Preparation and Characterization of Bio-based Activated Carbon from Fish Scales

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The object of this study was to prepare activated carbons containing nitrogenous functional groups by a chemical method from nitrogen-containing raw materials. Fish (*Ctenopharyngodon idellus*) scales were impregnated with phosphoric acid (H_3PO_4) and activated at varied temperatures. The adsorption ability, structural characteristics, surface chemistry, and morphology of the activated carbons were characterized by methylene blue and iodine values, nitrogen adsorption, the Boehm method, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). The total alkaline groups content of the activated carbon produced from fish scales was 0.4330 mmol/g, the total acidic groups was 1.68 mmol/g, the Brunauer–Emmett–Teller (BET) surface area was 501 cm^2/g, and the total pore volume was 0.284 cm^3/g. The average pore diameter was 1.94 nm under an activation temperature of 550 °C, an activation time of 1 h, and an impregnation ratio of 2. As a result of this study, nitrogenous functional groups that contained acid-base amphoteric adsorbent were produced.

Keywords: Activated carbon; Fish scales; H_3PO_4; Nitrogenous functional groups; Amphoteric adsorbent

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INTRODUCTION

Activated carbons with developed pore structures and excellent chemical properties have played an important role in the fields of adsorption (Lorenc-Grabowska *et al.* 2013), catalysis (Bedia *et al.* 2009), and electrochemistry (Choi *et al.* 2013). In order to fulfill the needs of practical applications, there has been increased interest in activated carbon with better performance, especially for the preparation and surface modification of nitrogen-containing activated carbons (Xie *et al.* 2003; Li *et al.* 2019). Generally, the surface chemical properties of activated carbon are mainly determined by oxygenous and nitrogenous functional groups (Yao *et al.* 2014). Due to the presence of oxygenous functional groups (carboxyl and phenolic hydroxyl groups), the surface of activated carbon is acidic. Nitrogenous functional groups that contain activated carbons have both acidic and basic functional groups (amine groups) on the surface, so they exhibit amphoteric characteristics (Lahaye 1998; Mangun *et al.* 1999; Fuente *et al.* 2003).

The traditional activated carbons almost have no nitrogenous functional groups, which can be attributed to the fact that they are commonly based on wood and coal as raw materials, and these have extremely low nitrogen content. To obtain activated carbons with nitrogenous functional groups many methods of adding an external nitrogen source have been used. There are usually three methods for the preparation of amphoteric nitrogenous functional groups with activated carbons. One method is directly activating the nitrogen-containing material with an activator such as phosphoric acid (H_3PO_4) (Oginni *et al.* 2019).

Lorenc-Grabowska *et al.* (2013) used nitric acid as an activator to treat the raw materials and perform a redox reaction. Palomo *et al.* (2017) used ammonia activation of raw materials at high temperature. Because the surface of the activated carbons contains different nitrogenous functional groups, its physical and chemical properties are optimized. All the activated carbon samples had different nitrogen contents (0.75 wt% to 42 wt%), so the surfaces of each sample had different basicities (Lorenc-Grabowska *et al.* 2013). Some researchers have shown that the presence of amide groups improves the adsorption and affinity of the carbon dioxide (CO_2) molecules (Pevida *et al.* 2008). In the field of electrochemistry, the presence of condensed nitrogen structures such as pyridine increases the capacitance, improves the charge transfer, and enhances the electrochemical reduction (Byrne *et al.* 2014).

In this work, fish (*Ctenopharyngodon idellus*) scales, a nitrogen-containing biomass, were used as raw materials, and it was indicated that carbon materials with nitrogenous functional groups would be produced by traditional methods. Fish scales are rich in protein and minerals, and they are mainly composed of protein and hydroxyapatite (Dai *et al.* 2018). In the fish scales, the contents of protein and ash were 70% and 30%, respectively. The proteins are mainly collagen and keratin. A small amount of globulin is also present. The ash is mainly hydroxyapatite and it contains a small amount of inorganic salts such as calcium carbonate, magnesium phosphate, and sodium phosphate (Liu *et al.* 2009). As the world depletes the supply of non-renewable resources, different raw materials must be sourced. China is the only country in the world where aquaculture exceeds fishing, and a large amount of waste such as fish scales are generated during processing. It is estimated that China's annual fish scale waste can reach 30×10^4 t (Dai *et al.* 2018). Fish scales were used in this work to prepare activated carbon, which is a good way to utilize waste resources and transform fish scales into high value-added activated carbon products.

