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Effect of Synthesis Conditions on Carbon Aerogels Material to Remove Pesticide in Cuu Long Delta Rivers

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Carbon aerogel is taken into account for a new material with many unique properties that can be applied in many different application fields. The properties of carbon aerogels are distributed across a wide range and are controlled by many conditions in the synthesis process. For each different application area, carbon aerogel is synthesized under different conditions to meet the required properties for materials such as: surface area, specific gravity, conductivity, pore size, etc. Therefore, the assessment of the quality of synthetic carbon aerogels will create a premise to guide them in appropriate fields. Besides, it is also possible to optimize the synthesis process to achieve materials of good quality, properties suitable for each specific requirement. The specific weight less than 0.5 g/cm^3. Specific surface area from 633 to 800 m^2/g. Pore size from 7 to 22 Å. With the properties of carbon aerogel materials synthesized, assess the adsorption capacity of carbon aerogel to treat heavy metals Fe, As and pesticides (Cypermethrin / DDT) in laboratory water samples and surface water samples taken from the rivers in the Cuu Long Delta. The results show that the ability to adsorb and process metals and pesticides is very good. Processing efficiency of iron and arsenic reaches 92 - 99 %. Meanwhile, the ability to absorb plant protection drugs Cypermethrin / DDT also reached 95 - 99 %.

1. Introduction

In the past years, the Cuu Long delta rivers has strongly developed, leading to an increase in industrial and agricultural waste, which is one of the risks of environmental pollution. The river system of the region receives industrial and domestic waste sources, a part of urban solid waste, industrial and hazardous waste, water from aquaculture and water from agricultural production with residual fertilizers and pesticides have seriously affected the surface water quality of the region. According to the monitoring report in recent years, the indicators of pollution often exceed the standard in surface water sources: total suspended solids (TSS), isoprothiolane, heavy metals (Fe, As) (Nga, 2011).

Plant protection drugs (pesticides) are preparations derived from chemicals, plants, animals, microorganisms and other preparations used to prevent and control organisms harmful to plant resources. Most pesticides have very high toxicity and greatly affect human health. There are a wide variety of treatment technologies such as precipitation, coagulation–flocculation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, bio-logical process, chemical reactions, adsorption and ion exchange that were involved in the wastewater treatment processes (Foo and Hameed, 2010). From these, adsorption process is recognized as the most efficient and promising fundamental approach in pesticide removing. In 2008, El-Sheikh et al. (2008) had carried out the research on carbon materials such as activated carbon, C18 cartridges as adsorbents, whilst Al-Degs et al. (2009) used multiwall carbon nanotubes in their study. In another research, Al-Qodah et al. (2017) had published their study on the shale ash as a new type of adsorbent, whilst Faur et al. (2015) used the carbon fibers to test the removal of pesticides from water samples. In 2017, Fan (2017) had carried out the study on chemical behavior of pesticide fungicide in lake.

Carbon aerogel is a special form in aerogel types. It is made up from pyrolysis of organic aerogels to remove functional groups and leave only carbon frames in the structure. Carbon aerogel can be made up from many types of organic gels. In 2018, Lebedev and colleagues fabricated the carbon aerogel using Resorcinol-Formaldehyde (Lebedev et al., 2018). In 2013, Rejitha and staffs had synthesised the carbon aerogel using

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the Phenol-Furfural, polyacrylonitrile as material (Rejitha et al., 2013). In another research, Tamon published the study of synthesis of carbon aerogel with the material of Melamine-Formaldehyde (Tamon et al., 1998). In organic aerogels used to synthesize carbon aerogels, the Resorcinol-Formaldehyde (RF) aerogel is great interest to scientists. Similar to activated carbon, carbon aerogel is processed to yield a very porous structure with a large surface area. The surface area of activated carbon is about 400 - 1,000 m^2/g and the pore volume is from 0.2 - 0.3 cm^3/g. Surface area of carbon aerogels is mainly due to small holes with a radius of less than 22 Å (Dat et al., 2018), so carbon aerogels are very effective in adsorption of organic compounds, pesticides, odor-causing loop compounds (non-polar compounds).

