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# Adsorption of Methylene Blue on Multi-Walled Carbon Nanotubes in Sodium Alginate Gel Beads

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Fang-Chang Tsai, Ning Ma, Lung-Chang Tsai,  
Chi-Min Shu, Tao Jiang, Hung-Chen Chang,  
Sheng Wen, Chi Zhang, Tai-Chin Chiang,  
Yung-Chuan Chu, Wei-Ting Chen, Shih-Hsin Chen,  
Han-Wen Xiao, Yao-Chi Shu and Gang Chang

Additional information is available at the end of the chapter

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## 1. Introduction

Surface water contamination by pollutants is common in highly industrialized countries due to direct discharge of industrial effluents into bodies of water or precipitation of air-borne pollutants into surface water [Murakamia et. al., 2008]. Dyes from the pollutants released along with industrial effluents are easily detected because of their inherently high visibility, meaning that concentrations as low as 0.005 mg/L can easily be detected and capture the attention of the public and the authorities [Ray et. al., 2003, Ray et. al., 2002]. Apart from the aesthetic problems caused by dyes, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water, which interferes with the growth of bacteria, such that bacteria levels are insufficient to biologically degrade impurities in the water [Pierce, 1994. Ledakowicz et. al., 2001]. Methylene blue (MB) and methyl violet are two common dyes that have been shown to induce harmful effects on living organisms during short periods of exposure [Hameed et. al., 2009]. Oral ingestion of MB results in a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis. The accidental consumption of large dose induces abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturation, and methemoglobinemia [Yasemin et. al., 2006]. Inhalation of methyl violet may cause irritation to the respiratory tract, vomiting, diarrhea, pain, headaches, and dizziness; long-term exposure may cause damage to the mucous membranes and gastrointestinal tract [Allen & Koumanova, 2005]. The majority of dyes

in this class are synthetic and usually composed of aromatic rings, which makes them carcinogenic and mutagenic [Ghosh & Bhattacharyya, 2002. Chen et. al., 2003]; they are inert and non-biodegradable when discharged into waste streams [Mittal & Gupta, 1996, Seshadri et. al., 1994]. With the social and economic development, the environmental consciousness of citizens and governing agencies was enhanced. Environmental pollution issues have garnered a considerable amount of attention throughout the world [Renmin et. al., 2005]. MB is a good representative of organic dyes that are difficult to degrade and substantially damage the environment due to their toxicity and dark color [Ho et. al., 2005].

Since carbon nanotube (CNT) was first discovered by S. Iijima in 1991, it has become an academic research subject of great interest [Olson, 1994]. CNT is the thinnest tubular structure humans can presently fabricate. It is lightweight and has high strength, high toughness, flexibility, high surface area, high thermal conductivity, and good electric conductivity and is chemically stable [Baughman et. al., 2002, Thostenson et. al., 2001, Banerjee et. al., 2005]. To fully exploit the superior mechanical, electrical and optical properties of multi-walled carbon nanotube (MWCNT), dispersion and adhesion to a polymeric matrix is a key issue [Iijima, 1991]. Both the dispersibility and matrix adhesion of MWCNT can be improved either by covalent or noncovalent functionalization. For covalent functionalization, several approaches studied, each having its advantages and drawbacks; examples of such methods include wet chemical methods with typical treatment times of up to 24 h [Sahoo et. al., 2010, Liu et. al., 1998, Chen et. al., 1998], treatment in air at elevated temperatures [Tsai et. al., 2010, Ajayan et. al., 1993], by ozone oxidation [Ago et. al., 1999, Mawhinney et. al., 2000] and treatment with low-pressure plasmas [Simmons et. al., 2006, Tseng et. al., 2006, Chen et. al., 2010, Zschoerper et. al., 2009].