EXPERIMENTAL

Preparation of the Activated Carbon Samples

The activated carbon samples were prepared *via* chemical activation, by using fish (*C. idellus*) scales as the precursor. First, the fish scales were boiled in water for a 0.5 h, rinsed repeatedly with water to remove the impurities, and dried. Ten grams of fish scales were impregnated with 85% H_3PO_4 (w/w) aqueous solution for 12 h at room temperature, and dried. The impregnation ratio value (H_3PO_4/fish scales mass ratio) was 2. Once the fish scales were impregnated and dried, they were placed in a muffle furnace at 550 °C for 1 h (Rosas *et al.* 2010). The obtained sample was washed with distilled water at a constant pH until elution was reached. The sample was then dried for 24 h (Palomo *et al.* 2017).

Morphology

The morphologies of the activated carbon specimens produced from fish scales were characterized using a Hitachi SU8010 scanning electron microscopy (SEM) (Tokyo, Japan). Double-sided adhesive tape was used to fix the activated carbon sample to the specimen stub. The carbon sample was transferred into the vacuum chamber, where the microscope scanned the sample with an electron beam (Oginni *et al.* 2019). Using the instrument software, the micrographs were obtained at a high voltage of 20 kV, the scanning internal was 15 mm, and the acquisition time was 100 s.

Surface Area and Pore Size Distribution

The nitrogen adsorption/desorption isotherms of the activated carbons were performed at 77.35 K. The Brunauer–Emmett–Teller (BET) method was used to calculate the surface area. The total pore volume was calculated using N_2 adsorption and the microspore volume was calculated by t-plot model. The pore size distributions of the sample were calculated by the Barret-Joyner-Halenda (BJH) model.

Elemental Composition and Surface Chemistry

The surface functional groups were analyzed by means of X-ray photoelectron spectroscopy (XPS), using the Boehm method. The XPS analyses of the samples were tested by a Kratos Analytical Ultra model X-ray photoelectron spectrometer (Spring Valley, NY, USA). The X-ray radiation source was Mg Kα (1253.6 eV) at 12 KV. For the analysis of the XPS peaks, the maximum of the C1s peak was set at 284.6 eV and used as reference for the other peaks (Bedia *et al.* 2011).

The Boehm titration method was used to determine the contents of the acidic and basic groups on the surface of the activated carbon. First, 0.05mol/L NaOH, Na_2CO_3, and $NaHCO_3$ standard solutions were configured, 2 g of activated carbon sample into a conical triangular flask of 100 mL volume. Then 25 mL of standard lye was added into the flask. After stirring for 24 h, the solids were filtered and washed with distilled water. Using methyl red as the end point indicator, the unreacted lye in the filtrate was titrated with the 0.05 mol/L HCl to the end point. The content of the corresponding groups was calculated according to the amount of alkali solution and HCl that was used (Boehm *et al*. 2002).

RESULTS AND DISCUSSION

The SEM images of the activated carbon produced from fish scales are shown in Fig. 1. As shown in Fig. 1a, all the activated carbons had a flaky structure, scattered randomly.

