Synthesis of Fe-SWCNHs via Arc-discharge in Water Method and Its Application on Antibiotics Adsorption

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ABSTRACT
The unique structures of SWCNHs motivate scientists and researchers to conduct various investigations on them. SWCNHs outstanding properties, i.e. high surface area and good chemical stability lead to several useful applications. Among various methods for synthesizing SWCNHs, Gas-Injected Arc-In-Water method (GI-AIW) is recognized as a good candidate because it is a simple, compact, and cost-effective method. Meanwhile, SWCNHs produced by the proposed method can be used to adsorb antibiotics because of their high specific surface area. In this study, GI-AIW method with unique configuration of graphite anode inserted with iron (Fe) wires was employed for synthesizing Fe-SWCNHs. The nitrogen gas flow rate of 8 L/min would lead to highest production yield (%) of SWCNH (varying from 4, 6, 8, and 10 L/min) about 7.7%. Tetracycline was employed as a target antibiotic due to its wide usage in Thai agricultural industry. Both of Fe-SWCNH and SWCNH have the antibiotic adsorption capability. However, the addition of Fe is found to worsen antibiotics adsorption capacity of SWCNHs from 25% to 21% approximately.

Keywords: Single-walled carbon nanohorn, Carbon nanomaterials, Arc discharge, Tetracyline, Antibiotics adsorption

INTRODUCTION
Single-walled carbon nanohorns (SWCNHs) are a member of carbon nanomaterials which possess unique structures which motivate scientists and researchers to conduct many challenging investigations [1]. In addition, several promising applications could be expected when SWCNHs are combined with some metal nanoparticles. There are many approaches proposed by various research teams to produce SWCNHs. For instance, gas-injected arc-in-water method (GI-AIW) is a simple method which can produce SWCNHs with high purity [2-3]. So far, some previous works have focused on experiments of SWCNH synthesis with effect of various metals which could be simply hybridized with SWCNHs [4-5]. Sano et al. [5] reports that incorporation of Patimum (Pt) nanoparticles would exert significant effect on particle size distribution of Pt-SWCNH. Moreover, due to the high surface area and chemical resistance, SWCNHs also used in hemoglobin adsorption [6] and glucose biosensor [7]. Recently, iron (Fe) hybridized with

SWCNHs was successfully synthesized by GI-AIW method [8]. Thus, in this work, we focus on the adsorption of antibiotics by using Fe-SWCNHs. The effect of nitrogen gas flow rate on production of SWCNHs was also examining. TEM (Transition Electron Microscope) micrographs with image processing was employed for determining the structure of carbon nanoparticles and roughly estimating particle size distribution (PSD) while BET (Brunauer–Emmett–Teller) was used to determine the surface area of SWCNHs and Ultraviolet–Visible spectroscopy was used to investigate the concentration of antibiotic which was sampling continuously until reaching the absorption capacity of Fe-SWCNHs on antibiotics.

EXPERIMENTAL PREOCEDURE

Pure graphite rods are used as cathode and anode as shown in Figure 1. The upper electrode was cathode which the length was 55 mm with two 2-mm diameter upper holes and single 10-mm diameter lower hole. The length of anode was 50 mm with 2-mm diameter. The anode had a single hole of 1-mm diameter. The diameter of Fe-wires which were used to insert in anode is 0.5 mm. The static holder was flexible that can move in three dimensional directions.

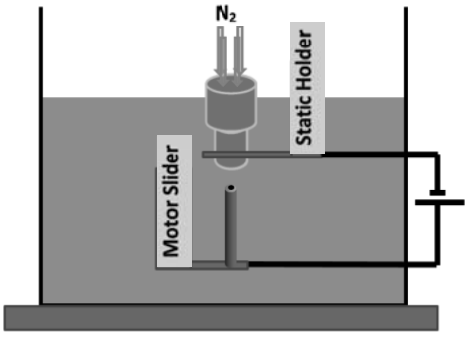


Figure 1. Schematic diagram of arc-discharge-in-water experimental apparatus

This work is roughly divided into three main parts; synthesis of SWCNHs and Fe-SWCNHs composite, characterization of product and adsorption of antibiotics by the SWCNHs and Fe-SWCNHs. The technique of arc-discharge in water was used as a method to synthesize Fe-SWCNH composite. The process begins with the preparation of electrodes both cathode and anode as mentioned above. Once the electrodes are prepared, they are set in the arc machine (as shown in Figure 1) under the distilled water of 3,000 mL. Optimization of the nitrogen gas flow rate was studied to get the most suitable condition for the maximum production yield of SWCNHs. Additionally, the insertion of Fe-wire into the anode is done to compare the production yield (%) of SWCNHs and the adsorption capacity of Tetracycline being adsorbed is determined between the SWCNHs and Fe-SWCNHs. In the real situation, the experimental setup takes some times. The connectors usually leaks, this can be solved by rounding up the thread more with adhesive tape. The coordination of the two electrodes are not easily matched, it should be fixed by invent new coordinator for sustainable usage as stated above. The synthesized SWCNHs floating on the top layer of water will be collected. The collected product is dried for 1 day in the oven with controlled temperature of 100˚C and then will be characterized further to analyze the structure to SWCNHs.