The aim of this paper was to investigate the feasibility of using carbon aerogels for pesticide removal from water surface in Cuu Long delta rivers by adsorption. Therefore, carbon aerogels were developed via a sol-gel process by the aqueous polycondensation of resorcinol with formaldehyde, using sodium carbonate as a base catalyst under frozen drying technique. The preparation conditions such as the catalyst concentration were investigated in this study, and the structure and properties of the products obtained were characterized by scanning electron microscope (SEM), thermo gravimetric analysis (TGA) and nitrogen sorption measurements.

2. Material and methods

2.1 Preparation of carbon aerogel

In order to prepare RF aerogels, resorcinol–formaldehyde (RF) solutions were prepared from resorcinol (R), formaldehyde (F), sodium carbonate (C). The synthesis conditions are presented: the molar ratio of resorcinol to formaldehyde (R/F) was fixed at 0.5, the RF content was fixed at 40 % in solution, the ratio of resorcinol and catalyst (R/C ratio) was changed: 500 and 1,000. Ultrasonic was applied into RF solution with a titanium alloy transducer (13 mm in diameter) at intensities 75 W/cm^2. The temperature of RF solution was controlled at 30 °C. When no cavitation bubbles were observed in high viscosity RF solution the ultrasonic irradiation was stopped then the RF solution was poured into the cylindrical glass tube followed by aging for 1-3 d at 75 °C in the oven. Before freeze drying, water in RF aerogels was replaced by solvent exchange with t-butanol for three times. The wet RF aerogels were freeze-dried step by step. The wet RF hydrogels were firstly frozen at -30 °C for 1 h, dried at -30 °C for 24 h, then at -10 °C for 24 h, and finally at 0 °C for 24 h, using a vacuum freeze-drying equipment. Finally, pyrolysis of the resultant RF aerogel was performed at 800 °C for 3 h under N_2 atmosphere (400 $cm^3.min^{-1}$), resulting in carbon aerogels. Carbon aerogels was further activated at 800 °C for 2 h a flow of CO_2 to increase its properties. The process for preparation of carbon aerogels showed in Figure 1 as follow:

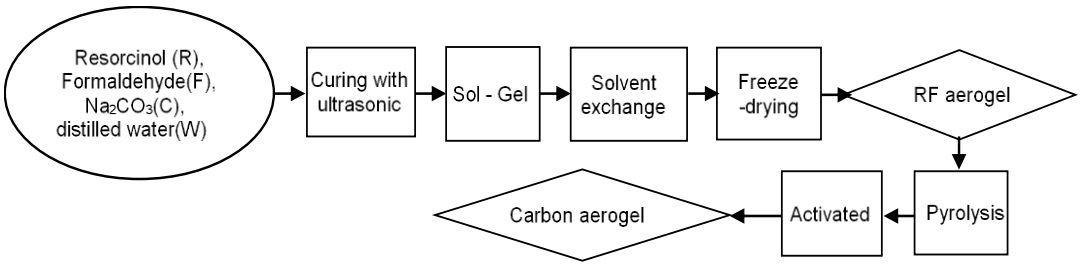

Figure 1: The flow chart of the preparation of carbon aerogels.

2.2 Characterization of carbon aerogels

Surface area and pore size distribution of carbon aerogel samples were characterized by analysis of nitrogen absorption-desorption. The samples were degassed under vacuum (0.01 bar) to 110 °C (for organic aerogels) and 200 °C (for carbon aerogels) for at least 10 h to remove all adsorbed species. Brunauer-EmmettTeller (BET) method was used for total surface area measurements, and t-plot method was used for estimating mesopore surface area. Pore size distribution were obtained by the Barret-Joyner-Halenda (BJH) method from desorption branch of the isotherms. Total pore volume was calculated from the adsorbed volume of nitrogen at P/P_0 of 0.99 (saturation pressure). Microstructure and morphology images of materials identified by Scanning electron microscopy (SEM).

