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## Azolla-derived hierarchical nanoporous carbons: From environmental concerns to industrial opportunities

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### ABSTRACT

Azolla biomass as a very fast growing fern was utilized to prepare hierarchically nanoporous activated carbons with high surface area and crystallinity. As-prepared activated carbons were characterized using powder X-ray diffraction (PXRD), Raman, Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS), N<sub>2</sub> sorption, scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM). XRD and FTIR results confirmed that CaCO<sub>3</sub> which is naturally present in azolla biomass is responsible for crystallinity of the final materials and in collaboration with NaOH as activation agent led to high surface area nanoporous carbons. Activation process increased the specific surface area of the initial char from about 3 m<sup>2</sup> g<sup>-1</sup> to 2680 m<sup>2</sup> g<sup>-1</sup>. Large ordered atomic layers domains of carbon were observed in HR-TEM. CO<sub>2</sub> adsorption capacity was investigated for the azolla-derived carbons which proved the high room temperature capture ability of near 7.18 mmol g<sup>-1</sup> at 1 bar and 12.5 mmol g<sup>-1</sup> at 20 bar. More significantly, extraordinary capacity of methylene blue uptake by about 4448 mg g<sup>-1</sup> has been observed in azolla-derived porous carbon which is the highest ever reported for water cleaning.

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### 1. Introduction

Nowadays, water and air pollution are among the most severe grand issues facing the mankind. Combustion of fossil fuels is still regarded as the main supply of energy worldwide, which increases the atmospheric concentration of carbon dioxide (CO<sub>2</sub>) to hazardous levels [1,2]. One of the major drastic effect of CO<sub>2</sub> is on water resources in which its dissolving in water and acidic rain lead to serious threats for marine organisms in tropical, open-oceans, coastal, deep-seas, and high-latitude sea ecosystems [3–5]. Therefore, due to its major contribution on water and air pollution, CO<sub>2</sub> emission mitigation has become an urgent aim in many countries [6,7]. In addition, improper disposal of industrial wastes such as organic dyes as other water pollutants must be avoided to protect the water resources. Thus, development of new materials that can be used in fields related to protection and cleaning of air and water is demanded.

Solid adsorptive materials provide a promising candidate for environmental applications of CO<sub>2</sub> capture and water cleaning due to their facile regeneration. Several types of solid adsorbents have been developed e.g. zeolites [8,9], porous polymer networks [10,11], metal-organic frameworks [12–15] and porous carbons [16–18] for CO<sub>2</sub> capture and water cleaning. Porous carbon materials are excellent candidates for CO<sub>2</sub> capture and water treatments due to their easy regeneration, low energy requirement, high adsorption capacity and selectivity [19–22].

Porous carbons are traditionally obtained by the pyrolysis of a variety of precursors which can be synthetic or natural [23–26]. Pyrolysis of natural source gives char which is then activated by physical (with CO<sub>2</sub> or steam) or chemical approaches in order to increase porosity and the number of small pores (meso- and micro-pores). Chemical activation can be done by acidic or basic agents. ZnCl<sub>2</sub> [27–29], FeCl<sub>3</sub> (in mixture with ZnCl<sub>2</sub> [30]), H<sub>2</sub>SO<sub>4</sub> [31], H<sub>3</sub>PO<sub>4</sub> [32] are some of the acids and KOH [33,34] and NaOH [35,36] are the main bases which have been studied for this purpose.

While the engineering of the specific properties of porous carbons is of great value, economically viable materials and procedures are needed for even more widespread usage of such materials. Taking advantage of lignocellulosic biomass has been widely

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studied for this task [37–39]. Conversion of these wastes to porous carbon not only can bring about value added commercial products, it will reduce the environmental challenges caused by open-air burning or dumping of them.

Azolla or fairy moss is a very fast growing fern which can be found floating on the surface of water (lakes, canals, ponds, slow moving streams, etc.). *Azolla filiculoides* is native to Americas and has been spread widely all around the world [40]. The thick mat (5–20 cm thick, in areas up to 10 hectares [41]) made by azolla not only prevents sunlight penetration, but also creates an anaerobic environment, making it impossible for most organisms to survive in the water below. Azolla infestations have severe impacts; they drastically decrease the biodiversity in their water ecosystem [42], decrease the quality of drinking water, increase evapotranspiration and promote the spreading of water related diseases [43]. A catastrophic environmental case happened in Anzali lagoon [44]. The challenging of presence of azolla with all its negative impacts can be faced with an opportunistic attitude. Application of azolla for industrial application especially in environmental fields, make it as an economically viable idea to change these environmental concerns to environmental opportunities. In this paper we report the application of azolla as cheap, non-toxic and abundant biomass for the synthesis of high surface area porous carbons. The prepared activated carbons were utilized to CO<sub>2</sub> capture and water cleaning treatment to change environmental concerns to beneficial environmental application

## 2. Experimental

### 2.1. Materials and synthesis

All chemicals and reagents, except Azolla were of analytical grade and used as received without any further purification. Sodium hydroxide (NaOH) was purchased from Merck. Nitric acid (37%) (HNO<sub>3</sub>) was purchased from Dr Mojallali<sup>TM</sup> Chemical Reagent Company. Azolla was obtained from Anzali lagoon and washed several times before treatment to ensure the removal of any contaminants.