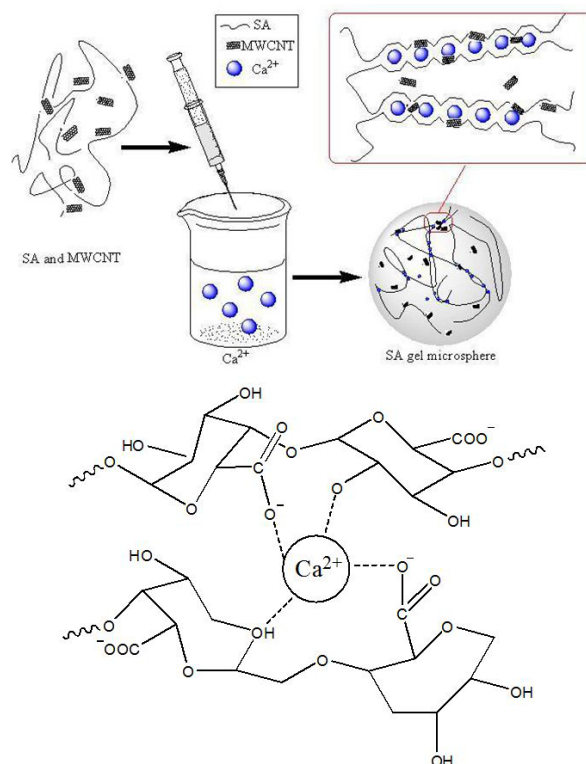
Alginate is a collective term for a family of exopolysaccharides produced mainly by brown seaweeds. It has been widely used in the food, biomedical, pharmaceutical, and sewage-treatment industries, preferentially as sodium alginate due to its solubility in cold water. In molecular terms, alginate is composed of (1–4)-linked  $\beta$ -D-mannuronic acid (M) unbranched binary copolymer and  $\alpha$ -L-guluronic acid (G) monomer residue, constituting M-, G-, and MG sequential block structures [Chen et. al., 2009]. Most applications that use alginate are based on its gel-forming ability through cation binding; the transition from water-soluble sodium alginate (SA) to water insoluble calcium alginate, for example. Divalent cations preferentially bind toward the G-block rather than the M-block [Moe et. al., 1995, Braccini et. al., 1999]. The composition of monomers and their sequential character (i.e., blackness) affects the gelatin behavior of alginate. In the presence of  $\text{Ca}^{2+}$ , G-rich samples generally form hard and brittle gels while M-rich samples form soft and elastic gels [Braccini & Perez, 2001, Courtois et. al., 1993, Thakur et. al., 1997, Pe'rez et. al., 1996]. The “egg-box” model has been accepted as a general model to describe gel formation [Morris et. al., 1978, Thom et. al., 1985]. Alginate is an excellent polymer flocculant and has been widely used in wastewater treatment.

This study reports for the first time the effect of the carboxylation method on CNT structure and property. The results can be used as reference for selecting the carboxylation method. Furthermore, the applicability of a new adsorbent, SA and MWCNT and the SA/MWCNT composite, for the sorption of MB dyes from an aqueous solution were investigated.

## 2. Experimental

### 2.1. Materials and methods

The SA, MB, and MWCNT were used as received from Fuchen Chemical Reagents Factory, Tianjin, China and Nanotechnologies Port Co., Ltd., Shenzhen, China. The MWCNTs were treated with a mixture of sulfuric and nitric acid under ultrasonic vibration, as seen in Table 1. According to the series reaction time in Table 1, the optimized ratio of the MWCNT to acid mixture is 3:1 by volume. Ultrasonic treatment was applied for the duration of varying reaction times. Filtration was conducted with a micropore filter and sand core filter. Pure de-ionized water (pure DI water) was used to rinse the filtrate until the pH of the aqueous solution was neutral. The compositions of the SA, MWCNT, and SA/MWCNT series specimens prepared in this study are summarized in Table 2. Ten milliliters of an aqueous solution of SA/MWCNT was added drop-wise to 50 mL of calcium chloride (10%, w/v) aqueous solution for 20 min, followed by the sampling of supernatant at the specified time intervals. The gel particles were pre-consolidated under a pressure of 8–30 kPa in a consolidation cell with an inner diameter of 2.0–3.0 mm to produce a packed gel bed to determine their expression characteristics. The schematic evolution of the SA and MWCNT in the microsphere, as a function of the calcium chloride, is shown in Figure 1. Other supplementary agents were of analytical grade (purity > 99.8 mass%) and all solutions were prepared with double distilled water.