2.3 Adsorption experiments

Carbon aerogels was synthesized, after analyzing and evaluating structural parameters, prepared 10-20 g for adsorption experiments. Samples of carbon aerogels with particle size smaller than 1 mm, specific gravity less than 1 g/cm^3, specific surface area of 600-800 m^2/g, average pore size of 18 - 22 Å. Water samples were prepared to conduct adsorption experiments to evaluate the effectiveness of TSS, Coliform; Fe, As heavy metals treatment and pesticides (Cypermethrin / DDT). Water flow Q was fixed of 0.25 L/min (water velocity V of 0.2 m/min). Effective treatment of Fe, As, combination of Fe / As and pesticides (Cypermethrin / DDT) was determined by taking samples at the specified volumes.

3. Results and discussion

3.1 Properties of carbon aerogels

3.1.1 Surface structure and particle size

Survey of catalytic concentrations (Na_2CO_3) affecting the surface properties and particle size of carbon aerogels. SEM shooting for two carbon aerogel samples has the ratio R/C of 1,000 and R/C of 500 (with the same ratio R/F of 0.5; RF/dd of 40 %; application of ultrasonic techniques in synthesizing sol - gel, freeze - dried with t-butanol solvent by step drying technique, pyrolysis at 800 °C (3 h) in nitrogen, activated at 800 °C (2 h) in CO_2) to determine surface properties and evaluation of particle size of these materials.
Figure 2 shows that carbon particles have a spherical-like form, joined together to form a chain, randomly arranged and subjected to catalytic effects during bonding. Figure 2a has high porosity, large size particles (about 50 nm), more uniform and less cohesive, large pores. Figure 2b has not high porosity, small particle size (about 20 nm), uneven, bound. The specific surface area of the material is calculated by the total surface area and the area of pores inside the particle, the small particle size will increase the surface area of the material, but the small pore size affects adsorption capacity. When the R/C ratio is high (low basal catalyst concentration), there is not much available germ in the gel, forming clusters with few branches and longer in the germ stage. When the gelation time is long enough, the clusters tend to stick to each other more, forming large sized particles. Large particles connected together create large-sized pores.

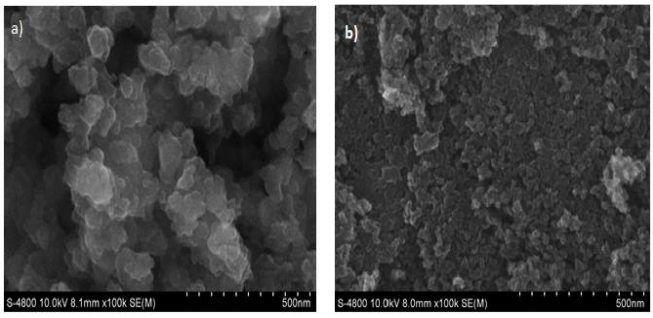

Figure 2: Properties of carbon aerogels: (a) SEM: R/C of 1,000, (b) R/C of 500

3.1.2 Distribution of pore size

Table 1 shows that the CA500 sample consists mainly of small pores (accounting for 83.95 %) and medium pores (13.24 %).

Table 1: Parameter of carbon aerogel: CA500 (R/C of500) and CA1000 (R/C of1000)

Samples	S_{BET} m^2/g	D_{pore} Å	V_{total} cm^3/g	V_{micro} cm^3/g	V_{meso} cm^3/g	V_{macro} cm^3/g	V_{micro} %	V_{meso} %	V_{macro} %
CA500	633.54	19.86	0.2403	0.2018	0.0318	0.0067	83.95	13.24	2.80
CA1000	779.06	22.24	0.3733	0.3353	0.0361	0.0019	89.82	9.67	0.51

While the CA1000 sample contains mainly small porous holes (89.82 %), medium pores and large pores have very few numbers. This result again confirms the speculation when observing the adsorption isotherm - nitrogen desorption. The pore diameter of CA500 is in the range of 0.7 nm to 1.7 nm. While, the CA1000 is about 0.8 nm to 1.7 nm so the material is small and has a small amount of average pore (average pore diameter of 2.2 nm). However, the total volume of pore and surface area of CA1000 is much larger than that of the CA500. The pore size of carbon aerogels is an important factor determining the adsorption capacity of the

material. Depending on the size of the pores determine which element may be adsorbed or not. The average pore diameter of the carbon aerogels after activation is 22 Å (the major size distribution in the range of 7 to 15 Å) is much larger than the adsorbed ions.

