Modification and Characterization of Ordered Mesoporous Carbons for Resorcinol Removal

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Table of Contents

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

EDS	Energy-Dispersive X-ray Spectroscopy
DTG	Differential Thermal Gravity
FT-IR	Fourier Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
ISS	International Space Station
Kv	Kilo-volt
mA	Milliampère
mg	Miligram
nm	Nanometer
OMCs	Ordered Mesoporous Carbons
PAA	Polyacrylic Acid
PSD	Pore Size Distribution
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TEOS	Tetraethoxysiliane
TGA	Thermogravimetric Analysis
TOC	Total Organic Carbon
WRS	Water Recycling System
XRD	X-ray Diffraction

CHAPTER 1: INTRODUCTION

1.1 Background

Water recovery system (WRS) is designed for the International Space Station (ISS) to provide portable water for space crew members. It consists of various units including vapor compression distillation, adsorption, and ion exchange (Guo *et al*. 2005). Among them, adsorption processes have played a key role in the life support systems. Currently, granular activated carbon (GAC) has been used in this adsorption process as an adsorbent because of its large specific surface area and multiple types of reactive surface sites. Materials with high adsorption capacity, less weight and volume for the adsorption unit used in WRS can fulfill long duration manned missions. Recently, mesoporous materials have attracted much attention because they have been widely explored for industrial applications as catalyst supports, electrochemical materials, and gas separation media.

Mesoporous materials are defined as natural or synthetic materials with a pore diameter of 2~50 nm, halfway between the pore sizes that define micro- and macro porous materials (Rouquerol *et al.* 1994). They have high-surface areas, regular frameworks and narrow pore size distributions (Titrici *et al.* 2007). All the above mean that they can be widely used as adsorbents, catalyst supports, electrode materials and energy storage media. Typical mesoporous materials include silica and carbon that have similarly-sized fine mesopores. One of the major mesoporous materials is ordered mesoporous carbon (OMC).

Compared with the regular activated carbon-based materials, OMC materials have a higher adsorption capacity and faster adsorption kinetics. Historically, activated carbon used for contaminant adsorbing has been limited by slow contaminant diffusion kinetics and the inaccessibility of sorption sites. Ordered mesoporous carbon, on the other hand, can overcome the limitations by increasing the pore size and the surface area. These show great potential for environmental improvement because of their ability to remove inorganic and organic contaminants from liquid and gas. So more and more researchers show great interests in the OMC material as a replacement of granular activated carbon used in the water and waste water treatment system.

In 1999, the first example of ordered mesoporous carbon was synthesized using MCM-48 as a template (Ryoo *et al*. 1999). Since then, various synthesis methods of OMC have sprung up. However, previous studies on the OMCs demonstrated that OMCs were still not selective for the specific contaminant. And practically, the adsorption capacity was not as good as expected. All these limitations narrowed the OMC's applications. Currently, the research priorities are mainly focused on the modification of the OMC. In general, the mesoporous structures of the OMC are highly dependent on the carbon precursor and the silica template, as well as the synthetic conditions. Apparently both the surface chemistry and the pore structure of the synthetic materials play a cooperative role in the specific application. To improve the performance of the adsorption, one important innovative method is to modify both the surface chemistry and pore structure. The idea of OMC modification primarily came from the modification of the activated carbon materials. The approaches that introducing function groups to the surface of the OMCs have been categorized in various ways: oxidation, reduction, and electrode methods (Han *et al.* 2003).

1.2 Study objectives

The overall objective of the study is to develop modified OMC materials with high adsorption capacity for organic contaminants removal. The specific objectives of this project are:

1. Investigate the influence of template quantity on the synthesis of ordered mesoporous

carbon. Prepare the OMCs with different amounts of silica template and analyze their adsorption capacities for removing organic matters in aqueous solutions.

2. Modify the ordered mesoporous carbons with various methods.
3. Test the property changes and improve the adsorption behavior of the OMCs and modified OMCs.

1.3 Study approach and processes

In this investigation, different ratios of silica template to carbon precursor were tested to study the effect of template amount affect during the initial stage of the OMCs' fabrication. Then different solutions were used to modify the mesoporous carbon materials by immersing method. Next, several characterizations have been applied to all the products to test their properties. Finally the adsorption capacities of the OMCs and modified OMCs were evaluated.

CHAPTER 2: LITERATURE REVIEW

2.1 Mesoporous materials

Porous materials are classified into different kinds by their porous size. According to IUPAC classification, micro porous materials have pore diameters of less than 2 nm and macro porous materials have pore diameters of greater than 50 nm; the mesoporous category thus lies in the middle.

A mesoporous material can be disordered or ordered in a mesostructure. Ordered mesoporous materials have inspired prominent research interests due to their unique properties and functionalities and potential applications in adsorption, separation, catalysis, sensors, drug delivery, energy conversion, and storage (Baton *et al.* 2006; Ma *et al.* 2000; Cheetham *et al.* 1999; Behrens 1993). Compared with their bulk counterparts, they can interact with atoms, ions, molecules, or even larger guest species not only at the external surface, but also through the whole internal pore system (Li *et al*. 2013)

Since the exciting discovery of this new material based on the supra molecular assembly chemistry in the early nineties, considerable work has been done to synthesize ordered mesoporous materials with diverse compositions, morphologies, and pore symmetries; meanwhile, tremendous effort has been devoted to elucidate the mechanism of mesostructure formation and explore their applications. In 1990, the first mesoporous material was reported by Yanagisawa *et al.* However, this type of materials did not attract much attention at that time. Until 1992, a group of Mobil Oil Company's scientists had investigated groundbreaking materials named M41S family of mesoporous silica, the world started to turn their attention to the mesoporous materials. Among the M41S family of nanostructured mesoporous materials, the hexagonal phase MCM-41 is the best known and most widely studied in this fields; MCM-41,-48, and -50 are all synthesized via a template mechanism using long chain surfactants under basic conditions. MCM-41 has a hexagonal structure with one-dimensional pore structure and MCM-48 displaying a cubic structure with a three-dimensional pore system (Fig. 1).

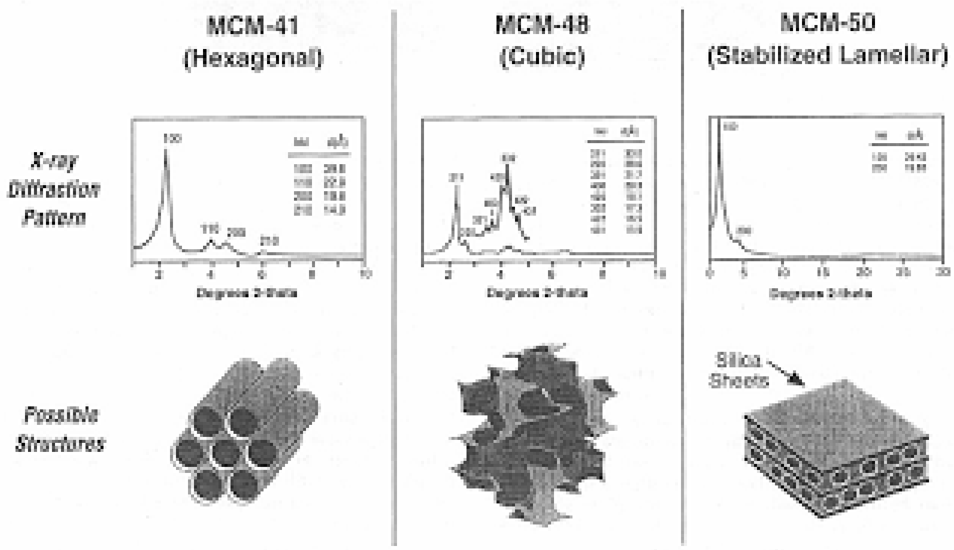


Fig. 1 The schematically structure of MCM-41, MCM-48 and MCM-50 (Sábado, 2010)

MCM-41 has attracted significant attention for its versatile industrial applicability. Scientific interest in the change of synthetic strategies, processing conditions and characterization methods has grown dramatically. In 1996, Inagaki and co-workers prepared a mesoporous silica designated as FSM-16 from a layered form of sodium silicate and cetyltrimethylammonium (CTA) surfactant cation. Ryoo *et al.* (1996) synthesized a stable mesoporous silica named KIT-1 using ethylenediaminetetraacetic acid with disordered interconnected pore channels. Several other researchers (Huo *et al*. 1995; Zhao *et al.* 1998; Lukens *et al.* 1999; Zhao *et al.* 1999; Feng *et al*. 2000) reported a series of acid-prepared meso-structured silica materials, named SBA-n (n = 1 - 3, 8, 11, 12, 14 - 16). Silica mesophases could also be used as templates for the synthesis of a variety of other materials such as ordered mesoporous carbons and polymers, as well as metallic and semiconductor nanowires.

It is interesting to notice that varied choices of precursor, template, reaction conditions, and synthetic pathway would result in novel meso-structured materials. All of these approaches are mainly based on intermolecular forces between the various silica sources and surfactant molecules via electrostatic, hydrogen-bonding, covalent, and van der Waals interactions.

2.2 Ordered mesoporous carbon materials

2.2.1 Synthesis of OMC

Ordered mesoporous carbon (OMC) materials, have attracted many interests because the potential industrial applications as catalyst supports, electrochemical materials, and gas separation media (Lee *et al.* 2006). This is mainly owing to their advantages of the large surface area, high stability, controllable pore texture, and tunable surface chemistry. Ryoo and coworkers (1999) first fabricated ordered mesoporous carbon material, CMK-1, by employing the ordered aluminosilicate MCM-48 as a template. In the same year, Hyeon *et al*. reported the synthesis of an OMC material, SNU-1. They used the same silica template MCM-48 but with phenolic resin as the carbon precursor. In the year of 2000, a highly ordered hexagonally structured mesoporous carbon, CMK-3, was produced by Ryoo's group by using SBA-15 as the silica template, which was also a hexagonally structured molecular sieve (Jun *et al.* 2000).

Based on all the reported synthesis of OMCs, the processes are similar. Carbon precursors are introduced into the channels of the mesoporous silicates through a solution-phase reaction. Then the in-situ polymerization is carried out under different conditions. The polymers are carbonized through carbonization. After the removal of the hard silica templates, mesoporous carbons replicate the ordered meso-structures of silicates (Fig. 2).

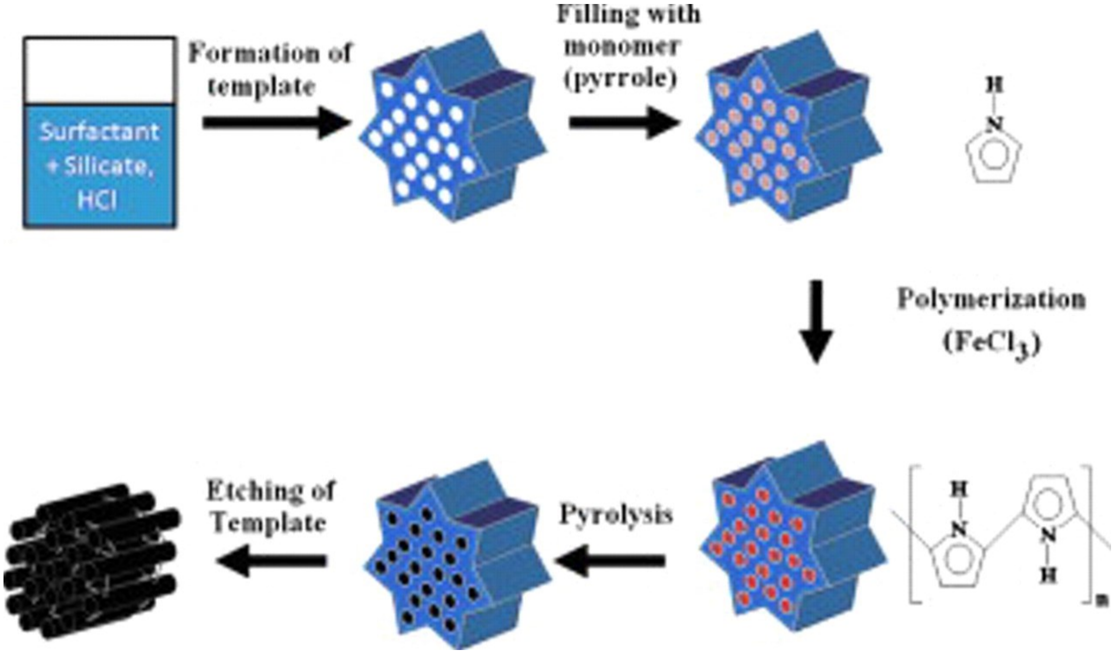


Fig. 2 Schematic illustration for the OMCs nano-casting strategy (Shrestha S. and Mustain W. E, 2010)

The pore size of an ordered carbon material is primarily determined by the pore wall thickness of the inorganic templates, which can be tailored by the synthetic conditions. Therefore, in order to vary the pore diameter of the carbon, one straightforward way is to synthesize the silica with different wall thickness. Of all the reported mesoporous carbons prepared by meso-structured silica materials, mesoporous carbons obtained from SBA-15 have attracted the most attention. Because of the well-ordered structure of SBA-15, the OMCs obtained as inverse replicas are highly ordered. The synthesis of ordered mesoporous carbons with large pores is a great challenge, although the availability of such materials would be very interesting both for fundamental research and practical applications.