**Figure 1.** The preparation process of the SA/MWCNT composite gel beads.

A-series reaction group	Mixed-acid treatment time (h)	Hydrogen peroxide treatment time (h)	B-series reaction group	Mixed-acid treatment time (h)	Hydrogen peroxide treatment time (h)
A0	0	0	B0	0	0
A1	1	0	B1	1	0.5
A2	2	0	B2	2	1
A3	4	0	B3	4	2
A4	6	0	B4	6	3
A5	8	0	B5	8	4

Table 1. Formulation for CNT carboxylation.

Sample		SA (%, w/v)	MWCNT (%, w/v)	CaCl <sub>2</sub> (%, w/w)
0#	SA <sub>0</sub> MWCNT <sub>0</sub>	0	0	0
1#	SA <sub>2</sub> MWCNT <sub>0</sub>	2	0	10
2#	SA <sub>2</sub> MWCNT <sub>0.03</sub>	2	0.03	10
3#	SA <sub>2</sub> MWCNT <sub>0.06</sub>	2	0.06	10
4#	SA <sub>2</sub> MWCNT <sub>0.09</sub>	2	0.09	10
5#	SA <sub>2</sub> MWCNT <sub>0.12</sub>	2	0.12	10
6#	SA <sub>2</sub> MWCNT <sub>0.15</sub>	2	0.15	10

Table 2. The composites of SA/MWCNT series samples.

2.2. MWCNT dispersed polarity

Six small reagent bottles were filled with 6 mL pure DI water, 4 mL toluene and a small amount of MWCNT derived as shown in Table 1. They were ultrasonically treated for 0.5 h, and then, after the solution was stored for 12 h, they were recovered and observed.

2.3. Particle size analysis

The particle size analysis measurements of MWCNT and modified MWCNT series specimens were recorded using a Dandong Bettersize Instruments Ltd. BT-9300H at 25°C and 50% relative humidity, wherein six scans with a size range of 0.1–340 μm were collected during each data measurement. Particle size analysis samples of powder specimens were collected using approximately 15 mL pure DI water and a small amount of MWCNT derived as shown in Table 1.

## 2.4. Adsorption property

All sorption measurements were performed by batch type with 50 mL of MB solution in a shaking incubator to form a final concentration of 50 mg/L ( $A_{665\text{ nm}} = 2.9966$ ) at room temperature for 3 h. The equilibrium MB concentration was measured by means of double beam ultraviolet–visible spectroscopy (Shanghai Precision & Scientific Instrument Co., Ltd, UV762, China), and the pH values of the solution were measured using a pH meter (Shanghai Yulong Instrument Co., Ltd., PHS-3 C, China) with a calomel and glass electrode (E201-9). The dye decolorization percentage was defined as follows:

$$\text{Decoloration percentage(\%)} = (A_0 - A) / A_0 \times 100\% \quad (1)$$

where  $A_0$  is the dye absorbance of the control specimen,  $A$  is the dye absorbance of the reacted sample.

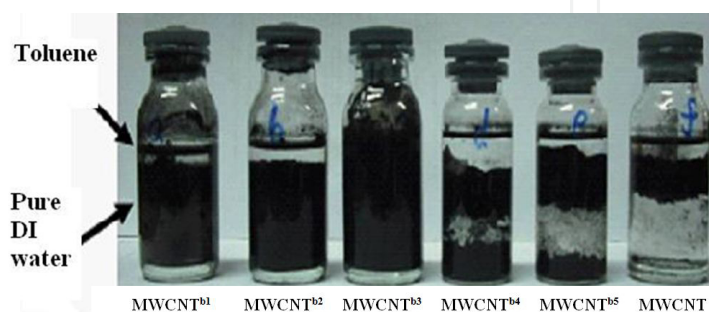
## 2.5. Electrical conductivity

To understand the electrical conductivity properties of MWCNT in SA specimens dispersed in MB solution, the electrical conductivity of the SA and SA/MWCNT solutions were measured at 25°C and 50% relative humidity using a conductivity meter (LIDA Instrument Factory, DDS-12A, China).