In the characterization stage, there are two main approaches which are mentioned above. In TEM (JEOL, JEM-2100 electron microscope) observation, the samples are selected to be viewed. The samples are the condition of nitrogen flow rate of 4, 6, 8, and 10 L/min and Fe-consisting samples, 1 iron wires. For the determination of average size and BET specific surface area of SWCNHs, nitrogen adsorption-desorption apparatus

was used (Quantachrome/ Autosorb-1, Thermo Finnigan/ Sorptomatic 1990).

The permanent magnetic bar was used to trap the Fe-SWCNH composite in separation process. The remaining solution

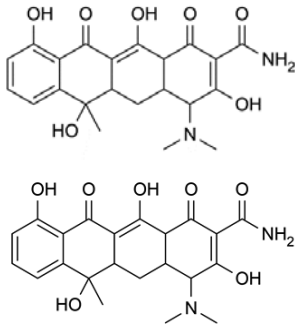


Figure 2. Schematic diagram for adsorption process

is analyzed by Ultraviolet–Visible. UV-Visible spectroscopy was used to determine the concentration of antibiotics remained as shown in Figure 2. From our preliminary studies, the time approaching equilibrium for CNTs adsorbing antibiotics is approximately 10 hours. Therefore, this duration time was fixed. Also, the assumption for antibiotics' adsorption was set. The antibiotics solution was not disturbed when sampling out to measure the adsorption capacity.

In the adsorption capacity study, Tetracycline was used as an antibiotic (TTC, ≥98% purity, Sigma Aldrich Co.). The structure of TTC is shown in Figure 3. The calibration curve of Tetracycline as an antibiotics was constructed to be used for calculation of the remaining concentration. The adsorption capacity curve was plotted and the time to equilibrium was evaluated. The reaction was assumed to be first order reaction [9]. This means that the rate of reaction was depended on only one reagent which was the combination of antibiotics and carbon nanohorns.

RESULTS AND DISCUSSIONS

The effect of N_2 gas flow rate on the production yield of pristine SWCNHs was

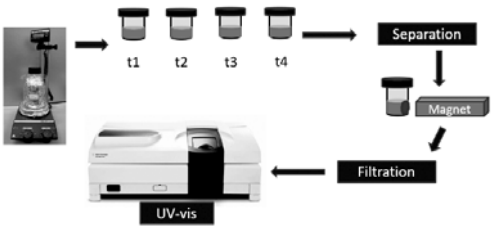


Figure 3. Molecular structure of Tetracycline (TCC).

demonstrated in Figure 4. The yield of SWCNHs was determined by equation (1). It was found that the highest production yield of SWCNHs was obtained at the flow rate of 8 L/min. It should be noted that the yield of SWCNHs depended on the quenching of carbon vapor in the cathode hole. Thus, at the lower flow rate, the quenching rate was low which let the carbon vapor is expelled into the outside zone of cathode cavity before the conversion of carbon vapor to SWCNHs. Therefore, the yield was low when the flow rate was decreased.

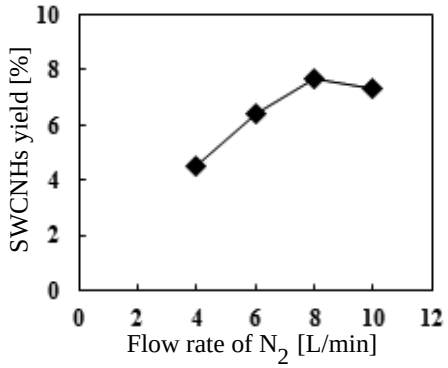


Figure 4. The effect of N_2 gas flow rate on the production yield of SWCNHs.

$$\text{Production Yield [\%]} = \frac{\text{Weight of SWCNHs}}{\text{Weight of consumed anode}} \times 100 \quad (1)$$

Beside the N_2 gas flow rate, the morphology of SWCNHs was observed by TEM images in Figure 5. The aggregates of SWCNH can be observed. It clearly shows that the morphology of SWCNHs does not change with the varied of N_2 gas flow rate.

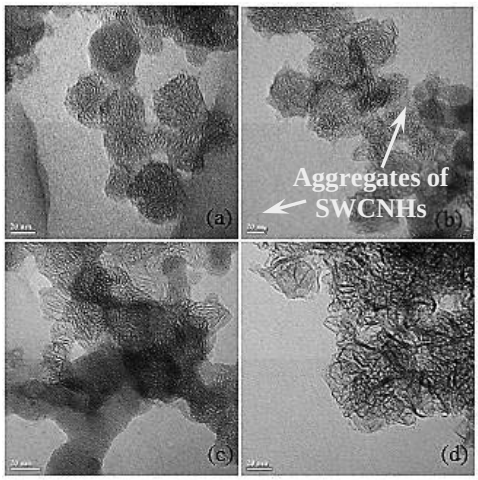


Figure 5. TEM images of SWCNHs synthesized at varied nitrogen gas flow rate of (a) 4 L/min, (b) 6 L/min, (c) 8 L/min and (d) 10 L/min.