2.3 Conventional activated carbon materials

The conventional carbon materials, such as activated carbon and carbon molecular sieves, are synthesized by pyrolysis and chemical activation of organic precursors, such as coal, wood, fruit shell, or polymers, at high temperatures (Bansal *et al.* 1988; Gaffney 1996). These carbon materials normally have large pore size distributions in both micropore and mesoporous ranges.

Activated carbon (AC) materials are outstanding adsorbents. They can absorb various kinds of organic and inorganic components. Typically, activated carbons have porous structures and large adsorption capacities. Those properties have played significant roles in their excellent adsorption behavior, which also lead to the comprehensive applications in chemical engineering and environmental engineering areas. Another advantage of the activated carbon is that it can be regenerated when it gets exhausted.

Even though these materials have been widely used in adsorption and separation, they have some limitations arising from the methods and materials used in their production. The key disadvantages associated with the conventional activated carbon materials are:

(1) Slow mass transfer of molecules because of space confinement imposed by small pore sizes,

(2) Low conductivity arising from the presence of enormous surface functional groups and defects.

(3) Collapse of porous structures during high-temperature treatments or carbonization.

In recent decades, a growing member of modifications is applied to the activated carbon materials to overcome these limitations. Generally, the superiorities of the activated carbons are mainly determined by their surface morphology and chemical properties. So the modification procedures usually change both the surface morphology and chemical properties. Meanwhile, electrochemical characters also affect the adsorption capacity significantly.

2.3.1 Modification of the physical structure

Structure properties are mainly determined the physical adsorption of the activated carbons. The properties included the pore volume, specific surface area and porous structurec. Granular activated carbons have high ash content, small porous size and surface area, those limit their adsorption capacities. So the modification of the physical structure is necessary. Typically, modification procedures are categorized as physical methods, chemical methods, and physical-chemistry methods.

2.3.1.1 Physical methods

Physical modifications are generally containing two steps: First, the raw materials are carbonized to remove the volatile component. Second, appropriate oxidative gases are introduced to activate the products. This step is concentrated on the structuring of micropores. The activation process flows with the two reactions (Han *et al.* 2003):

$$C + H_2O \rightarrow H_2 + CO$$

$$C + CO_2 \rightarrow 2CO$$

These two reactions can remove the carbon atoms inside the materials, so abundant micropore structures are created. Many factors can influence the physical activation processes, such as the properties of the raw materials, carbonization conditions and activation conditions (temperature, contacting time, active agents, etc.). Moreover, various catalysts are always introduced to the activation procedure to promote the efficiency of the reaction. For example, Japanese researchers use the Ⅷ metal elements as the catalysts for activation (Tsutsumi *et al.* 1993). Not only the reaction time is decreased significantly, but also the specific surface areas of the activated carbons reach to 2,000 – 2500 m^2/g. Typically transition metal chemicals include $Fe(NO)_3$, $Fe(OH)_3$, $FePO_4$, $FeBr_3$,$Fe_2(SO_4)_3$, and Fe_2O_3.

2.3.1.2 Chemical methods

Chemical modifications are primarily using chemicals to carbonize and activate the activated carbons. The purpose is to create more effective micro-porous structures. Widely used active agents include alkali metals, alkaline-earth metals, mineral salts, and acids. Currently, mostly mature chemical activators are KOH, NaOH, $ZnCl_2$, $CaCl_2$ and H_3PO_4. Among all of them, the super-activated carbon activated by KOH has the best characters (Teng H. *et al.* 1998).

When using the KOH as the activator, carbon and KOH react to form K_2CO_3, which will extend the pore size. Meanwhile, K_2CO_3 will decompose to K_2O and CO_2; those will also help to develop the pore size. On the other hand, K_2CO_3, K_2O and carbon will react to produce potassium. When the temperature reaches to the boiling point of potassium (762°C), potassium will spread in the carbon layer to affect the pore structures. The main reactions in this procedure are as follows (Han *et al.* 2003):

$$4KOH + C \rightarrow K_2CO_3 + K_2O + 3H_2$$

$$K_2O + C \rightarrow 2K + CO$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO$$

Plenty of studies were conducted using the chemical modifications. Zhang, *et al.* (2002) used the acid-alkali alternate modification to treat the granular activated carbon. The modified AC had a larger specific surface area, and the adsorption capacity to benzene was increased. This is mainly because that in this modification, the solutions removed the soluble substance in the AC without destroying the frame construction. In 2001, Zhan, *et al.* treated the AC made from coal tar with KOH. The resulting modified AC had a specific surface area of 3,886 m^2/g. The adsorption capacity was significantly increased.

2.3.1.3 Physical chemistry methods

Physical chemistry modification is the way to combine both the physical methods and the chemical methods together. Generally, the chemical modification is employed to the activated carbon first, and then follows with the physical modification. The combinations always succeed to get the substantial micro-porous structures.

In 1991, Caturla *et al.* used $ZnCl_2$ to activate the AC first, and then they further expanded the pore size of the materials by physical modification using CO_2.The product had a larger specific surface area up to 3000 m^2/g. Molina *et al.* (1996) introduced H_3PO_4 and CO_2 to treat the lignocellulose AC. The lignocellulose AC was first immersed by H_3PO_4 (68% - 85%) at 85°C for 2 h. The resulting product was calcined under N_2 flow at 450°C for 4 h. After washed with distilled water, the AC was partially gasified under CO_2 at 825°C. The producing AC had a specific surface area of 3,700 m^2/g.

2.3.2 Surface chemistry modifications

The surface chemical properties determine the chemical adsorption of the activated carbon. The main purpose is focused on the surface function group modification. Surface function groups can be categorized to oxygen function groups and nitrogen function groups. Also, oxygen function groups can be further divided to acid oxygen function groups and alkali oxygen groups. Acid function groups contain carboxyl, phenolic hydroxyl, ester, quinonyl and ring peroxide, and the first three groups are referred as the main acid oxygen groups. The acid oxide will motivate the AC with chemical polarity. Therefore, the resulting modified AC is limited by adsorbing the adsorbates with strong polarity. On the other hand, the alkali modified AC can easily adsorb the low polar substances or nonpolar substances. As a result, the change of the surface groups leads to the selectivity of adsorption behavior (Tamon *et al.* 1996).

In recent decades, more and more researchers pay attention to the surface chemical modifications. Introduction of oxygen function groups is one important area. Activated carbons can adsorb different nonpolar organics from the water effectively due to the hydrophobicity. But the removal of the polar organic from the water is limited by this property. Surface modifications can improve the surface polarity of the AC.

The surface chemical modification of activated carbon can be categorized to oxidative modification, reductive modification and loading-metal modification.

2.3.2.1 Oxidative modification

Oxidative modifications are mainly used strong oxidants to oxidize the activated carbons at a specific temperature. Currently, oxidative modifications are primarily concentrated on improvement of acid oxygen function groups. With the increase of the surface oxygen function groups, the surface polarity increases. Generally nitric acids are used as the strong oxidants. However, the nitric acids enhance the hydrophilia of the AC; this will decline the adsorption of organic contaminants due to their hydrophobic properties (Tamon *et al.* 1996).

Morwski *et al*. (1997) used the nitric acid to treat the AC with phenolic groups. Results showed the modified AC had a tremendous improvement on the removal of Trihalomethane spillout (THMs). In 1994, Vinke *et al*. applied both HNO_3 and HClO to modify the activated carbon. HNO_3 was a strong oxidant and produced lots of acid groups. At the same time, HClO was effective to adjust the surface acidity to the appropriate value. Activated carbon materials had much more homogeneous morphology with the oxidative modification (Tsutsumi *et al*. 1993).

Gao *et al.* (2000) investigated the modification of activated carbon fibers using HNO_3, H_2SO_4 and Cl_2. The results showed the adsorption of SO_2 was improved significantly. Aqueous and gaseous oxidation methods were used in this study. Both the two methods had increased the surface acid function groups and the ability of adsorbing SO_2 raised 65% and 32%. The Cl_2 treated AC increased SO_2 adsorption capacity up to 45%. It is obvious that the surface modification can enhance the adsorption potential of the activated carbon materials.

Fan *et al.* (1995) used the HNO_3, H_2O_2, and $(NH_4)_2S_2O_8$ to modify the activated carbon. The research studied the influence on the adsorption capacity from the surface properties and structures. It was found that the structure changed with different chemicals. HNO_3 modification had decreased the surface area, while the other two chemicals had increased the surface area.

2.3.2.2 Reductive modification

Strong reductive modifications are mainly used the deoxidizer to modify the surface function groups of the activated carbon. The oxygen alkali function groups will increase. This modification will cause the higher adsorption capacity for the nonpolar substances. Some scientists believe the alkalinity of the activated carbon is due to its Lewis alkali surface. The AC can be modified to get more alkali function groups under the N_2 or H_2 gas at high temperature (Menendez *et al.* 1996).

In 1994, Gao *et al.* used the hydrogen gas to modify the activated carbon. The modified AC had a decreased surface oxygen function groups, especially the acid function groups. This was primarily caused by the acid function group's pyrolysis under H_2 at high temperature.

Wan *et al.* (1999) employed the NH_3H_2O and aniline to modify the AC. The products had a higher adsorption capacity for Au(Ⅲ). When the AC was immersed in strong aqua ammonia and aniline solution, the surface acid function groups reacted with NH_3H_2O. With the removal of NH_3H_2O by heating, the pore size extended. The $AuCl^{4-}$ could go inside the apertures and decreased the electrostatic interactions. This may be the main reason for the improvement of the adsorption capacity.

2.3.2.3 Loading-metal modification

The principles of the loading-metal modification are mostly related to the reproducibility of the activated carbons. The metal ions are firstly adsorbed to AC, and then AC reduces the ions to low valence ions or simple substance. Due to the strong binding force between the metal ions and the adsorbates, the adsorption capacity is improved.

In 2001, Li *et al.* used three different metal aqueous solutions to immerse the AC for modification: $Cu(NO_3)_2$, $CuCl_2$ + HCl and $La(NO_3)_2$. The $Cu(NO_3)_2$ modified AC showed higher adsorption capacity for ethene. And with the increased of metal content, the adsorption capacity increased. When the metal content reached 2%, the adsorption capacity had a highest value. And then, the adsorption capacity decreased with the metal content increased. During the calcination procedure, Cu(Ⅱ) was reduced to Cu(Ⅰ), Cu(Ⅰ) could react with the ethene, so the adsorption capacity increased. However, when the metal content reached too high, the metal ions could block the pore structures, and then, the adsorption capacity decreased.

Fu *et al*. (2000) applied the immersing modification to activated carbon fiber with metal palladium and copper. Results showed that the modified AC with Pd(Ⅱ) had outstanding adsorption capacity for CO. With the increasing ratio of Pd(Ⅱ), the adsorption capacity increased.

Liu *et al.* (1996) used the H_2S to modify the activated carbon. The modification introduced C-S function groups to the surface of AC, which increased the adsorption capacity for Pb^{2+}. This was mainly due to the larger binding power between sulfur element and Pb^{2+} compared with that between oxygen element and Pb^{2+}.