## 3. Results and discussion

### 3.1. Carbon nanotube dispersed polarity

A typical photograph of the polarity of MWCNT and modified MWCNT specimens is shown in Fig. 2. Fig. 2 shows the dispersion of the modified MWCNT in aqueous and organic solvent solutions after being exposed to the treatments highlighted in Table 1 and then left undisturbed for 12 h. The figure shows that in the six groups of MWCNT, except the unmodified carbon nanotube, there always exists an interface of two phases that cannot be dissolved in one another. All five of the other groups show different extents of dispersion. MWCNT<sup>b3</sup> shows the most stable dispersion in aqueous phase; even after being aged for a week, it still maintained the state seen in Fig. 2.

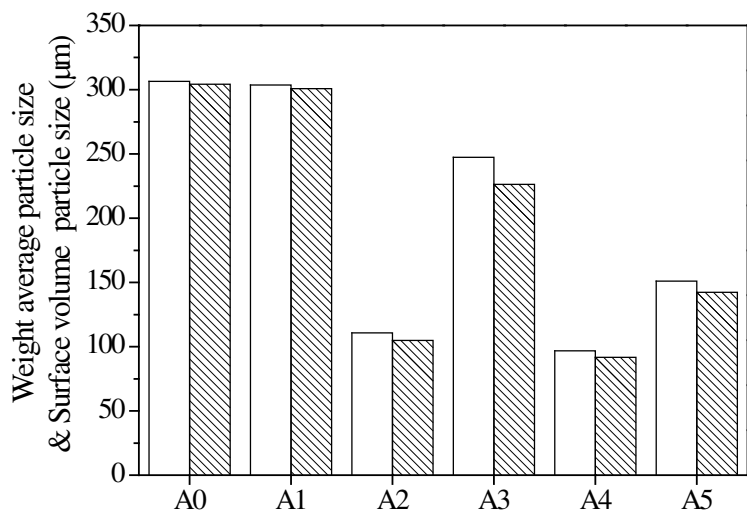


**Figure 2.** Photograph depicting the polarity of pure MWCNT specimens.

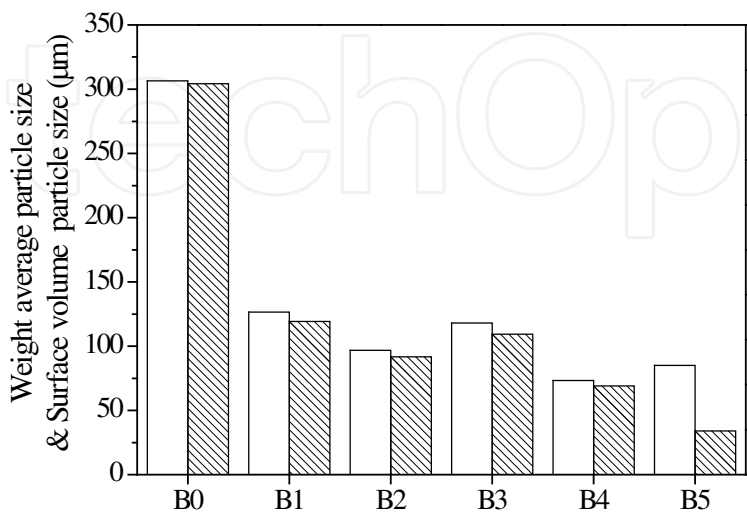


3.2. Particle Size Analysis

Particle size analysis was conducted on A-series and B-series of carboxylated MWCNT. Figs. 3 and 4 show that as carboxylation reaction time increases the extent of carbon nanotube shortening is increased; this is particularly true for the B-series, where the mixed-acid, hydrogen peroxide, and ultrasonic treatment times were all shortened. The B-series samples are much shorter than the A-series samples of MWCNT treated only with mixed-acid and ultrasonic treatment. This finding further corroborates the FT-IR results. With longer carboxylation reaction times the MWCNT is more severely damaged, inducing greater rupture on the C–C bond of the CNT. The higher activity at MWCNT ends facilitates bonding with free O and H from water or solution and the formation of carboxyl groups on the fracture site, increasing the functionalized carboxyl groups and the extent of MWCNT carboxylation.