In a typical synthesis air dried azolla was pre-carbonized under Ar atmosphere at 300 °C (T300). Then, 2 g of the obtained product was added to 6 g of solid NaOH and mixed until complete homogenization. This mixture was transferred to a tubular electric furnace and treated at 600 °C for 3 h under Ar atmosphere. The obtained black powder was washed with water (T36B sample). The T36B was washed with 1 M HNO<sub>3</sub> solution to remove the activation agent and other impurities. Next, the obtained powder was washed with deionized water until reaching neutral pH and dried at 80 °C for 5 h (T36A sample). T36A was further pyrolyzed at 800 °C under argon flow for 2 hours and named T368A. To investigate the effects of basic activation on the surface area and pore volume, an experiment was performed without activation step as T8A sample. In this experiment, dried azolla was firstly heat treated at 800 °C and then acid washed. To consider the effect of pre-carbonization and activation temperatures, T688A sample was prepared. Pre-carbonization and activation temperatures of 600 and 800 °C were used for this sample, respectively. Other parameters were similar to T368A. For all experiments, heating rate was 10 °C min<sup>-1</sup>.

### 3. Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Philips (Holland) PW1730 diffractometer with Cu K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation. Scanning Electron Microscopy was carried out on a VEGA\TESCAN (Czech Republic) at an acceleration voltage of 30 kV.

High Resolution Transmission Electron Microscopy (HR-TEM) images were obtained on a FEI (US) TITAN instrument operating at 300 kV. N<sub>2</sub> adsorption–desorption isotherms were recorded on a BELSORP mini II equipment at the liquid nitrogen temperature (77 K). The samples were degassed in vacuum at 150 °C for 6 h prior to the measurements. FTIR spectroscopy was performed on all samples in the range of 500–4000 cm<sup>-1</sup> with KBr pallets using a Shimadzu 8400s Spectrometer. Raman Spectroscopy was performed on a Takram micro Raman spectrometer (Teksan<sup>TM</sup>, Iran) equipped with a 532 nm laser as the excitation source at power of 90 mW. X-ray photoelectron spectroscopy (XPS) measurements were carried out for the carbon powders using an Al K $\alpha$  source (XPS Spectrometer Kratos AXIS Supra). The carbonaceous C 1s line (284.8 eV) was used as the reference to calibrate the binding energies. The absorbance of MB solution was measured using an UV-1700 (Shimadzu, Japan) UV–visible spectrophotometer to monitor absorbance at  $\lambda_{\text{max}} = 665 \text{ nm}$  corresponding to the maximum absorbance.

#### 3.1. CO<sub>2</sub> adsorption isotherms

CO<sub>2</sub> adsorptions at high pressures were carried out on a stainless steel absorption system up to 20 bar and 298 K. Schematic apparatus used for this experiment and detailed experimental description can be followed elsewhere [45].

#### 3.2. Dye adsorption

Adsorption experiments were carried out to investigate the adsorption behaviors of the prepared carbon powders. In a typical procedure, 5 mg carbon powder was added to a 50 ml MB aqueous solution (100 mg l<sup>-1</sup>). MB concentration was examined at different intervals by UV–vis absorption. Langmuir adsorption model was utilized to characterize the adsorption capacity of a sorbent for pollutants. Langmuir isotherm is represented as follows:

$$Q_e = \frac{Q_m K C_e}{(1 + K C_e)}$$

where  $Q_e$  (mg g<sup>-1</sup>) is the adsorbed amount of dyes at the equilibrium concentration,  $C_e$  (mg l<sup>-1</sup>) is the equilibrium solute concentration,  $Q_m$  (mg g<sup>-1</sup>) is the maximum adsorption capacity corresponding to complete monolayer coverage and  $K$  is the equilibrium constant. Initial concentration of MB solution in this experiment was 400 mg l<sup>-1</sup> and the experiments were continued until equilibrium.

## 4. Results and discussion

### 4.1. Carbonization

XRD patterns of the T300, T36B, 36A, T368A and T668A samples are depicted in Fig. 1. As it can be seen, XRD pattern of dried azolla at 300 °C (T300 sample) revealed peaks at 22.92°, 29.3°, 35.9°, 39.9°, 43.2°, 47.5°, 48.4° and 57.4°. The observed peaks are assigned to (012), (101), (110), (200), (002), (211), (112), (202), (310) and (103) reflections of calcium carbonate (CaCO<sub>3</sub>) (JCPDS card no. 01-086-0174). Activation of T300 with NaOH as activation agent at 600 °C under Ar atmosphere followed by washing with deionized water led to black powders (T36B sample). XRD pattern of T36B shows similar XRD peaks compared to T300. Sharpness of appeared reflections for CaCO<sub>3</sub> could be due to high temperature treatment; this finding shows that CaCO<sub>3</sub> remained in the carbonized sample, T36B. Acid washing of the obtained black powder after carbonization at 600 °C with HNO<sub>3</sub> solution resulted in the elimination of the observed peaks related to CaCO<sub>3</sub> (T36A). Heating of T36A at 800 °C under Ar atmosphere, led to T368A carbon

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