2.4 Modification of the mesoporous carbon

As discussed in the previous sections, the conventional activated carbon materials have three prime limitations due to their producing technologies and the materials used. Ordered mesoporous carbons, on the contrary, have overcome such limitations by the innovation of the synthetic processes. Typically, OMCs are produced by the replication synthesis with pre-synthesized hard templates. The templates mainly serve as molds for replication of mesoporous carbon materials, and there is no significant chemical interaction taking place between templates and carbon precursors. The corresponding porous structures are predetermined by the templates. Owing to the intensive research on mesoporous inorganic materials conducted over the past decades (Ciesla and Schuth, 1999), the synthetic methods replicating templates have been proven to be the most successful methods for the preparation of mesoporous carbon with well-defined pore structure and narrow pore size distributions.

Both activated carbon and ordered mesoporous carbon materials have high surface area and could be used as adsorbents. The similar properties determine that their modification technologies can be adopted by each other. Since the modification of the activated carbon had already developed for years and the modified technology trends to be mature, it is possible to apply the surface modifications to the ordered mesoporous carbon for the adsorption capacity improvements.

The chemical modification of carbon surface is not difficult due to the high reactivity of carbon, but OMC materials have well-ordered structures, which can be damaged by the modifying methods. The adsorption capacity of OMCs can be varied from the reference of the activated carbon.

In 2011, Guo, *et al.* used nitrogen gas to modify the ordered mesoporous carbon to enhance the electrocatalytic activity of platinum. The materials were synthesized via the 900°C carbonization of polyaniline-coated mesoporous carbon. Pyridinic nitrogen and quaternary nitrogen generated disorders and curvatures on the surface of graphitic carbon layers with nitrogen atoms replacing carbon atoms at the edges and the interior of carbon stacking, and thus offering beneficial anchoring sites for $PtCl_6^{2-}$ ions. Pyridinic nitrogen and pyrrolic nitrogen offered p electrons to the sp2 hybridized graphitic carbon layers, decreasing the inner electrical resistance of the catalytic carbon layer, enhancing the rate of proton diffusion, and transporting more free electrons to oxidative platinum. Due to the advantageous modification of the electronic structure of carbon atoms, platinum nanoparticles with a narrow size distribution were homogenously dispersed onto the surface of nitrogen-modified ordered mesoporous carbon, as evidenced by TEM images.

Sanchez *et al.* (2013) synthesized the ordered mesoporous carbon by chemical vapor deposition using SBA-15 silica as solid template and propylene as carbon precursor. The OMCs were modified by means of HNO_3 and H_2O_2 under different oxidation conditions. More oxygen functional groups were introduced into the surface by using HNO_3 than by means of H_2O_2, but the original surface texture and structural arrangement were kept unchanged in both cases.

Another OMC prepared through the pyrolysis of used cigarette filters was chemically modified with nitric acid to enhance its surface acidity (Soltani *et al.* 2014). The analysis of variance (ANOVA) showed that both acid concentration and contact time had significant effects on the BET surface area. The proximate analysis confirmed a considerable reduction in total ash content of the surface-modified char compared to the non-modified char. A 57.8% increase in the surface acidity compared to the non-modified char was further confirmed by Boehm titration.

CHAPTER 3: MATERIALS AND METHODS

3.1 Preparation of silica template

Silica templates (SBA-15) were synthesized under acid condition using oxide surfactant chemical: Pluronic P123 (BASF). The silica source was tetraethyl orthosilicate (TEOS, Aldrich). In a typical aqueous solution, 100 ml of concentrated hydrochloride acid (HCL, 37%) was added into 525 ml of distilled water. Then 20 grams of triblock copolymer Pluronic P123 (EO20PO70EO20, BASF) was added in the mixture. The mixture was magnetic stirred for 1 hr. After Pluronic P123 was completely dissolved, 46.5 ml of tetraethylorthosilicate (TEOS, 98%, Aldrich) was added to the homogenous solution with vigorous stirring for 10 mins. The resulting mixture was placed in a constant temperature water bath (Premiere Thermostatic water bath HH-4) for 4 hrs at 40°C, followed by aging for 24 hrs at 90°C. After the aging procedure, the solid product was washed with 80 ~ 90°C hot distilled water, and dried in an oven at 105°C overnight. After drying, the product was calcined in a muffle furnace at 550°C for 8 hrs. The white silica template SBA-15 was obtained and stored in the desiccator for the next preparation of OMC. Fig.3 shows the flow chart of the synthesis of silica template.

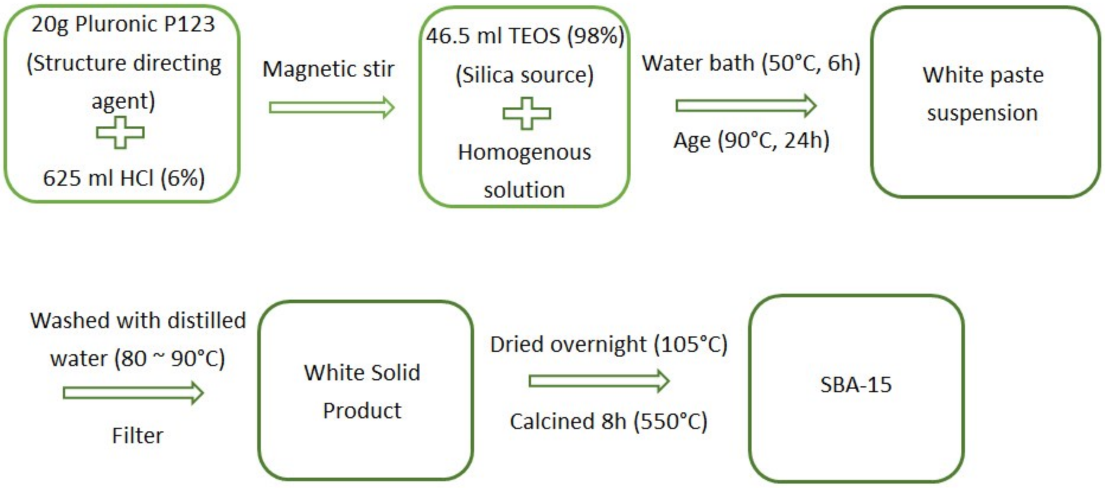


Fig. 3 Flow chart of the synthesis of silica template

3.2 Preparation of corresponding ordered mesoporous carbons (OMCs)

The synthesis of OMC was accomplished by in situ polymerization of acrylic acid in the mesoporous structure of the silica template SBA-15 (hexagonal structure) in an aqueous solution. Acrylic Acid was commonly selected as the carbon precursor due to its fast polymerization kinetics. 2.2-azobisisobutyronitrile (AIBN) was used as the free radical initiator. Free radical polymerization is a classic chain reaction, wherein initiator thermolysis introduces free radicals at a moderate rate. The closed propagation sequence involves repeated alkyl radical addition to monomer, thereby increasing macro-radical molecular weight. Radical-radical combination and/or disproportionation terminate the propagation sequence to give non-radical products (Chern, 2006). The reactions are listed below:

Intiation:

$$In_2 \xrightarrow{k_d} In\cdot + In\cdot$$

Proipagation:

$$In\cdot + M \xrightarrow{k_{p,1}} M_1\cdot$$

$$M_1\cdot + M \xrightarrow{k_{p,2}} M_2\cdot$$

$$M_2\cdot + M \xrightarrow{k_{p,3}} M_3\cdot$$

$$M_i\cdot + M \xrightarrow{k_{p,i+1}} M_{i+1}\cdot$$

Termination:

$$M_m\cdot + M_n\cdot \xrightarrow{k_{t,d:m,n}} P_m + P_n$$

Where, *In* is the initiator; *M* is the monomer; *k* is the rate constant; *P* is the Polymer;

During the initiation reaction, AIBN decomposed, eliminating a molecule of nitrogen gas to form two 2-cyanoprop-2-yl radicals, these radicals could initiate the polymerization for acrylic acid. Fig.4 illustrates the reaction of acrylic acid polymerization.

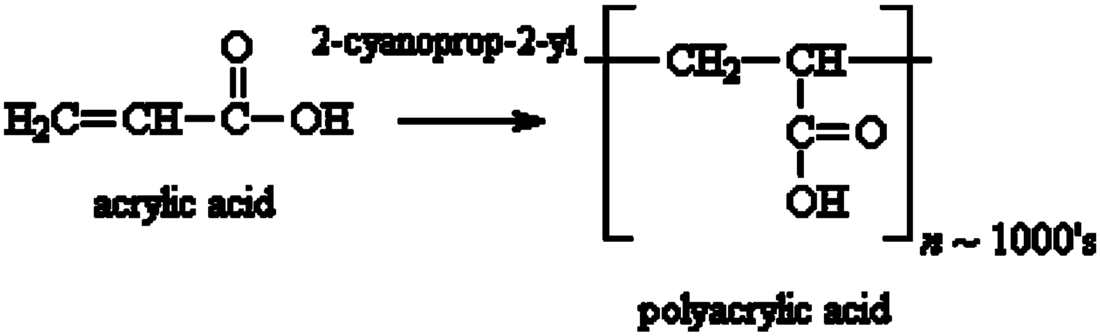


Fig. 4 Acrylic acid polymerization reaction

Different ratios of SBA-15 to acrylic acid were mixed to test the impact of the silica template on the structure of the synthesized OMCs. Ninety (90) ml of acrylic acid (>99%, Aldrich) was added into 180 ml of distilled water to form the acrylic acid aqueous solution. Then different weight of SBA-15 (3g [OMC1], 6g [OMC2], 9g [OMC3] and 12g [OMC4]) were added into the acrylic acid aqueous solution with magnetic stirring. After 30 minutes, 0.06 g of 2.2-azobisisobutyronitrile (AIBN) were added and stirred for 15 mins. Then the mixture was heated in the water bath (70°C) for in situ polymerization with continuously stirring from beginning to end. The mixture of the polyacrylic acid (PAA) and the silica template was dried by oven at 200°C overnight. Afterwards, the composite was heated under N_2 flow at a temperature ramp rate of 5°C min^{-1} to 700°C and held for 8 hrs for carbonization. The resulting carbon–silica composite was immersed in 50 ml 48% HF (Aldrich) at room temperature with magnetic stirring for 24 hrs to remove the silica template. The OMC was then washed with distilled water (1500 ml) to remove the residual HF and dried in the oven at 90 ~100°C overnight. Fig. 5 shows the strategy of synthesis of silica templates and ordered mesoporous carbons (OMCs)

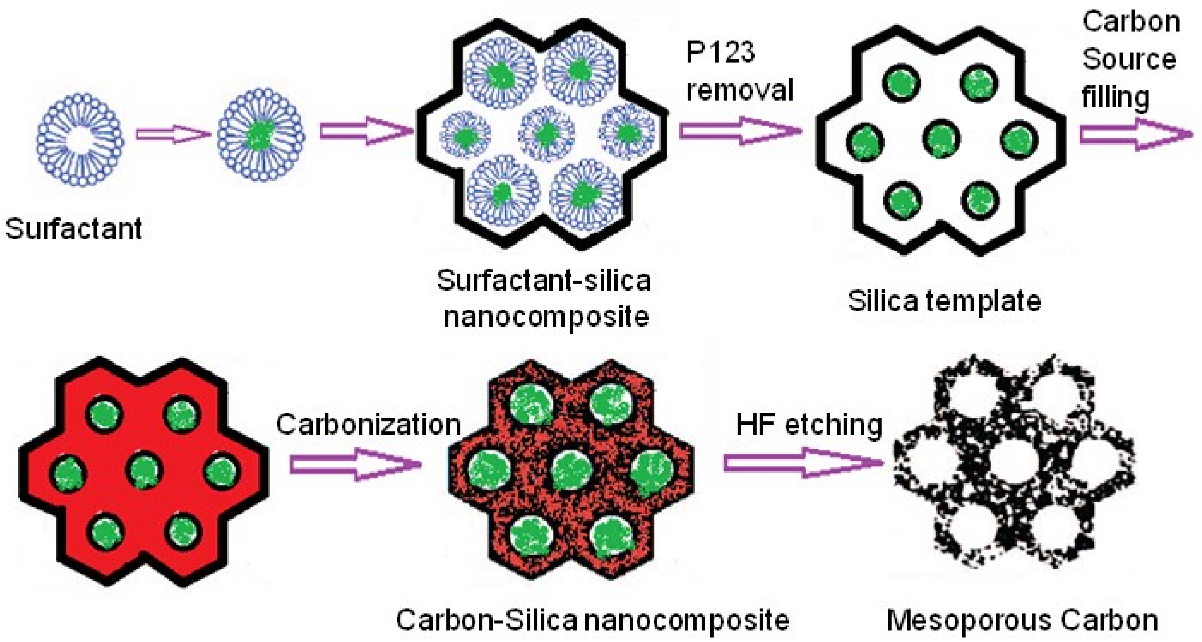


Fig. 5 Schematic illustration for the OMCs nano-casting strategy, viewing from perpendicular direction (100) (Lu Lin, 2011)

3.3 Modification of the ordered mesoporous carbons (OMCs)

The modification of the ordered mesoporous carbons (OMCs) is adopted from the modification of activated carbon materials. Based on the previous study, surface reduction procedure could improve the hydrophobic of the carbon, which will lead the enhancement of the adsorption capacity of the organic component in the aqueous solution (Han *et al.* 2003). In this study, four different aqueous solutions were used to modify the OMCs.