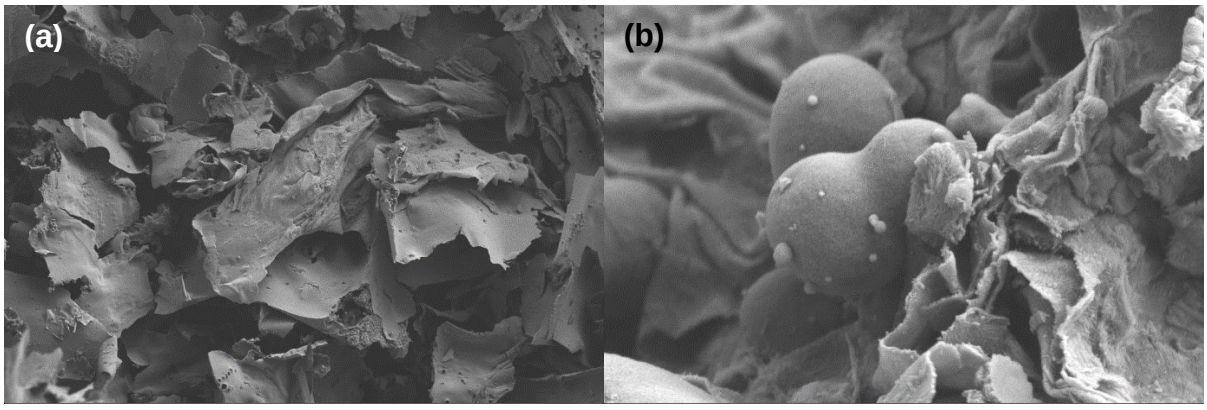

Fig. 1. SEM images of the activated carbons produced from grass carp scales at a a) 10 μm scale and a b) 200 nm scale

The surface was relatively smooth and flat, and there were some holes, which is an indication that the original structural characteristics of the fish scales were retained after activation by H_3PO_4. Figure 1b shows that the exterior surface of the activated carbons had certain granular materials.

The adsorption amount of iodine and methylene blue to the activated carbons are shown in Table 1. As the temperature of preparation was increased, the adsorption amount of the activated carbons to iodine and methylene blue tended to increase and then decreased. The optimal adsorption capacity was observed at 550 °C. It can be seen from the adsorption of the iodine that the activated carbon developed a microporous structure. The adsorption of the methylene blue indicated that the activated carbon had an appreciable content of mesopores.

Table 1. Properties of the Activated Carbon Produced from Fish Scales under Different Conditions

Temp (°C)	Iodine Adsorption Value (mg/g)	Methylene Blue Decolorization (mg/g)
400	350.35	91.50
450	344.98	104.00
500	481.16	150.00
550	936.46	213.00
600	716.58	170.50
650	511.37	148.00

Table 2. BET Surface Area Parameters of the Activated Carbon Produced from Fish Scales

	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
Fish Scales	6.5633	0.0142	6.6484
Microporous	427.565	0.1844	-
Mesoporous	30.5325	0.0533	
Total	501.356	0.2836	1.9364

Figure 2 depicts the N_2 adsorption-desorption isotherms at 77.35 K for the activated carbons that were prepared in this work. The BET surface areas of the activated carbons were assessed by the isotherms. The isotherm for the activated carbon can be classified as type IV in the entire relative pressure range, which indicates a highly porous structure, with microporous and mesoporous characteristics. The activated carbons produced from fish scales adsorbed more nitrogen in the initial part of the isotherm. It is also indicated that the activated carbons contained many microporous structures. When the relative pressure was in the range of 0.4 to 0.8, the upward trend of the adsorption capacity slowed down. The N_2 adsorption-desorption isotherms show a hysteresis loop, which is associated with capillary condensation that takes place in the mesoporous. This indicated that there were almost no large pore structures in activated carbons (Kumagai *et al.* 2010)

