



Title	A novel adsorbent obtained by inserting carbon nanotubes into cavities of diatomite and applications for organic dye elimination from contaminated water
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Citation	Journal of Hazardous Materials, 177(1-3), 138-145 <a href="https://doi.org/10.1016/j.jhazmat.2009.12.007">https://doi.org/10.1016/j.jhazmat.2009.12.007</a>
Issue Date	2010-05-15
Doc URL	<a href="https://hdl.handle.net/2115/42973">https://hdl.handle.net/2115/42973</a>
Type	journal article
File Information	JHM177-1-3_138-145.pdf



**A novel adsorbent obtained by inserting carbon nanotubes into cavities of diatomite and applications for organic dye elimination from contaminated water**

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## **Abstract**

A novel approach is described for establishing adsorbents for elimination of water-soluble organic dyes by using multi-walled carbon nanotubes (MWCNTs) as the adsorptive sites. Agglomerates of MWCNTs were dispersed into individual tubes (*dispersed-MWCNTs*) using sodium *n*-dodecyl itaconate mixed with 3-(N,N-dimethylmyristylammonio)-propanesulfonate as the dispersants. The resultant *dispersed-MWCNTs* were inserted into cavities of diatomite to form composites of diatomite/MWCNTs. These composites were finally immobilized onto the cell walls of flexible polyurethane foams (PUF) through an *in situ* PUF formation process to produce the foam-like CNT-based adsorbent. Ethidium bromide, acridine orange, methylene blue, eosin B, and eosin Y were chosen to represent typical water-soluble organic dyes for studying the adsorptive capabilities of the foam-like CNT-based adsorbent. For comparisons, adsorptive experiments were also carried out by using agglomerates of the sole MWCNTs as adsorbents. The foam-like CNT-based adsorbents were found to have higher adsorptive capacities than the CNT agglomerates for all five dyes; in addition, they are macro-sized, durable, flexible, hydrophilic and easy to use. Adsorption isotherms plotted based on the Langmuir equation gave linear results, suggesting that the foam-like CNT-based adsorbent functioned in the Langmuir adsorption manner. The foam-like CNT-based adsorbents are reusable after regeneration with aqueous ethanol solution.

*Keywords:* Carbon nanotubes, diatomite, polyurethane foam, adsorbent, water-soluble organic dye

## **1. Introduction**

Dyes typify a class of colored chemicals long used in textile, leather, paper, plastic, and the other industries. Wastewaters and/or effluents discharged from these industrial practices often contain a certain amount of dyes, especially water-soluble, organic dyes, because of the inability to completely remove the highly water-soluble dyes using common coagulation processes. Water-soluble organic dyes, especially compounds with aromatic backbones [1], are suspected carcinogens and known to exert potent acute and/or chronic effects on exposed organisms, depending on exposure time and dye concentration. The water-soluble organic dyes can also adsorb/reflect sunlight, which can inhibit the growth of bacteria to levels sufficient to biologically degrade impurities. Moreover, the human eye can easily detect water-soluble organic dyes, resulting in aesthetic contamination even at very low concentrations.

Elimination of residual water-soluble organic dyes from wastewaters discharged from industrial colorants is therefore important to avoid possible environmental contaminations by dyes. Physical adsorption, because of its low cost, high efficiency, easy handling, wide variety of adsorbents, and high stabilities toward the adsorbents, has become the mostly widely used method for eliminating dyes from wastewaters. Meanwhile, other methods, such as solvent extraction [2], photocatalytic degradation [3], and biodegradation [4], have also demonstrated high potential for applications.

Carbon-based materials typify a class of significantly and widely used engineering adsorbents. Using new and advanced carbon-based materials as the adsorbents often yields a physical adsorption system with high adsorptive capabilities. In recent years, efforts targeting adsorbent development have turned to nano-structured carbon-based materials because of their extraordinary mechanical, electrical, thermal, and structural

properties. Carbon nanotubes (CNTs), including both the multi-walled types [5] and the single-walled types [6, 7], represent a fascinating new member in the family of carbon-based materials. CNTs are cylindrically shaped, graphite-like,  $sp^2$ -bonded, entirely carbon materials. Their large specific surface areas and sharper curvatures together with their high thermal and chemical stabilities make them ideal for application to the adsorption of pollutant chemicals, especially chemicals with aromatic backbones.