NaOH solution: The OMCs (0.10 g) were mixed with 10 ml of NaOH solution (0.1%) for 3 hrs at 90°C. After that, the mixture was filtered and washed until the water attained the same pH value as the distilled water employed. After that, the solid product was dried in the oven at 105°C overnight.

Urea solution: The OMCs (0.10 g) were mixed with 10 ml of aqueous solution containing 2.0 g of urea ($(NH_2)_2CO$>99.5%, Riedel) for 5 hrs at 90 °C. After that, the sample was dried and pyrolysed in a horizontal tubular furnace in a flow of dry nitrogen with a flow rate of 85 mL/min until a final temperature of 500°C for 2 hrs. The sample was cooled below 50°C before removing from the furnace. The carbonized sample was washed, with 1 L of distilled water and stirred at 80 °C for 1 hr. The sample was filtered and oven dried at 100°C overnight.

Aluminum chloride solution: The OMCs (0.10 g) were mixed with 10 ml aluminum chloride (1 mol/L) solution for 6 hrs at room temperature. After stirring, the solid product was filtered and put it in the oven (120°C) over night.

Ammonium hydroxide solution: OMCs (0.10g) were immersed with 10 ml ammonium hydroxide (30%) and placed in the incubator shaker (New Brunswick Scientific). The shaker was set at 60°C with 110r/min and allowed to shake for 3 hrs. The mixture was filtered and the solid product was then calcined in the protection of N_2 at 500°C for 2.5 hrs.

3.4 Structure characterization

3.4.1 X-ray diffraction (XRD) analysis

Small angle X-ray diffraction patterns were obtained on a Diano 2100E instrument operated at 45 Kv and 30 mA and using Cu Ka12 radiation (k=1.5418). Measurements were carried out to obtain resolved XRD patterns at 2θ angles from 0.5° to 3.5°. The scanning rate was 0.03°/step, and 15 second/step. The aperture slit (solar slit) was 0.4°.

3.4.2 Transmission electron microscopy (TEM)

TEM images were obtained using a Hitachi 7600 Transmission Electron Microscopy (Hitachi America Ltd., Tarrytown, New York). The acceleration voltage was 100 Kv. The samples were prepared by dispersing a large number of particles in ethanol with an ultrasonic bath for 15 min and then a few drops of the resulting suspension were placed on a holey carbon film supported on a Cu grid.

3.4.3 BET surface area measurements

The specific surface area (SSA) was carried out with the nitrogen adsorption and desorption processes by Micormeritics system. The measurement was taken at -196 °C using Flowsorb Ⅲ surface area analyzer (Micormeritics).

3.4.4 Fourier transform infrared spectroscopy (FT-IR)

The surface functional groups were qualitatively measured with Fourier transform infrared spectroscopy (FT-IR). Ordered mesoporous carbon materials (0.01 g) were scanned in a range from 4000 to 600 cm^{-1} using a Perkin Elmer Spectrum 100 series spectrometer.

3.4.5 Thermogravimetric analysis (TGA)

Thermogravimetric Analysis (TGA) was conducted for all the OMCs to find their thermal stability. The experiments were conducted under an air flow with the rate of 100ml/min. All the samples were heated from room temperature to 800°C with rate of 20°C/min. The analysis was using the SDT 2960 DSC-TGA analyzer (TA Instruments, Inc.).

3.4.6 Energy-dispersive X-ray spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS) was used primarily to determine the element composition of the carbon materials. EDS measurements were conducted on a JEOL 6300 Scanning Electronic Microscopy (JEOL Ltd., Tokyo, Japan) using conventional sample preparation and imaging techniques with an acceleration voltage of 25 Kv.

3.5 Batch adsorption study

Batch adsorption experiments were carried out in 250 mL conical flasks placed in an E24 Incubator Shaker (New Brunswick Scientific). Resorcinol, a typical TOC model compound, was selected to evaluate the adsorption behavior of the OMCs. The adsorption capacities of the OMCs were measured by the adsorption of resorcinol. The adsorption studies were conducted at

25°C with the pH range of 5-8. UV-Vis Absorption Spectrophotometer (Varian) was used to measure the resorcinol concentrations.

One sample of the same concentration solution (blank) without OMC was prepared and treated under the same conditions as the solutions containing adsorbent. This blank was used as a reference to establish the initial concentration for the solutions containing OMCs. The mixture of OMCs and resorcinol solutions was placed in a shaker (200 rpm, room temperature) for 24 hrs. After the adsorption was completed, the conical flasks were removed and solution filtered using a 0.45 μm glass filter paper. The filtered solution was analyzed for the final concentration of resorcinol. The amount of resorcinol adsorbed by OMCs can be determined by subtracting the final concentration from the initial concentration using the following formula:

$$q = \frac{(C_i - C_f)\, V}{M}$$

Where, q is the adsorption capacity (mg/g);

Ci is the initial concentration of resorcinol in solution (mg/L);

Cf is the final concentration of resorcinol in treated solution (mg/L);

V is the volume of the solution taken (L);

M is the weight of the adsorbent OMCs (g).

CHAPTER 4: RESULTS AND DISSCUSIONS

4.1 Effect of the amount of SBA-15 on OMC synthesis

Ordered mesoporous carbon was fabricated using the silica template SBA-15. The amount of the silica template may have a significant effect to the adsorption capacity of OMC. In this investigation, different amount of SBA-15 was used for the OMC's preparation.

XRD Analysis:

The XRD patterns of silica templates and ordered mesoporous carbons are presented in Fig. 6.

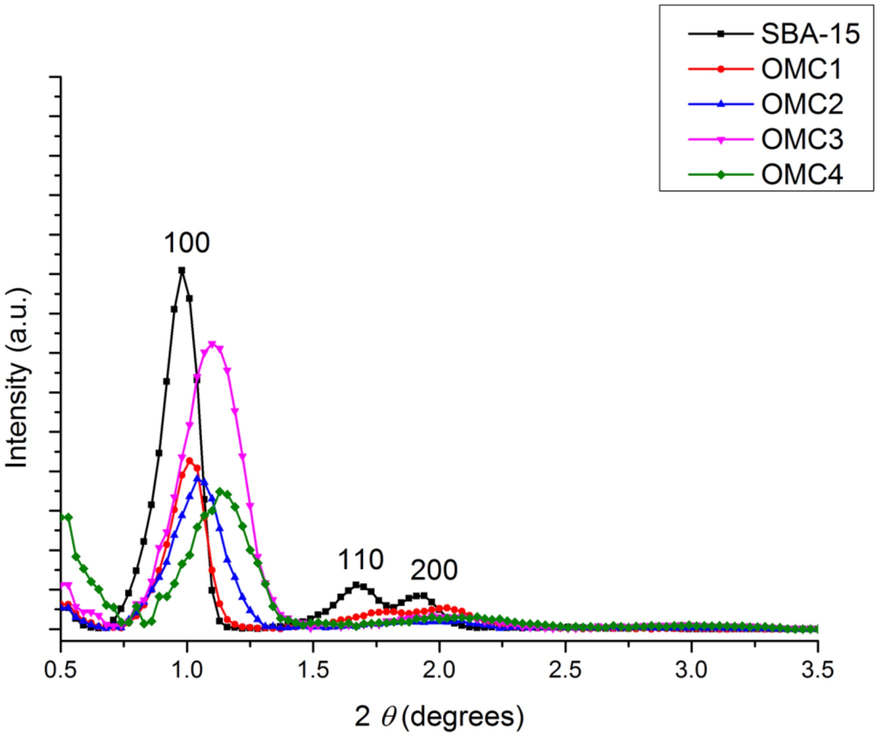


Fig. 6 XRD patterns of SBA-15 and ordered mesoporous carbon

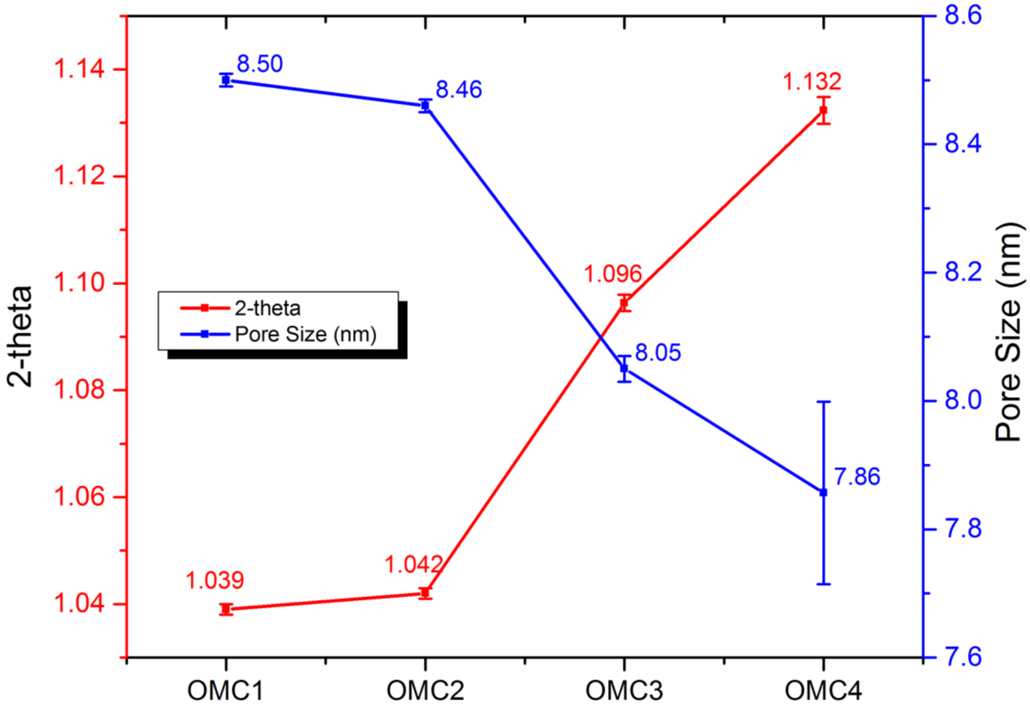


Fig. 7 Two-theta degrees of ordered mesoporous carbons

It can be seen that the SBA-15 has three clear diffraction peaks indexed as (100), (110), and (200), which indicates a well-ordered two-dimensional (2D) hexagonal structure. Similar results were reported by Bazula *et al* (2008). The OMCs have the similar structure replicating from the silica templates. But due to the defect of the polymerization and high temperature damage from carbonization procedure, the intensity of the carbon materials are gradually reduced at the peak of (100) diffraction. It is clear that the OMC3 has the highest intensity. This indicated that it has the best ordered structure. Fig. 7 illustrates the $2\boldsymbol{\theta}$ degrees of the mesoporous carbons change with the increasing amount of silica template. From the graph, it is obvious that with the increasing ratio of the silica template, the peak of (100) diffraction has shifted to a larger degree. That means OMC4 > OMC3 > OMC2 > OMC1. Based on Bragg's law (Kacher *et al.* 2009), this means the decrease of the pore size. This may result from the inhomogeneous distribution caused by increase of silica template. Table 1 confirms the pore size results from the Jade 6 Analysis.

