increased surface acidity of the carbonized materials.

The sites responsible for the adsorption of cation is due to the $-\text{COOH}$ groups which has strong complexing properties forming heterocyclic chelates with M^+ ions depending on the pH of liquid phase [23]. Peaks at 1400 cm^{-1} appears after adsorption of Cr(III) on OCWS and OCBS which was due to formation of ester like groups. Cr^{3+} ions adsorb on the carbon surface forming heterocyclic chelates with $-\text{COOH}$ groups. This will create an ester like groups which is supported by the appearance of peak at 1400 cm^{-1} after adsorption of Cr(III) on OCWS and OCBS in Fig. 4.

The results of Boehm titrations and FTIR analyses suggest that the number of carbonyl groups, of which there are very small amounts initially in the carbonized materials, was increased by oxidation with nitric acid. As described by Chingombe et al. [22], carbon materials consist of condensed aromatic structures. In the case of modification by oxidation, the reaction is most likely to occur on the aliphatic side chains of aromatic rings because such sites are highly susceptible to oxidation as shown in (1).



(1)

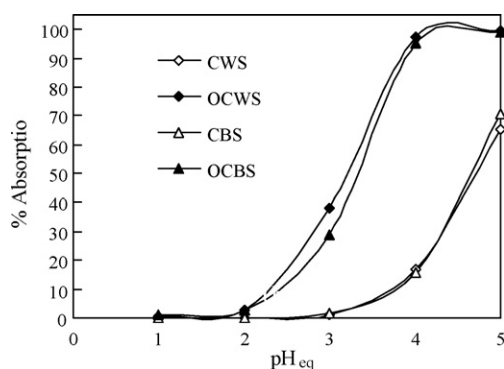


Fig. 5. Effect of equilibrium pH on the adsorption of Cr(III) on carbons. Weight of adsorbent = 25 mg; volume of Cr(III) solution = 15 mL; initial concentration of Cr(III) = 0.5 mmol/L; shaking time = 24 h.

3.6. Effect of the pH on adsorption of Cr(III)

Fig. 5 shows the effect of pH on the adsorption of Cr(III) on oxidized and unoxidized carbon samples. The adsorption of Cr(III) was tested over a pH range of 1–5. At pH values higher than 5, adsorption tests were difficult due to the formation of chromium hydroxide precipitates. The percent adsorption of Cr(III) increases with increasing pH, suggesting that the adsorption takes place according to a cation exchange mechanism, which is considered to be caused by the abundance of carboxylic functional groups on the carbon surface.

In Fig. 5, the pH at which the adsorption of Cr(III) takes place is shifted to lower pH values by about 1.5 pH units between the oxidized carbon materials and the unoxidized ones, which is attributed to the increase of carboxylic groups by the nitric acid oxidation in agreement with the results of the Boehm titrations.

3.7. Adsorption isotherms

Fig. 6 shows the adsorption isotherms for Cr(III) on the tested samples at pH 5. The amount of adsorption increases rapidly with increasing Cr(III) concentration at low Cr(III) concentrations and slowly reaches a constant value corresponding to each sample at high Cr(III) concentrations, as expected for Langmuir-type adsorption curves. From the constant values, the maximum adsorption capacities were evaluated as 0.30, 1.00, 0.29 and 0.93 mmol/g for CWS, OCWS, CBS and OCBS, respectively, suggesting that oxidation has increased the maximum adsorption capacity by 3.33 and 3.20 times for CWS and CBS, respectively, which can be correlated to the increases in the density of carboxylic groups on the surface of CWS and CBS.

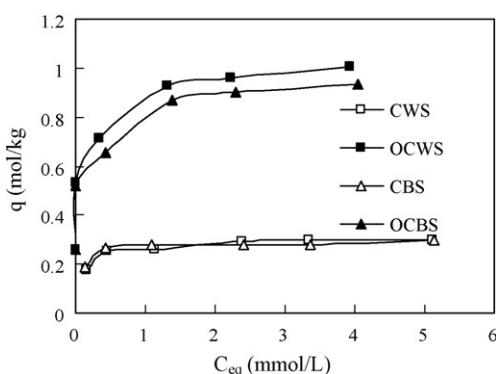


Fig. 6. Adsorption isotherms for Cr(III) on carbons. Weight of adsorbent = 25 mg; volume of Cr(III) solution = 15 mL; shaking time = 24 h; pH 5.