Two major difficulties have arisen with the use of CNTs for adsorption applications. Immobilization is an initial problem, which is commonly overcome using the traditional packing technique; for instance, by packing the agglomerates of multi-walled CNTs (MWCNTs) into a column. A column packed with MWCNTs can provide a flow system for continuously treating the liquid and/or gaseous effluents, but such a system often requires a high-pressure pumping system, which in turn diminishes the overall treating capacity of the adsorptive system. To overcome this difficulty, in earlier studies, we used cross-linked alginate hydrogels to encapsulate MWCNTs to create large-sized CNT-based adsorbents (> 400  $\mu$ m). This kind of CNT-based adsorbent could absorb chemical pollutants with the simple addition of the beads to the wastewaters [8], without requiring a high-pressure pumping system. However, the capability of the cross-linked alginate hydrogels for encapsulating MWCNTs was poor (<0.1 wt %), and they still exhibited low mechanical strength.

Enlargement of the effective surface areas of CNTs has been another important step in producing CNT-based adsorbents with high adsorptive efficiency. CNTs, because of the high aspect ratio of each tube and the strong van der Waals attractions among the tubes, often occur as large-sized agglomerates (often up to few mm) of many individual tubes. Adsorption of chemicals of higher molecular weights, such as the

water-soluble organic dyes, occurs mainly over the outermost surfaces of the CNT agglomerates. In other words, the innermost tubes often make no contribution to the adsorption of such chemicals. Dispersion of the agglomerates of CNTs into individual tubes can maximize the adsorptive surfaces; however, difficulties persist in keeping the CNTs in the individual forms while the tubes are packed or immobilized.

In this study, a novel approach was established for the creation of a CNT-based adsorbent with high adsorptive efficiency and high mechanical strength. This goal was achieved by using diatomite (diatomaceous earth) as a micro-reverser (container of micro-size) and polyurethane polymers as binders. The agglomerates of MWCNTs of the chemical vapor deposition (CVD) products were first dispersed into individual tubes (designated here as *dispersed-MWCNTs*) in water using sodium *n*-dodecyl glyceryl itaconate, an anionic type of surfactant, used in combination with 3-(*N,N*-dimethylmyristylammonio)-propanesulfonate, a zwitterionic type of surfactant, as the dispersant. These *dispersed-MWCNTs* were then packed into the cavities of diatomite.

Diatomite is a naturally occurring clay from geological deposits composed predominantly of the fossilized skeletons of unicellular organisms, particularly diatoms. Because of its porous morphologies, diatomite has long been applied as a filter aid, filler, insulator, and catalyst support. Chemically modified diatomite also can eliminate water-soluble organic dyes, such as methylene blue, but naturally occurring diatomite has a lesser ability to absorb these dyes [9]. To the best of our knowledge, this study describes the first use of diatomite as the micro-container for MWCNTs maintained in their individual forms.

The resulting diatomite/MWCNT composites were finally immobilized on the cell walls of polyurethane foams (PUF) using the diatomite/MWCNT as additives during

PUF formation for preparing a foam-like, ternary type of adsorbent for adsorption of water-soluble dyes.

## **2. Experimental**

### **2.1. Materials**

Powders of agglomerates of MWCNTs with loose agglomerate sizes of 0.1–1 mm (trade name, Baytubes C150P) were purchased from Bayer MaterialScience (Germany). Wall number was 3 – 15; outer diameter distribution, 5 – 20 nm; and inner diameter distribution, 2 – 6 nm, as recommended by the manufacturer. Typical water-soluble, organic dyes, ethidium bromide, acridine orange, methylene blue, eosin B, and eosin Y were purchased from Acros Organic (New Jersey, USA). Table 1 gives the molecular structures together with other information regarding these dyes.

Diatomite was obtained from Eagle-Picher Filtration & Minerals, Inc. (USA, MW-27; average particle diameter, 13.0  $\mu\text{m}$ ; bulk specific gravity, 0.19  $\text{g}/\text{cm}^3$ ; brightness, 90; and pH 10; as recommended by the manufacturer). The specific area is found to be 1.4  $\text{m}^2/\text{g}$  based on the Brunauer-Emmett-Teller (BET) method.

NB-9000B, used as the binder for preparing the flexible, foam-type of the ternary adsorbent, was provided by INOAC Corporation (Nagoya, Japan).

Spectrophotometric measurements of the contents of the dyes were carried out using the UV-Vis-NIR spectrophotometer V570 (Jasco, Inc., Japan) with a scan rate of 10–4000  $\text{nm}/\text{min}$  and a spectral resolution of 0.025 – 2  $\text{nm}$ .