Table 1 Pore size of SBA-15 and OMCs

Sample	SBA-15	OMC 1	OMC 2	OMC 3	OMC 4
nm	9.01	8.49	8.46	8.05	7.79

Transmission Electron Microscopy

Transmission electron microscopy (TEM) analysis illustrates the well-ordered hexagonal arrays channels of the SBA-15 and OMCs. Fig. 8 shows the TEM image of the silica template. Fig. 8 (a) confirmed the parallel array of SBA-15 template and Fig. 8 (b) shows the picture from the perpendicular direction. The diameter of silica rods was about 9.01 nm. The hexagonal-ordered structures of SBA-15 were similar to those described in Skar's (2013) results. Fig. 9 shows the TEM images of ordered mesoporous carbons. Even though the OMCs were made from different ratios of templates to carbon precursor, the TEM results showed that all of the carbon materials have the highly ordered structure. Compared with the OMCs from other literature (Guo *et al.* 2013), it was clear that the structure of ordered mesoporous carbon was faithfully duplicated from the structure of the silica template. The XRD and TEM images showed all the silica template and OMCs had similar ordered mesopore structures.

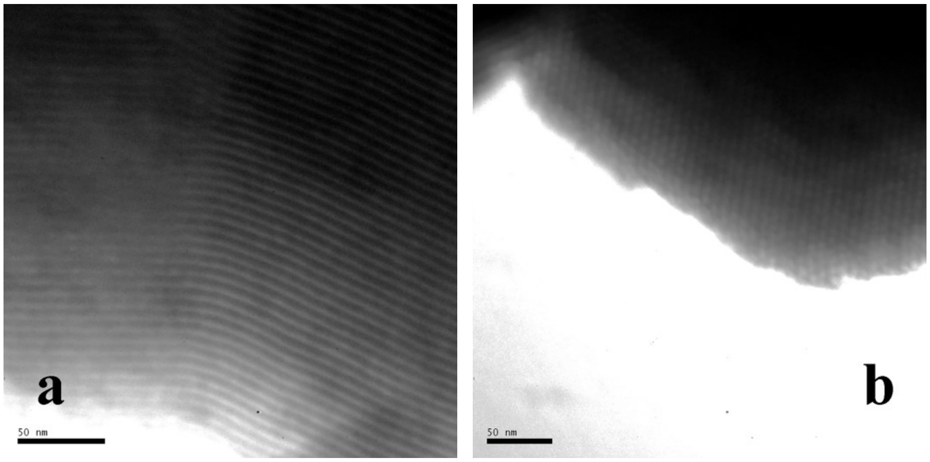


Fig. 8 TEM images of SBA-15: (a) channel direction (b) perpendicular direction

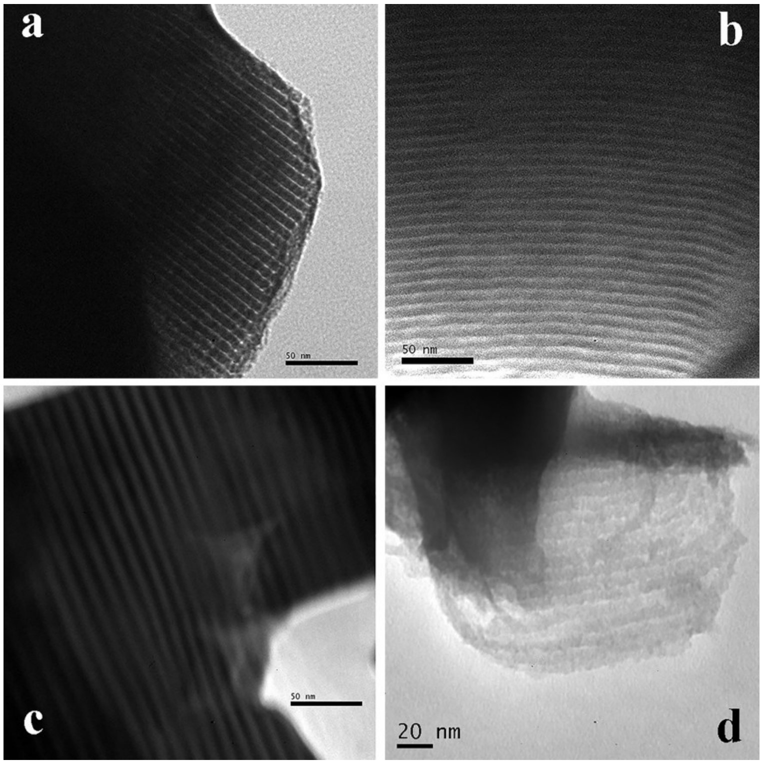


Fig. 9 TEM image of ordered mesoporous carbons: (a) OMC1 (b) OMC2 (c) OMC3 (d) OMC4

BET Surface Area Measurements.

The specific surface areas (SSA) of SBA-15 templates and OMCs are listed in Table 2.

Table 2 Specific surface areas of the OMCs and SBA-15

Sample	SBA-15	OMC 1	OMC 2	OMC 3	OMC 4
m^2/g	524.81	467.02	705.53	854.08	849.62

From Table 2, it can be seen that the OMC3 has the largest surface area. The general trend is OMC3 > OMC4 > OMC2 > OMC1. It is apparently that the increase of silica template to carbon precursor ratio can result in a larger surface area. This may indicate that effective structure of the OMC is closely related to the quantity of silica template. Besides, the table shows the SBA-15's surface area fell between the OMC2 and OMC1, this probably indicates the hexagonal structures in OMC1 are less than that in SBA-15. Similar phenomenon was reported by Ramanathan *et al.* (2013). Ramanathan used different method to change the ratios of silica to the carbon precursor, and the morphology analysis indicated that the reduction of silica templates would cause the decrease of the SSA. Conversely, the increasing ratio of silica templates to carbon precursor could increase the carbon material's specific surface area.

FT-IR Analysis

FT-IR spectral analysis allows the identification of different functional groups and chemical bonds on the surface of OMC. Fig. 10 shows the FTIR spectra of the OMCs. A set of peaks emerging in the region between 3600 and 3900 cm^{-1} can be attributed to the O–H and C–H stretching vibrations. This could be due to surface hydroxylic groups and chemisorbed water (Swiatkowski *et al.*2004). The strong peaks showed in 2000 ~ 2400 cm^{-1} could be related to C–O group (Cansado *et al.*2012). This probably associated with the polymerization of the acrylic acid. The C=O bond related to COOH group can be found around 1700 cm^{-1}. The band located at 1570 cm^{-1} is assigned to stretching vibration of the C=C bond due to the incomplete polymerization, Fujimori *et al* (2014) reported the same conclusion in their study. In the lower region of the spectra, the clear band around 1050 cm^{-1} could be due to antisymmetric stretching vibrations of C–O–C group or also to the out-of-plane C–H bending. From the figure, it can be seen that all OMCs have the similar chemical bonds. The function groups are similar for OMCs made from different SBA-15 to acrylic acid ratios.

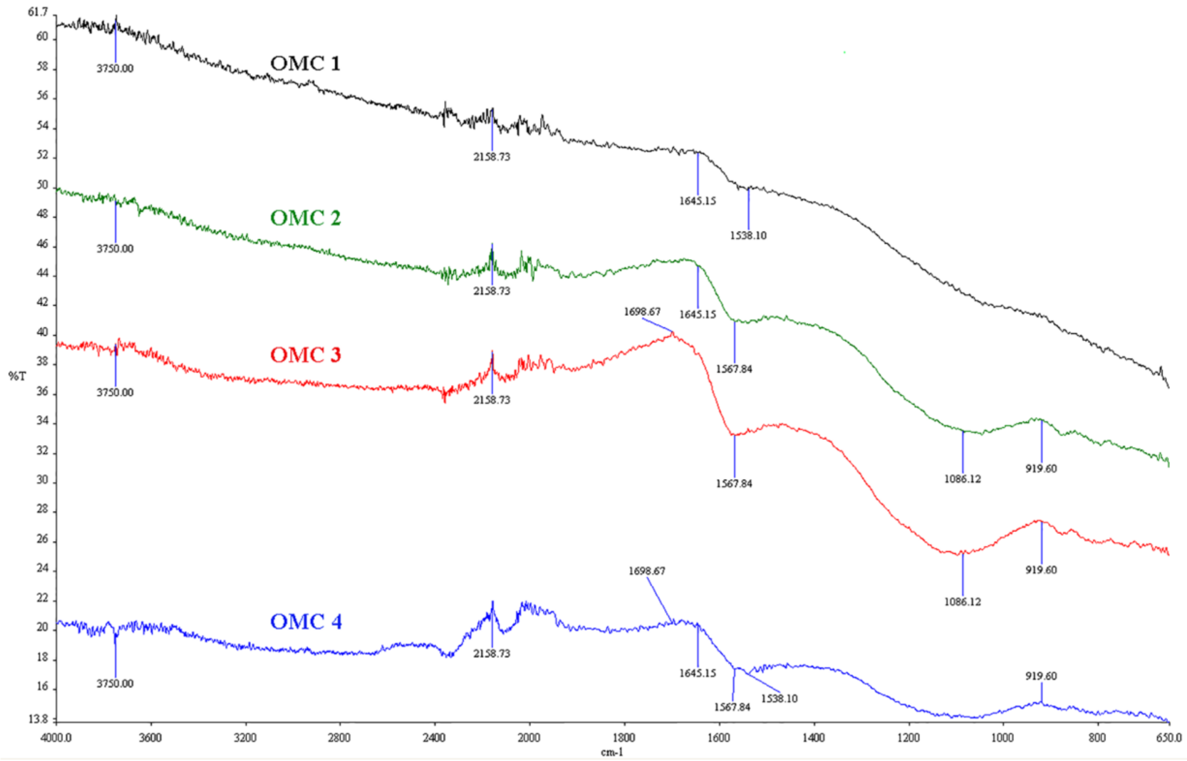


Fig. 10 FT-IR spectra of different OMCs

Batch Adsorption Study

The adsorption capacities of four different OMCs for resorcinol removal are shown in Fig. 11.

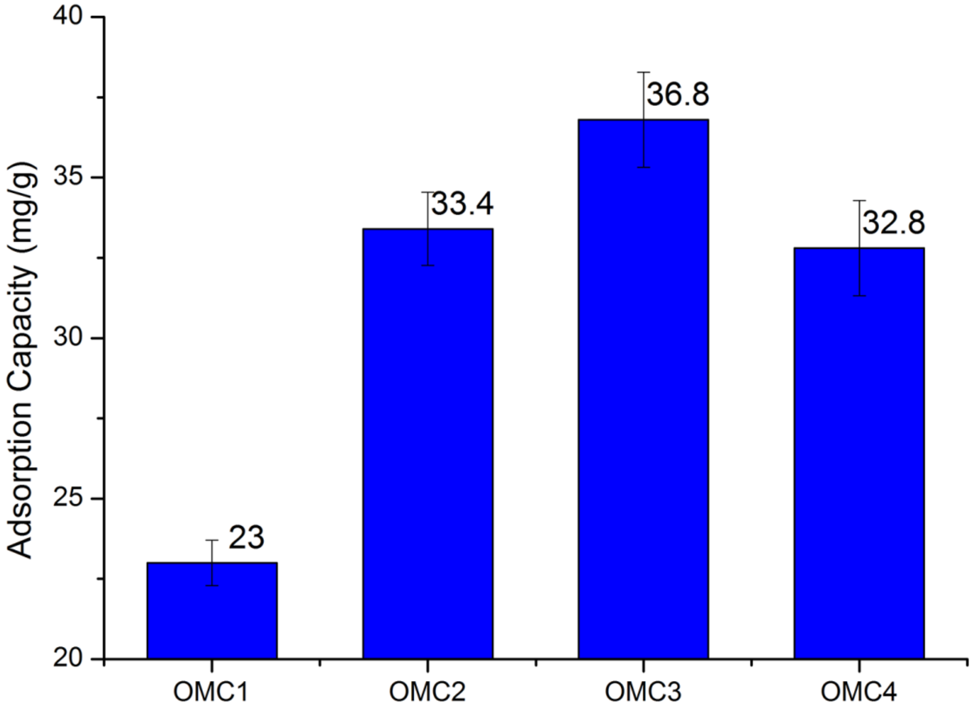


Fig. 11 Adsorption capacity of different OMCs

The adsorption capacity of OMC3 made with SBA-15 to carbon precursor ratio of 3:1 is 36.8 mg/g. That is 10% more than that of OMC2, 12% more than that of OMC4 and 60% more than that of the OMC1. It is noticed that the adsorption capacity increased by increasing the amount of silica template, and it reached the highest point when the ratio of silica template to carbon precursor reaches 3:1. After that, the adsorption capacity dropped with the increase of the silica template. Based on the FTIR analysis, all four ordered mesoporous carbons have similar surface function groups; besides, the morphologic structures are almost the same from the TEM images. So the increase of the adsorption capacity could be mainly due to the increase of the specific surface area. It probably indicates that more templates can produce more effective and highly ordered structure, leading to the increase of the surface area of OMC.