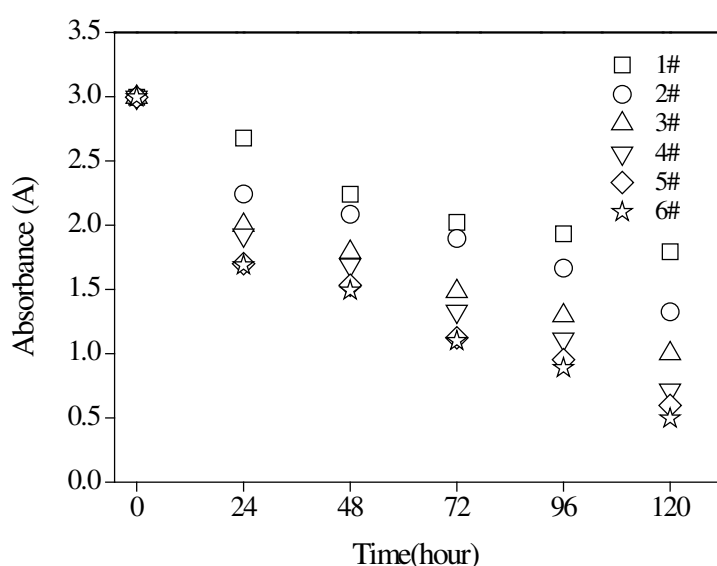
**Figure 3.** The A-series of MWCNT specimens on weight average particle size (white column) and surface volume particle size (slash column) measured at 25°C.



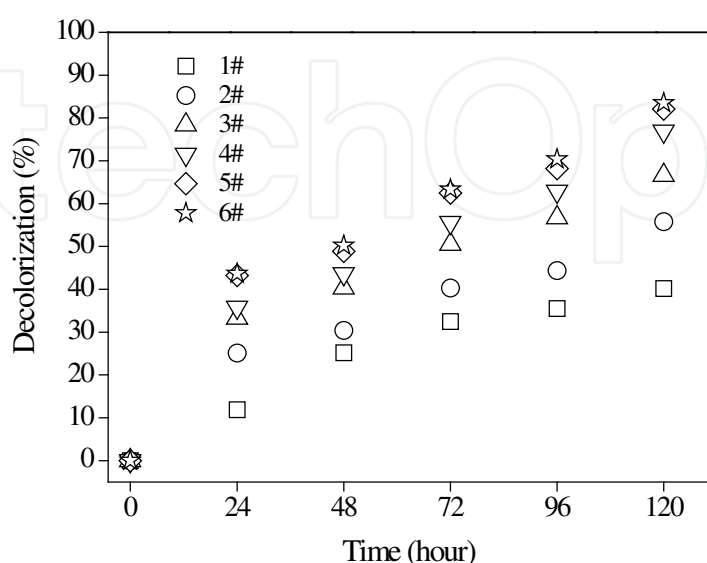
**Figure 4.** The B-series of MWCNT specimens on weight average particle size (white column) and surface volume particle size (slash column) measured at 25°C.

### 3.3. Adsorption property

As shown in Figs. 5, 6, and 7, the absorption of MB increased with time. The decolorization of sample 1 (SA<sub>2</sub>MWCNT<sub>0</sub>) reached 40.16% after 120 h, meaning that SA itself has the ability to absorb MB. Compared with sample #1, the decolorizations of 2#, 3#, 4#, 5#, and 6# ordered by increasing content of MWCNT, were 55.78, 66.62, 76.9, 82.06, and 83.46%, respectively, when tested under the same conditions. This trend of increased decolorization with increased MWCNT concentration is attributed to the fact that the surface of MWCNT has substantial amounts of carbonyl that reacted with MB (see Fig. 8). Another reason for this decolorization may be due to the large specific surface area of MWCNT that greatly affects adsorption ability. Voids present in the MWCNT may also favor of the adsorption of MB.