3.2 Adsorption of carbon aerogels

3.2.1 The maximum filtration rate and TSS / Coliforms treatment efficiency

Figure 3 shows the effectiveness of TSS and coliform treatment were performed on the basis of fixing the selected filter velocity v of 12 m/h (Q of 0.25 L/min). The efficiency of TSS treatment in about 50 L of filtered water in the range of 95 - 98 % corresponds to the post-treatment TSS concentration of about 2 - 5 mg/L. The efficiency of coliform treatment in about 50 L of filtered water in about 95 - 100 % corresponding to coliform after treatment reaches about 0 - 30 bacteria/mL.

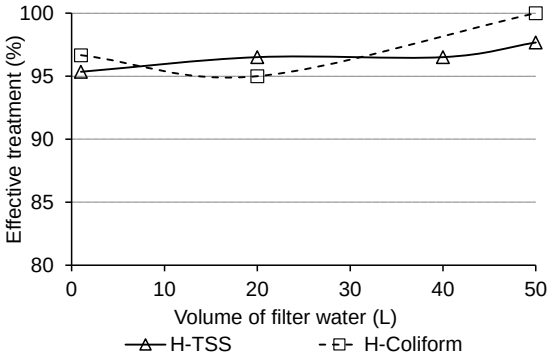

Figure 3: The maximum filtration rate (a) and TSS / Coliforms treatment efficiency

3.2.2 The efficiency of heavy metal (Fe, As) treatment

The efficiency of Fe treatment increases when increasing the number of carbon aerogel modules (Figure 4). The sample M1.Fe3-11 with concentration of Fe was 2.7 mg/L, EC was 125 µS/cm. Sample M1.Fe3-22 with concentration of Fe was 2.8 mg/L, EC was 210 µS/cm. Sample M2.Fe3-11 with concentration of Fe was 2.8 m/l, EC was 121 µS/cm. Sample M2.Fe3-22 with concentration of Fe was 3.0 mg/l, EC was 215 µS/cm. When the conductivity (EC) increases from 110 µS/cm to 220 µS/cm, the efficiency of Fe treatment is reduced by 1 carbon aerogel module. In addition to 2 carbon aerogel modules, the efficiency of Fe treatment is equivalent for both cases of conductivity. When applying 2 carbon aerogel modules, Fe processing capacity is over 90 % and can handle up to 50 L of water.

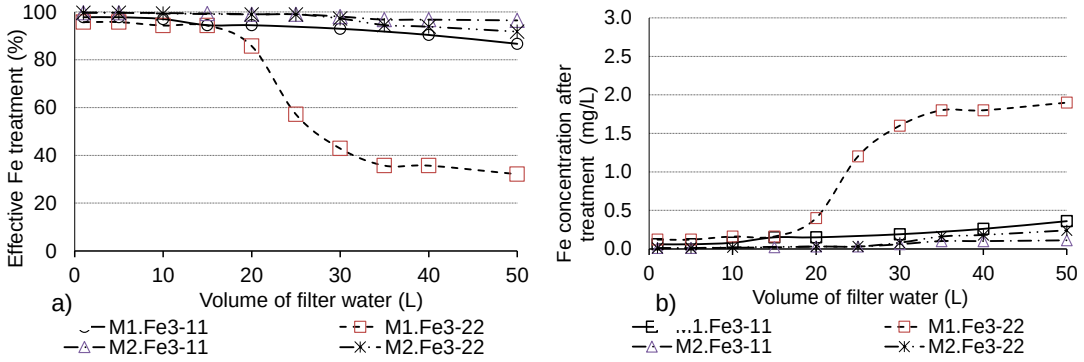

Figure 4: Effective treatment (a) and concentration after treatment (b) of Fe.