4.2 Effect of surface modification

It is clear that both the surface chemistry and the pore structure of the mesoporous material play a cooperative role in adsorption. To improve the adsorption capacity of OMC, modifications of both surface chemistry and pore structure may be necessary. OMC3 with the higher adsorption capacity was used as the original OMC for the surface modifications.

XRD Analysis

The SAXRD patterns of all the modified OMCs can be found in Fig. 12. It can be seen that the modifications have reduced the intensity of peak at (100) diffraction. This could be due to the erosion effect from the modifying procedures. The peak of (100) diffraction had shift to left; this meant that the pore size of the two modified OMCs had increased. With regard to the $2\boldsymbol{\theta}$ in Fig. 13, the NaOH and urea modifications caused the decrease of the two theta angle. On the contrary, the $AlCl_3$ modified OMC's peak shifted to a larger degree, which meant the decrease of the pore size. The NH_3H_2O modified OMC had the similar pore size with the original carbon materials. Based on the analysis of Jade 6, the pore size distributions of all the modified OMCs are listed in Table 3. It has the same conclusions with the XRD results.

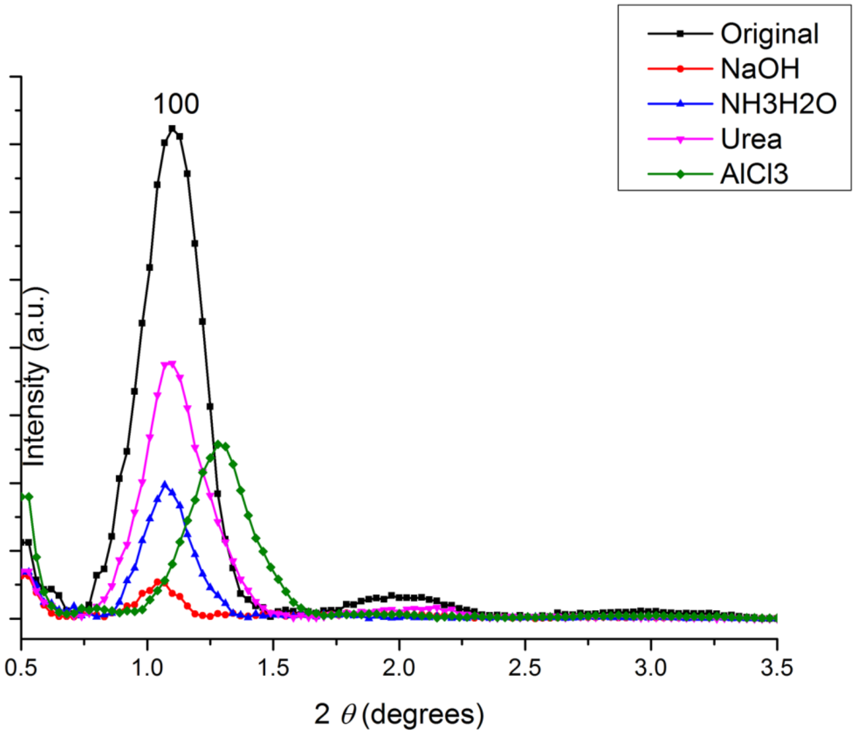


Fig. 12 XRD patterns of modified OMC

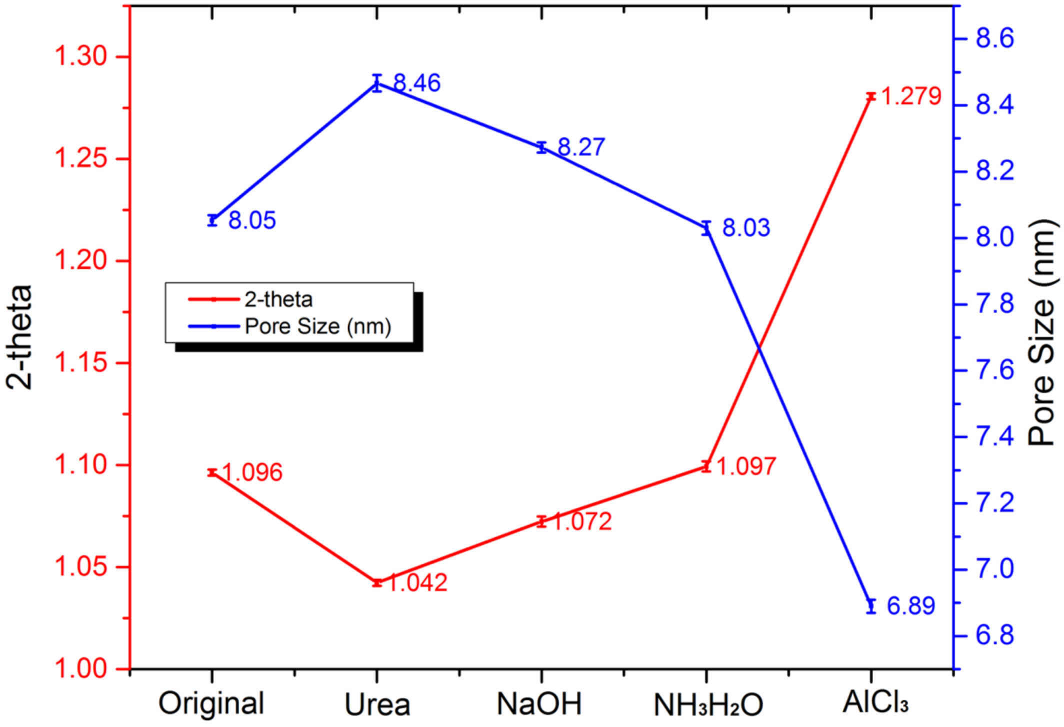


Fig. 13 Two-theta degrees and pore size of modified OMCs

Table 3 Pore size of original OMC and modified OMCs

Sample	Original	NaOH	Urea	NH_3H_2O	$AlCl_3$
nm	8.05	8.23	8.47	8.03	6.89

Transmission Electron Microscopy

The TEM images of the modified OMCs are showed in Fig. 14.

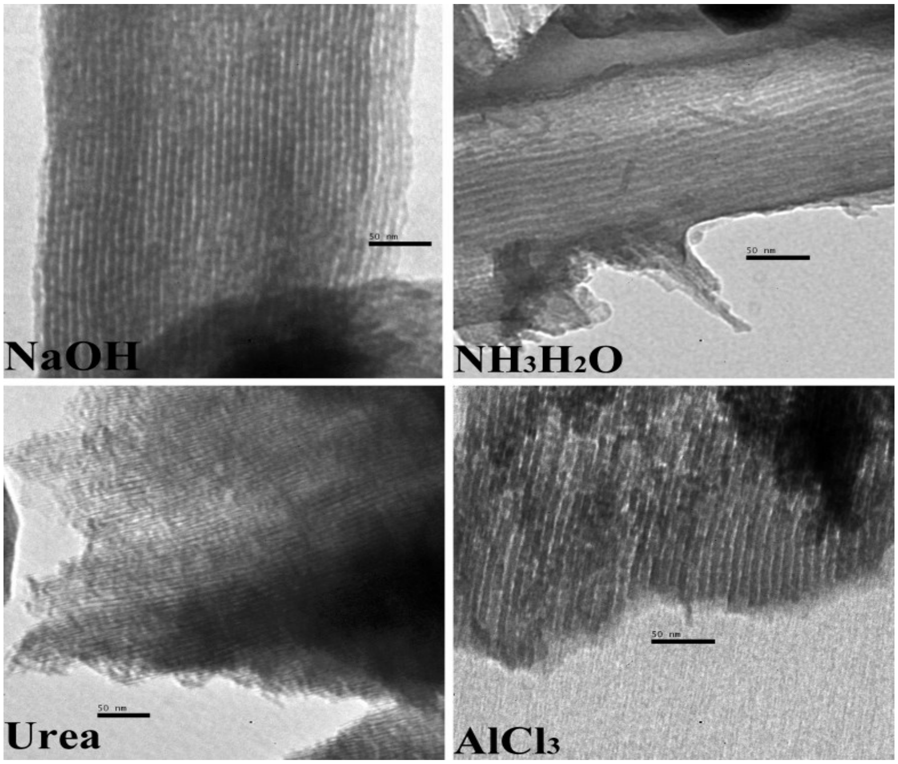


Fig. 14 TEM images of modified OMCs

After the treatments, the images of modified OMC show that the morphologies are essentially the same as that before modification, and the parallel channels are still preserved. The collapse of pore structure was observed, which is similar to the description reported by Bazula *et al.* (2008). The pore sizes of the modified OMCs did not change a lot except the $AlCl_3$

modification. This result was consistent with that reported by Guo *et al.* (2013). The reason of the phenomenon is probably because the $AlCl_3$ solution has a complex chemical property. Also, the concentration of the $AlCl_3$ is higher than the other three solutions used for the modification.

BET Surface Area Measurements

BET surface area analysis was carried out to all the modified OMCs. Table 4 shows the results.

Table 4 Specific surface areas of the modified OMCs

Sample	OMC 3	NaOH	Urea	NH_3H_2O	$AlCl_3$
m^2/g	854.08	745.56	723.38	767.10	511.19

Table 4 shows that all the modified OMC materials have smaller SSA than that of the original OMC. The immersing modification decreased the surface area. The decrease of the SSA should be mainly due to the damage of the pore structure from the modification. The different properties of the immersing solutions result in the different decreases in the surface area. This phenomenon is quite similar to that reported by Pevida *et al.* (2008). In their study, the ammonia treatment of activated carbon resulted in lower BET surface areas, comparing with the parent material. Also, Cansado *et al.* (2012) and Fujimori *et al.* (2014) found that the modifications usually decrease the surface area of activated carbon due to the shrinkage of the oxidation effect and the block of the micropores. The modification procedures could damage the highly ordered structures and cause the collapse of the ordered structures. As a result, all the modified OMCs had smaller specific surface areas.

FT-IR Analysis

The FT-IR spectra of original ordered mesoporous carbon and modified OMC are shown in Fig 15.

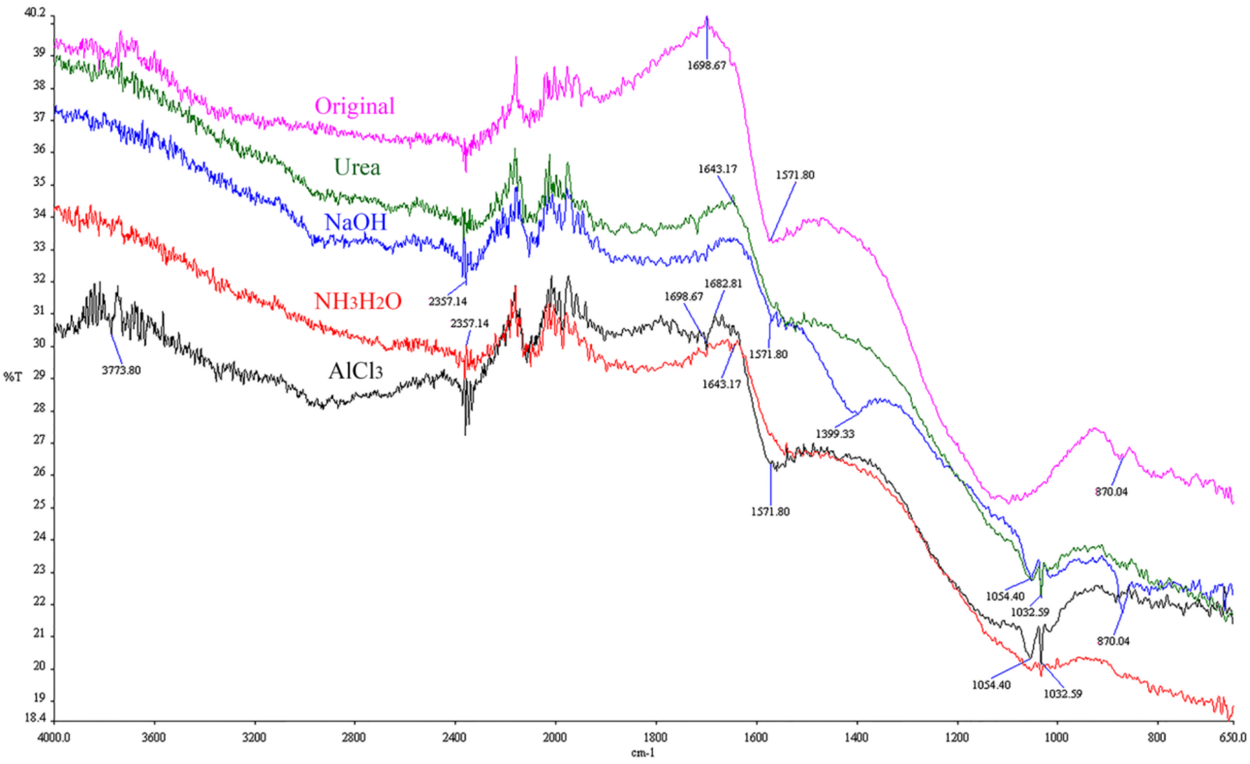


Fig. 15 The FT-IR spectra of OMC and modified OMCs

Compared with original OMC, the NaOH treated OMC presented strenuous vibration around 1400 cm^{-1} and 1050 cm^{-1}. The broad band in 1400 cm^{-1} consisted of a series of overlapping absorption bands ascribable to the deformation vibration of the surface hydroxyl groups. The new peak around 1030 cm^{-1} indicated the enhancement of the C–H stretching vibration from the C=C group. Dehydration may occurred due to the strong alkalinity of the sodium hydroxide solution.