**Figure 5.** Absorbance of MB by SA/MWCNT microsphere, determined at 25°C.

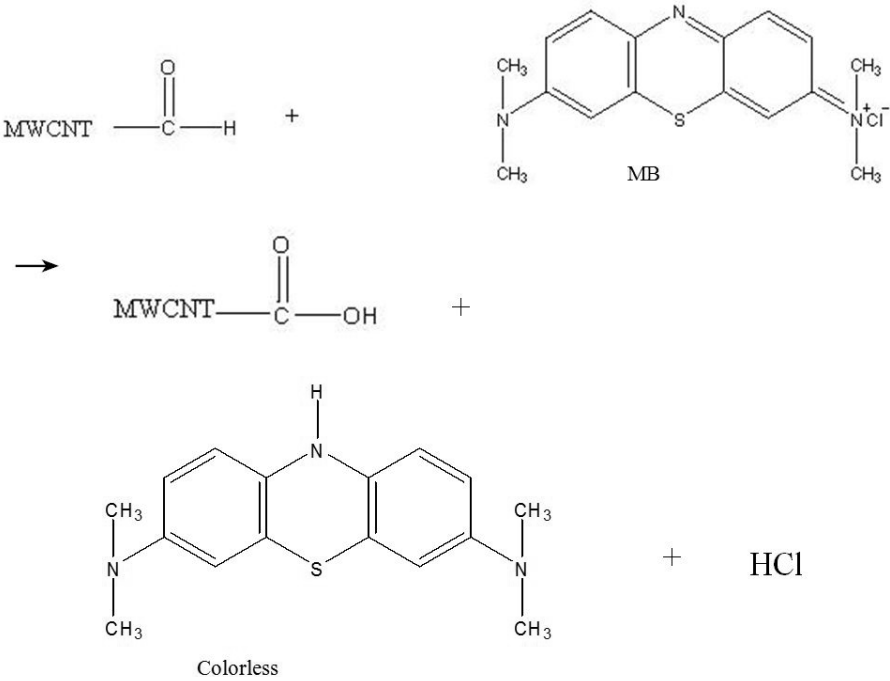


**Figure 6.** Decolorization of MB by SA/MWCNT microsphere determined at 25°C.



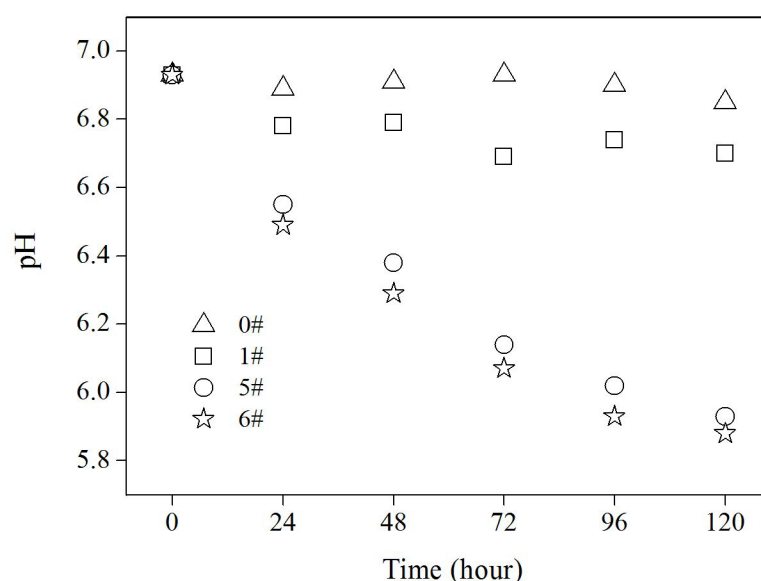


**Figure 7.** The photograph of MB absorption by different amounts of MWCNT.



**Figure 8.** Reaction of MB by SA/MWCNT microsphere determined at 25°C.

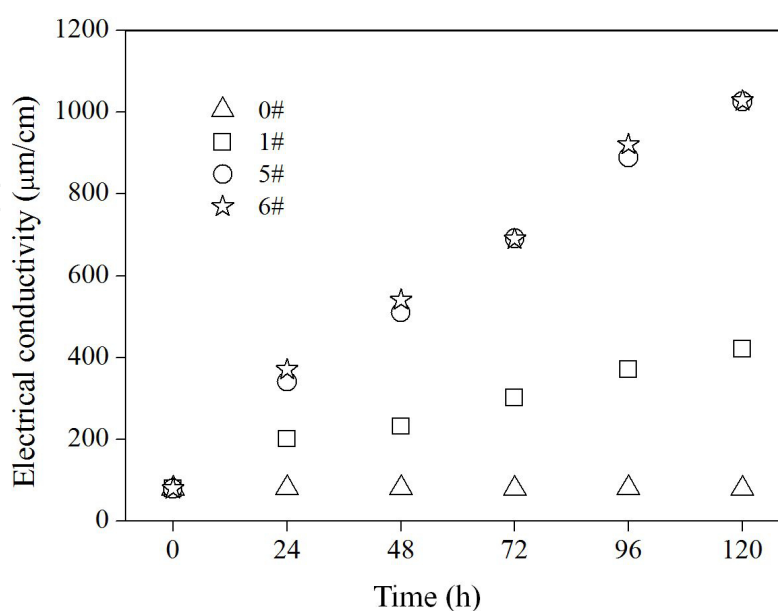
The pH values decreased appreciably in samples 5# and 6# over the course of 120 h. The reason for this decrease may be the same as the reasons for decolorization previously mentioned (see Fig. 9), but the pH value of the original sample (50 mL of MB solution) was virtually unchanged. The reaction generated much more HCl that decreased the pH values, but the reaction rate eventually diminished after 120 h because there was less HCl generated and the adsorption of MWCNT surfaces was also nearly complete.



**Figure 9.** pH values of MB by SA/MWCNT microsphere determined at 25°C.

### 3.4. Electrical conductivity

The electrical conductivity was initially fixed at 79.3  $\mu\text{S}/\text{cm}$  for the original sample, but increased considerably with increasing reaction time. The electrical conductivity of samples 5#, 6# increased sharply over the course of 120 h, but the electrical conductivity of the original sample (50 mL of MB solution) remained virtually unchanged, indicating that the original sample was stable.