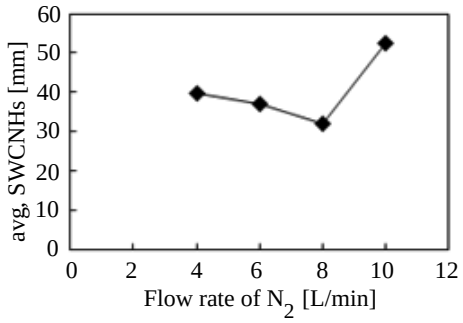
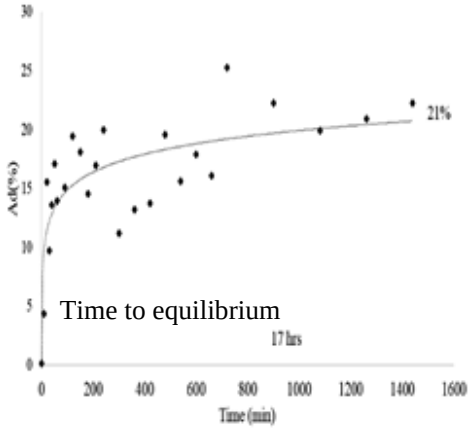


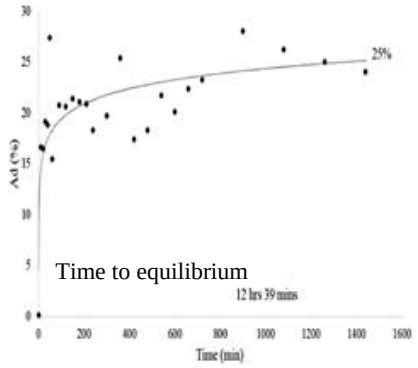
Figure 6. The effect of N_2 gas flow rate on average diameter of SWCNHs ($\Phi_{avg,\ SWCNHs}$ [nm]).

Moreover, the average particles size of SWCNHs was characterized by N_2 adsorption apparatus. Figure 6 shows the effect of N_2 gas flow rate on the average size of SWCNH's diameter. The aggregates of SWCNHs have an average diameter of about 30 to 50 nm.

The preliminary test of the TTC adsorption by using SWCNHs was also examined. In this work, SWCHs dispersed with iron (Fe) nanoparticles was also used to compare with pristine SWCNHs. The TTC sampling time was systematically allocated for 1 day in each of the Fe-SWCNHs and SWCNHs. The adsorption capacity of Fe-SWCNHs and SWCNHs was shown in Figure 7.



(a) Fe-SWCNHs



(b) SWCNHs

Figure 7. TTC adsorption capacity of (a) Fe-SWCNHs and (b) SWCNHs representing with percentage of adsorption capacity and time to equilibrium.

It can be observed that the addition of Fe-wire into the graphite rod did not promote the adsorption capacity and also extend more time of adsorption equilibrium time. This result suggested the imperfect mixing of the SWCNHs and water. However, in the process, the turbulence and the most proper mixing was observed while performing the experiments. Therefore, the surface area of Fe-SWCNHs and SWCNHs before and after adsorption was determined because the adsorption capacity depends on the surface area of adsorbent. The results from Table 1 indicated that SWCNHs have larger area than SWCNHs. Therefore, the iron nanoparticles occupied inside SWCNHs aggregates did not enhance the TTC adsorption. Thus, the adsorption capacity of Fe-SWCNHs was lower.

Table 1. Adsorption capacity (Ads [%]), adsorption time (Ads. Time [hrs]) and BET surface area of before and after adsorption of Fe-SWCNHs and SWCNHs.

Sample	Ads [%]	Ads. Time [hrs]	A_{BET} (before) [m^2g^{-1}]	A_{BET} (after) [m^2g^{-1}]
Fe-SWCNHs	21	17	115.55	76.96
SWCNHs	25	12	212.15	100.52

To enhance efficiency of antibiotics adsorption of SWCNHs, other kinds of metals should be inserted instead of Fe. However, the presence of Fe aids the process of separation of Fe-SWCNHs from antibiotics solution because of its magnetisms. We suggested that new sample holder, current and voltage detector, and nanoparticle collector must be established in order to increase the production SWCNHs. The main point should be focused on the alignment of the anode and cathode rod. They must be held tightly by sample holder in the center of each other. For the characterization and adsorption parts, the interpretation of graphs getting from BET area analyzer is crucial. The hysteresis loop of adsorption and desorption must be completely closed. The factors in adsorption part are emphasizing on the uniform distribution of antibiotics and SWCNHs. Since SWCNHs are hydrophobic that is insoluble in water, they must be confirmed the well-mixed behavior.

CONCLUSION

SWCNHs were synthesized by arc-in-water with nitrogen gas injection. In the experiments, SWCNHs was synthesized at the highest production yield of 7.7% at 8 L/min nitrogen gas flow rate. It had potential to adsorb antibiotics with limited efficiency due to the problems in synthesis part. In composition, Fe-SWCNHs had an impact on reduction of specific surface area and the ability of SWCNHs in adsorption of antibiotics.

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