In the FTIR spectra of the ammonia treated OMC, weak peaks around 2400 cm^{-1} could be assigned to the loss of C–O–C groups, which was mainly due to the alkalinity of the ammonium hydroxide. The similar reduction appeared around the 1700 cm^{-1} could be attributed to the stretching vibrations of C=O moieties in carboxylic, ester or lactonic groups. Swiatkowski *et al* (2004) reported the similar results in the modification of activated carbons with ammonium hydroxide.

OMC modified by urea presented almost the same peaks with the original samples. Despite the similarity of the FTIR spectra profiles, a deformation vibration of surface carboxylic groups appeared at 1640 cm^{-1}. However, Cansado *et al*. (2012) reported a band at 1270 cm^{-1} was displayed in urea modified AC. The difference of the carbon precursor and structures might lead to these differences.

The black line shows the 2R spectrum of OMC modified by $AlCl_3$. The intense vibrations at 3600~4000 cm^{-1} could be associated with the introduction of O–H group. Meanwhile, the aluminum chloride strengthened the C–O–C group at 1050 cm^{-1}. It agrees with the conclusion reported by Bazula *et al*. (2008).

Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was carried out to estimate the stability of OMC and modified OMCs. The weight loss of all the OMCs and modified OMCs are showed in Fig. 16. The results of TGA curve showed that the original carbons decomposed at temperature range of 510°C – 650°C with total weight loss of 98%. Gao *et al.* (2008) reported the similar results when they investigated the photo-electro-catalysis enhancement on carbon nanotubes. From the graph, it can be seen that the $AlCl_3$ modification leads to a huge residual, this is probably due to the introduction of aluminum ion. The other three modified OMCs are similar with the original OMC without any residuals.

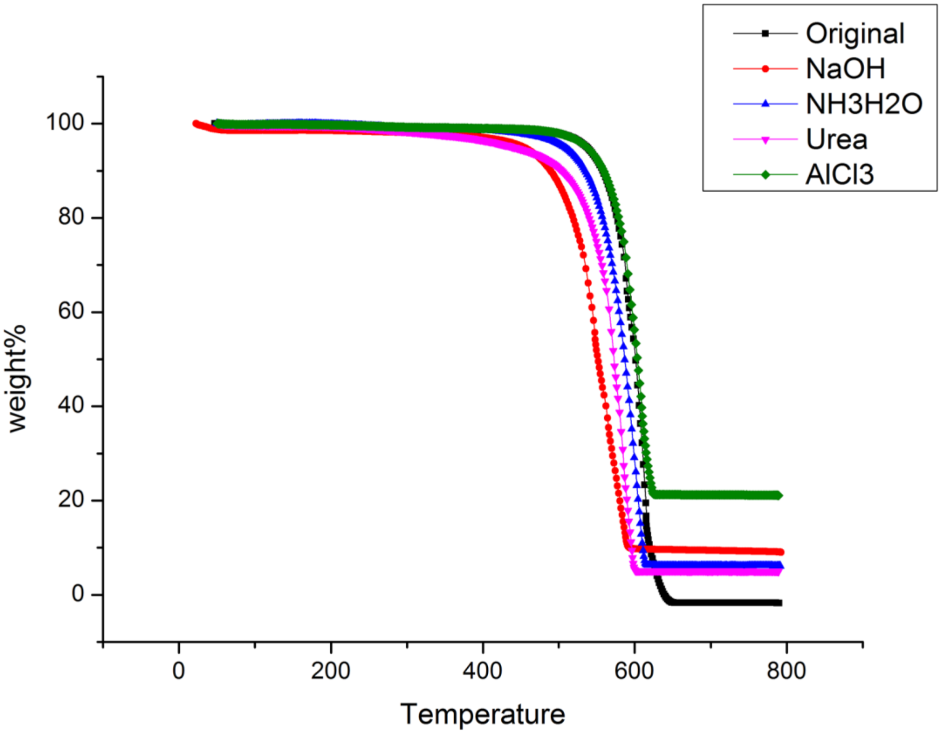


Fig. 16 TGA of the modified OMC

Differential thermal gravity (DTG) results are showed in Fig. 17. The DTG shows urea, NaOH and NH_3H_2O have declined the thermal stability of the OMC, while the $AlCl_3$ modification has increased the thermal stability.

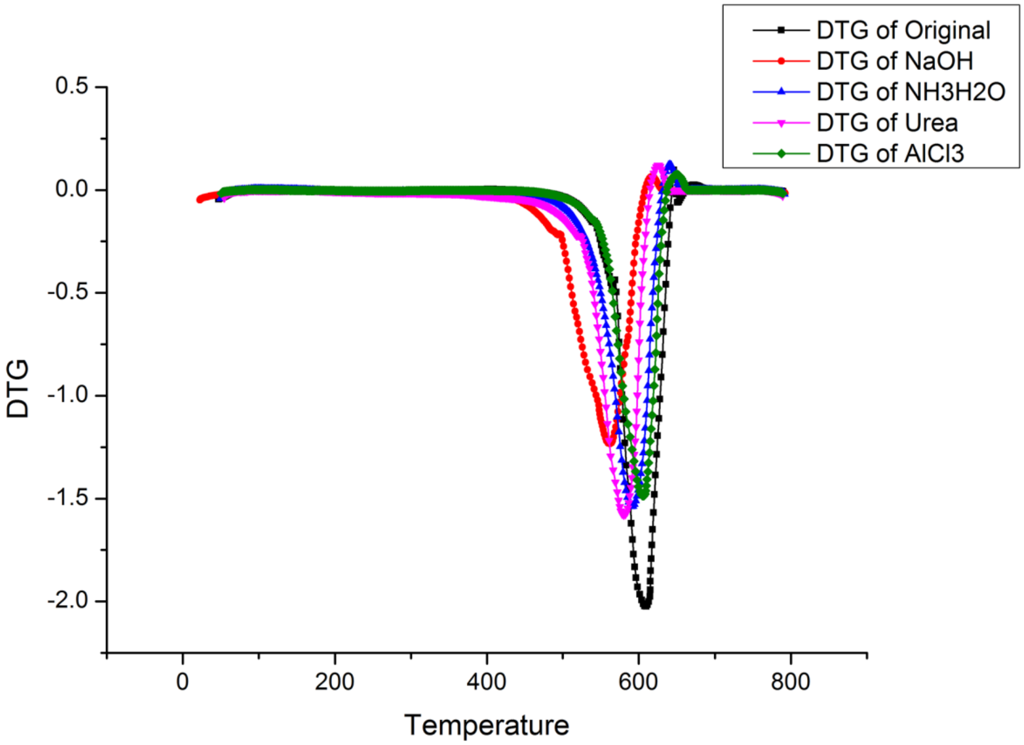


Fig. 17 DTG of the modified OMCs

Adsorption Study

The adsorption capacities of four modified OMCs are shown in Fig. 18. The OMC modified by NH_3H_2O has the highest adsorption capacity of 40.6 mg/g. Compared with the original OMC3, although modified samples have smaller surface area, their adsorption capacities were not all decreased. The phenomenon demonstrates that the modification procedures have complex effects on the OMCs. TEM results showed the damage of the well-ordered hexagonal structures, which may reduce the adsorption capacity of the materials. Bazula *et al* (2008) verified this point in their study. On the other hand, the surface modification has introduced various function groups to the OMCs. Swiatkowski *et al* (2004) believed the hydrogenant function groups, such as hydroxyl, could increase adsorption capacity of the adsorbent. Based on the results from the batch adsorption tests, the introduced function groups play the dominant role in the adsorption behavior.

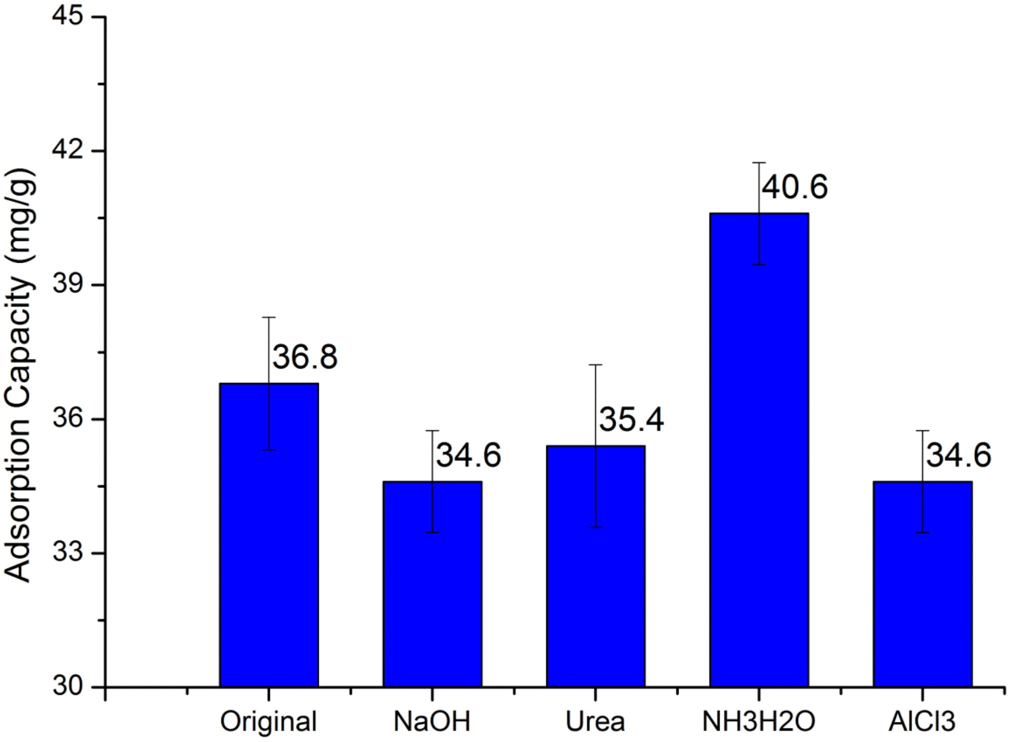
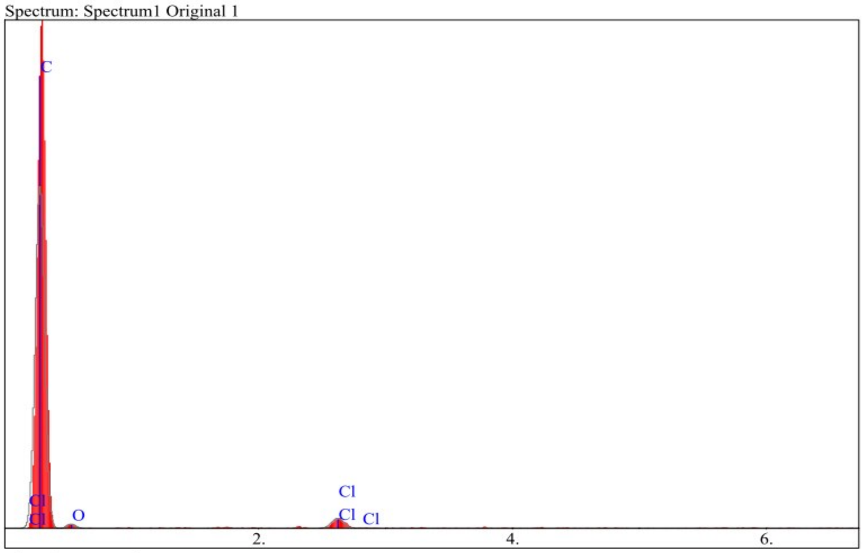