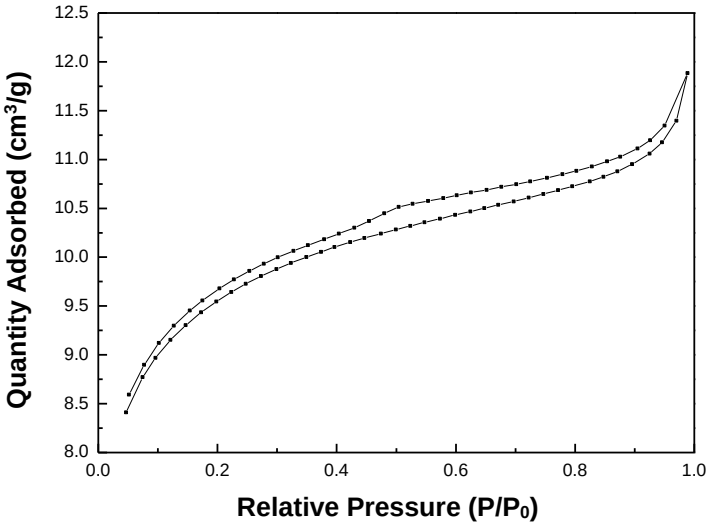

Fig. 2. The N_2 adsorption-desorption isotherms at 77.35 K

The pore size distribution is an intrinsic property of the activated carbon, which influences its adsorption performance (Oginni *et al.* 2019). The surface areas of the activated carbon produced from the fish scales was 501 m^2/g, the total pore volume was 0.244 cm^3/g, and the average pore size was 1.94 nm (Table 2). The surface area and the pore volume were the most influential characteristics of the microporous structure, which indicates that the activated carbon had a developed pore structure, a large surface area, and a large pore volume. This is conducive to the physical adsorption capacity of the activated carbon. Compared with wood waste activated by H_3PO_4 (with a surface area of more than 1000 m^2/g, a pore volume of more than 0.56 cm^3/g , an average pore size of more than 1.9 nm), the surface area and total pore volume of fish scales activated carbon are lower, and the average pore size are similar (Mohammed *et al*. 2018). These findings imply that H_3PO_4 is also an effective activator for activation of fish scale.

Table 3. Contents of the Functional Groups

Temp (°C)	400	450	500	550	600	650
Acidity mmol/g	2.1304	1.7043	1.2764	1.7166	1.3923	1.1291
Basicity mmol/g	0.4181	0.3162	0.3034	0.4587	0.4056	0.3458

The contents of the surface functional groups of the activated carbons are shown in Table 3. By using different temperatures of activation, it was possible to produce a string of similar functional groups. As the temperature was increased from 400 °C to 550 °C, the basicity of the activated carbons increased from 0.418 to 0.459 mmol/g. As the temperature was increased from 550 °C to 650 °C, the basicity decreased from 0.459 to 0.346 mmol/g. The changes in the amount of acidic functional groups are consistent with the changes in the basic functional groups. The results showed that oxygenous acidic functional groups and nitrogenous basic functional groups such as amines may be present in activated carbons produced from fish scales.

The surface element distribution and the surface nitrogenous functional groups of the activated carbons were further analyzed by XPS. Four obvious peaks emerged in the samples around 133.1, 284.6, 400.1, and 532.1 eV, corresponding to P2p, C1s, N1s, and O1s, respectively. The C1s, N1s, and P2p spectra for the activated carbons were deconvoluted, as shown in Fig. 3. To conduct an in-depth analysis, the C1s spectra consisted of a major graphitic carbon peak at a mean binding energy of 284.6 eV and three types of carbon atoms were linked to oxygen and nitrogen. Peak 1 (284.6) consisted of C-C/C=C bonds, peak 2 (285.7 eV) consisted of phenolic, alcohol, ether, or C=N groups, and peak 3 (287.5 eV) consisted of C=O or C-N bonds (Biniak *et al.* 1997). This was according to data from the N1s spectra, which was inferred from the corresponding functional groups at peak 1 (399.8 eV)-N-pyridonic (N-5) (Lorenc-Grabowska *et al.* 2013). This shows that the nitrogen atoms are well preserved after treatment. The P2p spectra shows one type of phosphorus atom: peak 1 (133.5 eV)-phosphate and pyrophosphate (Oginni *et al.* 2019). The result suggested that P atom was successfully deposited in the activated carbon samples.