Table 2

Estimated Langmuir isotherm parameters for Cr(III) adsorption at 30 °C and at pH 5.

Langmuir isotherm equation $1/q_e = 1/\theta \cdot b \cdot C_e + 1/\theta$	Estimated isotherm parameters		
	R^2	θ	b
CWS	0.98	8.54	0.30
OCWS	0.93	142.05	0.93
CBS	0.97	128.51	0.29
OCBS	0.96	44.44	0.85

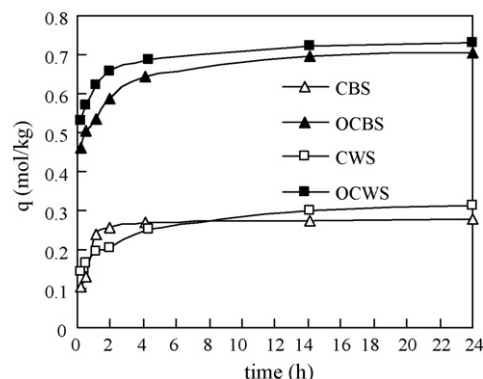


Fig. 7. Effect of contact time on adsorption of Cr(III) on carbons. Weight of adsorbent = 25 mg; Volume of Cr(III) solution = 15 mL; Initial concentration of Cr(III) = 2 mmol/L; pH 5.

Table 2 shows the result of the Langmuir plot for the data shown in Fig. 6. The Langmuir equation is represented as follows [24]:

$$\frac{1}{q_e} = \frac{1}{\theta \cdot b \cdot C_e} + \frac{1}{\theta} \quad (2)$$

where C_e is the equilibrium concentration (mmol/L) and q_e the amount adsorbed at equilibrium (mmol/g). The Langmuir constants, θ and b , which are related to the adsorption capacity and heat of adsorption, respectively were calculated as listed in Table 2. The high correlation coefficients as shown in Table 2 suggests that the Langmuir isotherm well describes the Cr(III) adsorption.

3.8. Effect of contact time

Fig. 7 shows the effect of contact time on the adsorption of Cr(III) on carbons. It shows that the rate of adsorption on all type of carbons studied were very fast and equilibrium was achieved within 4 h contact time. The very fast kinetic and enhanced adsorption capacity makes oxidized CBS and CWS more preferable adsorbent.

3.9. Comparison of the oxidized carbon with other adsorbents

Table 3 summarizes the comparison of the maximum adsorption capacities for various adsorbents for Cr(III) reported in the liter-

Table 3

Comparison of the maximum adsorption capacity for Cr(III) on different adsorbents.

Adsorbent	pH	Temperature (°C)	Adsorption capacity [mmol/g]	Reference
Activated carbon	5.0	25	0.76	[25]
Diatomite	6.0	30	0.54	[26]
Lignin	5.0	20	0.34	[27]
Lignite based humic acid	4.1	20	0.29	[23]
Turkish brown coal	4.5	25	0.26	[28]
Zeolites		28	0.05	[29]
OCWS	5.0	30	1.00	This work
OCBS	5.0	30	0.93	This work

ature including the oxidized carbons in this work. It can be seen that the carbon produced after oxidation of carbonized barley and wheat straw by a simple process are superior to many other adsorbent for trivalent chromium adsorption, indicating that it can be promising alternative for Cr(III) ion removal from industrial effluent. The significantly high adsorption capacities of these adsorbents are attributable to introduction of acidic functional group by oxidation method.

4. Conclusions

The chemical modification employed in the present work only slightly changed the specific surface area but significantly changed the surface chemical structure. Acidic surface functional groups were introduced by nitric acid oxidation, which was confirmed by FTIR analysis and measurement of surface functional groups by means of the Boehm method. The decrease in PZC after oxidation also supports the fact that acidic groups have been introduced. The surface modification produced carbon samples with a very different chemical nature but a similar porous structure. As shown by the BJH plots, the pore size distribution is almost the same before and after the oxidation. The only difference was a small decrease in the volume of the pores, which was also verified by the nitrogen adsorption–desorption isotherms, suggesting that the carbon materials maintain a microporous structure even after oxidation. However a slight decrease in the surface area took place after oxidation. The adsorption tests for Cr(III) at different pH values and Cr(III) concentrations showed that the oxidized straw carbons exhibit a high efficiency for Cr(III) ions in comparison to the unoxidized carbons. Thus the carbon materials prepared from waste straw can be modified into good cation ion exchanging adsorbents by the simple method of oxidation.

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