The arsenic treatment experiment was carried out on 2 carbon aerogel modules with 2 input water sources with EC was 110 µS/cm and EC was 220 µS/cm. Figure 5 shows both test samples achieved a high level of treatment in 50 L of filtered water. Sample M2.As100-11 with concentration of As was 85 µg/L, EC was 115 µS/cm. Sample M2.As100-22 with concentration of As was 94 µg/L, EC was 224 µS/cm This result is similar to that obtained from the iron type test with 2 serial modules. The efficiency of arsenic types of two experiments reached from 94 - 97 % for samples with EC about 110 µS/cm and from 93 - 95 % for samples with EC about 220 µS/cm.

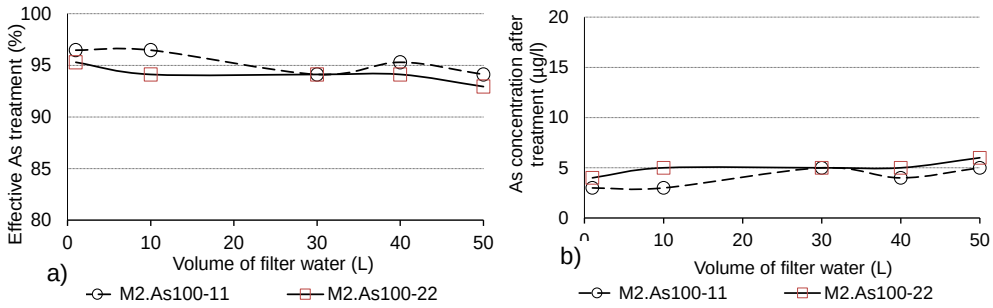

Figure 5: Effective treatment (a) and concentration after treatment (b) of As.

Figure 6 shows the efficiency of iron (3.2 mg/L) and arsenic (90 µg/L) at the same time with EC was 202 µS/cm in 50 L of filtered water. The targets of iron and arsenic of treated water are below the standard of direct drinking water, specifically: iron in the range of 0.01 - 0.24 mg/L, corresponding to the processing efficiency of 92 - 99 %, arsenic about 3 - 6 µg/L corresponds to processing efficiency of 93 - 97 %. This result demonstrates the application of two modules capable of handling 50 L of water with an input water source of iron about 3 mg/L, arsenic about 100 µg/L and EC about 220 µS/cm.

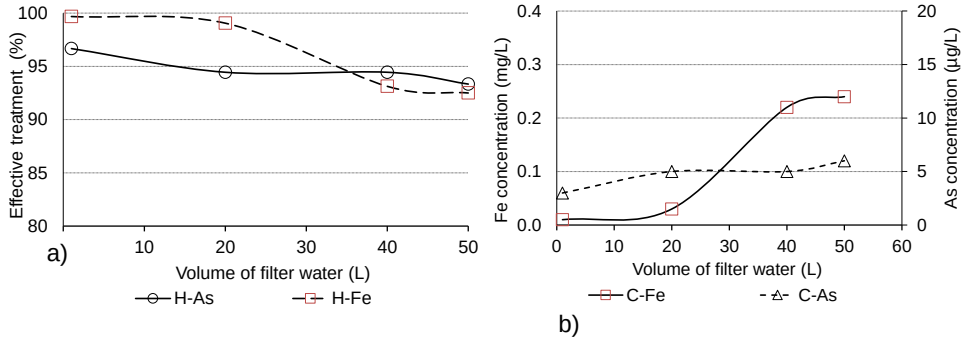

Figure 6: Effective treatment (a) and concentration after treatment (b) of mixtures Fe and As.

3.2.3 The efficiency of pesticide treatment (Cypermethrin / DDT)

Figure 7 shows the efficiency of pesticide treatment (Cypermethrin / DDT) with the effective remove pesticide and the concentration. Carbon aerogel was used to adsorb pesticide and chlorine. The experiment was performed on 01 module with water source with concentration of Cypermethrin was 10.8 µg/L and DDT was 14.2 µg/L. The effectiveness of pesticide absorption of the samples was high, 96 - 97 % for DDT and 95 - 96 % for Cypermethrin. This result is consistent with the theoretical basis of very high adsorption capacity of carbon aerogel for DDT and Cypermethrin.