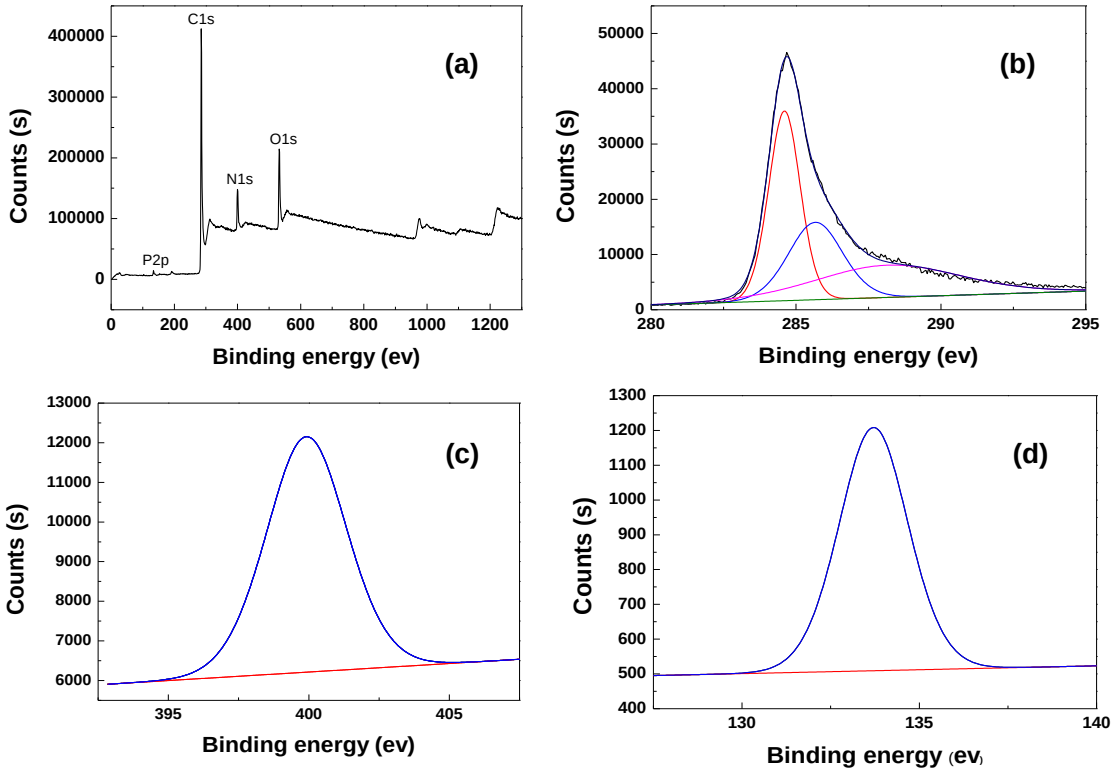

Fig3. The XPS images of the activated samples from the a) XPS survey, the b) C1s peak, the c) N1s peak, and the d) P2p peak

CONCLUSIONS

1. In this paper, porous nitrogenous activated carbons were successfully obtained *via* activating fish scales with H_3PO_4. The adsorption value of the methylene blue was 213 mg/g, and the adsorption value of the iodine was 936 mg/g. The samples exhibited an ultrahigh specific surface area of 501 cm^2/g. The total pore volume was 0.284 cc/g, the average pore diameter was 1.94 nm, and the microporous ratio was 85.3%.

2. The series characterization of the activated carbon samples produced from fish scales showed that the surface of the activated carbon had abundant functional groups. The basicity and acidity of the activated carbon prepared are 0.459 and 1.717 mmol/g, respectively. Phenolic, alcohol, ether, N-pyridonic, phosphate, and pyrophosphate functional groups were present in the activated carbon. These results showed that nitrogenous functional groups carbon materials can be produced by traditional methods which dealt with nitrogen-contained raw materials.
3. Activated carbon produced from fish scales was found to have a developed pore structure, large surface areas, and excellent adsorption performance. These characteristics provide this activated carbon with huge potential applications in the adsorption, catalysis, and electrochemical fields.

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