**Figure 10.** Electrical conductivity of MB by SA/MWCNT microsphere determined at 25°C.

## 4. Conclusions

This study effectively analyzed the adsorption of MB using gel beads prepared by sol-gel with SA and MWCNT. The formation conditions and mechanism of adsorption of the gel beads were also discussed. The decolorization of MB showed that the stability and reusability of SA/MWCNT could prove potentially advantageous in wastewater treatment.

## Author details

Fang-Chang Tsai<sup>1\*</sup>, Ning Ma<sup>1</sup>, Lung-Chang Tsai<sup>2</sup>, Chi-Min Shu<sup>2</sup>, Tao Jiang<sup>1</sup>, Hung-Chen Chang<sup>3</sup>, Sheng Wen<sup>4</sup>, Chi Zhang<sup>1</sup>, Tai-Chin Chiang<sup>2</sup>, Yung-Chuan Chu<sup>2</sup>, Wei-Ting Chen<sup>2</sup>, Shih-Hsin Chen<sup>5</sup>, Han-Wen Xiao<sup>1</sup>, Yao-Chi Shu<sup>6</sup> and Gang Chang<sup>1</sup>

\*Address all correspondence to: tfc0323@gmail.com

1 Ministry of Education Key Laboratory for the Green Preparation and Application of Functional Materials, Faculty of Materials Science and Engineering, Hubei University, P. R. China

2 Department of Safety, Health, and Environmental Engineering, National Yunlin University of Science and Technology, Douliou, Yunlin, Taiwan ROC

3 Department of Chemical and Materials Engineering, National Chin-yi University of Technology, Taichung, Taiwan ROC

4 Faculty of Chemistry and Materials Science, Hubei Engineering University, P. R. China

5 Department of Food Science, National I-Lan University, I-Lan, Taiwan ROC

6 Department of Cosmetic Applications & Management, Lee Ming Institute of Technology, Taipei, Taiwan ROC

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