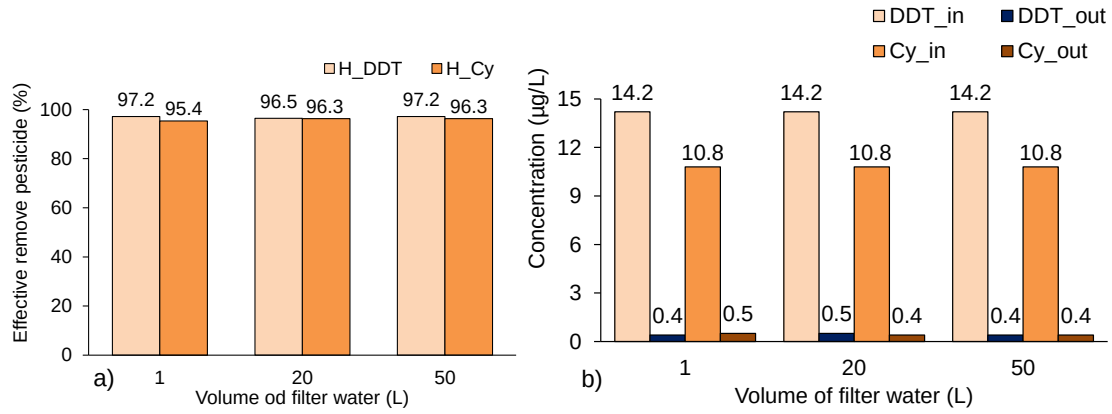

Figure 7: The efficiency of pesticide treatment (Cypermethrin / DDT). (a) Effective remove pesticide (%); (b) concentration (µg/L)

3.2.4 The treatment efficiency of carbon aerogels on surface water in Tien River

Figure 8 shows the removal efficiency of carbon aerogel for surface water on turbidity was from 190 to 3 NTU and counted as 98.4 %. For the TSS, removal efficiency was about 99 %. The Fe was of 97 %, the Cypermethrin was removed 10.0 to 0.4 µg/L and calculated as 96 %. The coliform was removed from 600 to 30 bacteria/mL, and efficiency was of 95 %.

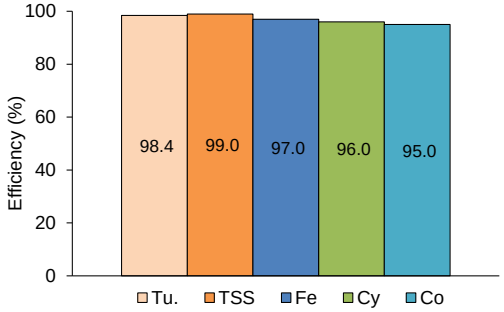

Figure 8:1 Removal efficiency of carbon aerogel for surface water on turbidity, TSS, Fe, Cypermethrin, coliform

4. Conclusion

Carbon aerogel was synthesized from resorcinol and formaldehyde under room temperature gel applied ultrasonic technique and freeze-drying with step drying technique. A part of carbon aerogel has a similar structure of graphite when synthesized at a high pyrolysis temperature. Specific weight: <0.5 g/cm^3. Specific surface area: 633–800 m^2/g. Pore size: 7–22 Å. Material structure were determined by scanning electron microscopy (SEM) and nitrogen absorption measurement. Assess the adsorption capacity of carbon aerogel to treat heavy metals Fe, As and pesticides (Cypermethrin / DDT) in laboratory water samples and surface water samples taken from the rivers in Cuu Long Delta. The results show that the ability to adsorb and process metals and pesticides is very good. Processing efficiency of iron and arsenic reaches 92-99 %. The ability to absorb plant protection drugs Cypermethrin / DDT also reached 95-99 %.

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