Fig. 18 Adsorption capacity of modified OMC *vs* original OMC

Energy-dispersive X-ray spectroscopy (EDS) measurement

Fig. 19 and Fig. 20 show the energy-dispersive X-ray spectroscopy (EDS) results of the original OMC and NH_3H_2O-modified OMC. It is obviously that the main component in the both the original OMC and modified OMC are carbon elements. The carbon content is 93.7% in the original OMC and 95.2% in the modified OMC. Also, oxygen elements are about 4.3% in the original OMC and 4.7% in the modified OMC. The ratios of oxygen to carbon are 0.046: 1 in the original carbon and 0.05: 1 in the modified carbon. This indicates the oxygen containing groups was introduced into the modified OMC after the ammonia hydroxide modification. It is reported that the increase of oxygen groups could increase the adsorption capacity of carbon materials because of the heterogeneity (Guo *et al*, 2013). However, since the change of the oxygen element is not significant, the increase of adsorption capacity may be due to the hydrophobic increase from the ammonia hydroxide modification. In addition, Fig. 19 indicates that there is chloride element in original OMC; it is probably because the hydrochloric acid residual was remained in the sample.

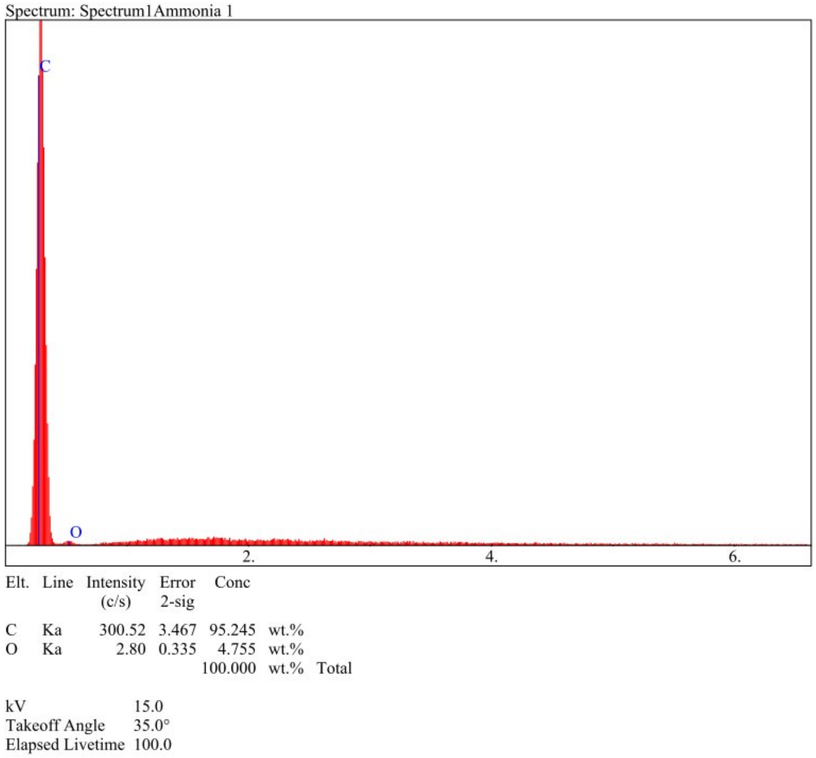


```
Elt.  Line  Intensity  Error   Conc
             (c/s)     2-sig

C     Ka     273.04   3.305   93.706  wt.%
O     Ka       3.10   0.352    4.335  wt.%
Cl    Ka       9.96   0.631    1.959  wt.%
                             100.000  wt.%  Total

kV                 15.0
Takeoff Angle      35.0°
Elapsed Livetime  100.0
```

Fig. 19 The element composition of original OMC (OMC3)



```
Elt.  Line  Intensity  Error    Conc
             (c/s)     2-sig

C     Ka      300.52   3.467   95.245  wt.%
O     Ka        2.80   0.335    4.755  wt.%
                              100.000  wt.%  Total

kV                  15.0
Takeoff Angle       35.0°
Elapsed Livetime  100.0
```

Fig. 20 The element composition of NH_3H_2O modified OMC

CHAPTER 5: CONCLUSIONS

5.1 Conclusion

First, ordered mesoporous carbons were made from four different ratios of silica template to carbon precursor acrylic acid. Second, the ordered mesoporous carbons were modified using four different aqueous solutions. The adsorption capacities of OMCs and modified OMCs were measured by removal of resorcinol from aqueous solution. The following conclusions can be drawn from this research:

1. Ordered mesoporous carbons with tunable mesoporous sizes were synthesized under different ratio of silica template to carbon precursor. Four different ratios (SBA-15 : Acrylic Acid) were 1:1, 2:1, 3:1 and 4:1. The corresponding ordered mesoporous carbons (OMCs) faithfully copied the structure of silica templates. The XRD and TEM experiments showed that ordered mesoporous carbons retain the highly ordered structure. The intensity of ordered mesoporous carbons was lower than the corresponding silica template because of the partial structure shrinkage during the carbonization process.
2. The XRD measurement showed that the pore sizes of the OMCs decreased with the increase ratio of the silica template to carbon precursor. Among all the OMCs, the OMC made at 3:1 had the best ordered structure. Also, the BET surface area analysis and adsorption behavior tests showed that the OMC3 had the larger specific surface area and higher adsorption capacity of 36.8 mg/g.
3. The modification of ordered mesoporous carbon using immersing methods did not destroy the ordered mesoporous structure. But all the modifying procedures eroded the surface of the original OMC and decreased the specific surface area. FT-IR tests and EDS results showed the change and increase of the oxygen function group by the modifications.

4. All OMCs could remove resorcinol from water, but the modified OMC by ammonia hydroxide solution had better performance than that of the original carbons with the adsorption capacity of 40.6 mg/g.

5.2 Future work

Based on the current research, future work can be carried out in the following directions:

1. Prepare silica templates under different condition to form a 3D structure.
2. Try different kinds of carbon resources like acrylamide, phenolic resin, etc.
3. Use different surfactant, pH and calcined time to produce the different silica templates.
4. Study other chemicals, such as $ZnCl_2$, $KMnO_4$, in the surface modification of ordered mesoporous carbon.
5. Characterize the other parameters, such as wall thickness, pore volume, pore size distribution, of the silica template and ordered mesoporous carbons.

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APPENDIX A

MATERIAL PREPARATION AND MEASUREMENT PROCEDURE FOR BATCH ADSORPTION STUDY

Ⅰ Material Preparation

A. Resorcinol solution

The resorcinol solution includes stock solution and intermediate solution, and standard solution. The intermediate solution must be prepared daily, and the standard solution must be prepared within 2 h of use.

1. Dissolve 100 mg resorcinol in freshly boiled and cooled distilled water and dilute to 100 mL; the concentration of stock solution is 1000 mg/L.
2. Dilute 2.00 mL stock solution in freshly boiled and cooled distilled water to 200 mL; the concentration of intermediate solution is 10 mg/L.
3. Dilute 10 mL, 20 mL, 30 mL, 40 mL, and 50 mL intermediate solution in freshly boiled and cooled distilled water to 100 mL, respectively. Then the concentrations of five standard solution are a = 1 mg/L, b = 2 mg/L, c = 3 mg/L, d = 4 mg/L, and e = 5 mg/L.

B. Auxiliary reagents

The auxiliary reagents include phosphate buffer solution, ammonium hydroxide solution, 4-aminoantipyrine solution, and potassium ferricyanide solution.

1. Phosphate buffer solution: dissolve 104.5 g K_2HPO_4 and 72.3 g KH_2PO_4 in water and dilute to 1 L. The pH should keep at 6.8.
2. Ammonium hydroxide (NH_4OH) solution 0.5 *N*: dilute 35 mL fresh NH_4OH to 1 L with water.
3. 4-aminoantipyrine solution: dissolve 2.0 g 4-aminoantipyrine in water and dilute to 100

mL. It should be prepared daily.

4. Potassium ferricyanide solution: Dissolve 8.0 g $K_3Fe(CN)_6$ in water and dilute to 100 mL. Filter if necessary. It should be stored in a brown glass bottle and be prepared weekly.

Ⅱ.Procedures

1. Scale 10 mg different OMCs, and then put into a 250 mL beaker with 5 mg/L resorcinol solution, respectively (this solution is prepared by diluting 50 mL intermediate solution in freshly boiled and cooled distilled water to 100 mL). And leave one solution untreated, as a comparison.
2. Transfer all the samples from Procedure 1 into 250 mL flasks. Then place them on an E24 Incubator Shaker (shaking speed: 200 rpm; temperature: 25°C). After 24 h, the samples are removed and filtered.
3. Prepare a series of 100 mL resorcinol standard solutions containing 0.1 mg, 0.2 mg, 0.3 mg, 0.4 mg, and 0.5 mg resorcinol, respectively, and a 100 mL distilled water as a blank one.
4. Treat sample, blank, and standards as follows: Add 2.5 mL 0.5*N* NH_4OH solution and immediately adjust to pH 7.9 ± 0.1 with 1.5 mL phosphate buffer solution. Add 1.0 mL 4-aminoantipyrine solution and mix well, then add 1.0 mL $K_3Fe\ (CN)_6$ solution and mix well. Let the color develop for 15 min. The solution should be clear and light yellow. After 15 min, transfer to 5 cm cells and read the absorbance of sample and standards against the blank at 500 nm.
5. Finally, plot absorbance against milligram resorcinol concentration. Construct a calibration curve only using standard resorcinol solution. Use calibration curve and absorbance of samples to obtain resorcinol concentration in samples.

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ABSTRACT

Ordered mesoporous carbon (OMC) materials have attracted great interests from NASA due to their remarkable properties, such as high specific surface area, regular and tunable pore size. These features show great potential for being used in the water recovery system (WRS) in the International Space Station (ISS) as potential adsorbents. Various methods have been explored on the OMC preparation and modification to achieve better adsorption results. In this research, acrylic acid was used as a carbon precursor to synthesize OMC using a common silica mesoporous template (SBA-15). The influence of silica template amount was tested by using different ratios of SBA-15 to acrylic acid. The modification processes were conducted by immersing methods using four different aqueous solutions: 30% ammonium hydroxide, 0.1% sodium hydroxide, 1 mol/L aluminum chloride, and 0.02 g/mL urea solution. BET-SSA, FT-IR, TEM, TGA, and XRD were used to characterize the structures of OMCs and modified OMCs. It demonstrated that all the products had well-ordered hexagonal structure. The modifying procedures had eroded the surface of the OMC, but the highly ordered structures had been preserved based on the TEM and XRD results. FT-IR analysis indicated that the functional groups were introduced to the surface of the modified OMCs, which affected the adsorption capacity significantly. Resorcinol, a typical total organic carbon (TOC) model compound, was selected to evaluate the adsorption behavior of the OMCs and modified OMCs. Adsorption study illustrates that OMC produced by 3:1 ratio of SBA-15 to acrylic acid showed a higher adsorption

capacity than that of OMCs produced with other ratios. The ammonium hydroxide modified OMC had the highest adsorption capacity of 40.6 mg/g for resorcinol removal, compared with that of the other three modified OMCs.

BIOGRAPHICAL SKETCH

Hanlong Ren was born in Henan province, China on June, 1988. He obtained his Bachelor of Science in Environmental Engineering from Jilin University (J.L.U) in China in Fall 2011. He entered the University of Louisiana at Lafayette to pursue a Master of Science in Engineering, Civil Engineering option. He completed his M.S. degree in Fall 2014.