### **2.2. Preparation of *dispersed*-MWCNTs**

Sodium *n*-dodecyl itaconate, an anionic surfactant that serves as a dispersant, was synthesized in the laboratory by essentially the same procedures as described in previous reports [10]. 3-(*N,N*-Dimethylmyristylammonio)-propanesulfonate, a zwitterionic surfactant that serves as a wetting agent, was obtained from Fluka (Germany). The as-received agglomerated MWCNTs were dispersed into individual tubes, namely, the *dispersed*-MWCNTs, in water, through the following steps. Briefly, 26 g of the CNT powders were introduced into 2000 mL of an aqueous solution containing 5 g of 3-(*N,N*-dimethylmyristylammonio)-propanesulfonate, to prepare the raw MWCNT suspension. This suspension was then used as the precursor for preparing the *dispersed*-MWCNTs by adding 10 g of sodium *n*-dodecyl itaconate as the dispersant. Three essential strategies are involved in the preparation of the *dispersed*-MWCNTs, as follows. (i) Wetting of MWCNTs: Air and moisture were displaced from the surfaces of the CNT aggregates by replacing them with the wetting agent. This objective was accomplished in the process of preparing the raw MWCNT suspensions, and the best wetting efficiencies were obtained using 3-(*N,N*-dimethylmyristylammonio)-propanesulfonate. (ii) Grinding of the “wetted CNT aggregates”: CNT aggregates, after being well wetted by the wetting agent, were easily dispersed into individual tubes by very mild mechanical shear forces through the use of a continuously operating bead-mill system. (iii) Addition of a certain amount of anionic surfactant: The addition of anionic surfactant, 10 g of sodium *n*-dodecyl itaconate, in this study, substantially enhanced the stability of the MWCNT suspension. Our MWCNT suspensions were found to be stable exceeding 18 months. This was monitored by measuring the mean diameter of MWCNTs in the suspensions using a dynamic light scattering size distribution analyzer.

### **2.3. Packing of *dispersed*-MWCNTs using diatomite and fabrication of the foam-like adsorbent**

The diatomite was first washed thoroughly using deionized-water/ethanol (50/50) to eliminate possible impurities, followed by filtration and drying. A total of 100 g of the diatomite was added to 2 L of the *dispersed*-MWCNT suspension containing 1.3 wt% MWCNTs; after shaking gently for 24 h, the mixture was freeze dried to produce the diatomite/MWCNT composites. About 12.5 g of these diatomite/CNT composites, 50 mL deionized water, and 50 g NB-9000B (a polyisocyanate type of pre-polymer of polyurethane foam) were then mixed vigorously to produce the foam-like CNT-based adsorbent. This adsorbent was washed by deionized water and 50% ethanol aqueous solution, and then dried at 80°C before being used for the morphological observation and adsorptive studies.

### **2.4. Adsorptive studies**

The adsorptive experiments were conducted by the addition of approximately 100 mg of the foam-like CNT-based adsorbent to 50 mL of aqueous solutions containing the model dye. The solutions were shaken at 200 rpm for a certain period of time. Fractions of the dye solutions were sampled, and their absorbance was measured using the Jasco V570 UV-Vis-NIR spectrophotometer during the time courses. The content of the dye was calculated using a standard curve based on the Lambert-Beer law.

## **3 Results and Discussion**

### **3.1. Analysis of the *dispersed*-MWCNTs**

Aqueous suspensions containing the *dispersed*-MWCNTs were analyzed using a dynamic light-scattering size-distribution analyzer. Fig. 1 shows a typical result of the averages of five measurements for particle size distributions; the mean volume diameters at 10%, 30%, 50%, 70%, 90%, and 95% of the accumulative curve were 0.0347, 0.0514, 0.0694, 0.0971, 0.1601, and 0.1990  $\mu\text{m}$ , respectively, suggesting that the MWCNTs in the suspensions occurred at the tubular level for dispersion.

Direct evidence showing dispersal of the CNT agglomerates into the tubular level was also observed using scanning electron microscopy (SEM) (Fig. 2).

### 3.2. Packing of the *dispersed*-MWCNTs using diatomite

Fig. 3 shows a typical SEM images; MWCNTs retained/packed into the cavities of the diatomite were observed. A few of the *dispersed*-MWCNTs were also found on the outer surfaces of the diatomite, but most were retained in the cavities. In other words, the diatomite functioned as “micro-cage” in which the *dispersed*-MWCNTs were retained. To our best knowledge, this is the first use of diatomite as the “micro-cage” for packing MWCNTs.

Fig. 4 shows a typical result regarding the measurement obtained using thermogravimetric analysis (TG-A) of the specific content for MWCNTs in the composite of the diatomite/*dispersed*-MWCNTs. The overall content for MWCNTs was found to be 25.6 wt%; for the diatomite, it was calculated from the TG-A curve as 61.7 wt%.

Raman spectroscopic data (Fig. 5) for MWCNTs found in the composite of diatomite/*dispersed*-MWCNTs were identical to those for the as-received MWCNTs. Note that at higher detection sensitivity, three intrinsic peaks between 800 – 1100  $\text{cm}^{-1}$  were observed for the entire diatomite samples; these peaks however were not observed

for MWCNTs and for the diatomite/*dispersed*-MWCNTs, because of the lower detection sensitivity. Moreover, the average value of the BET (Brunauer-Emmett-Teller) specific areas of three measurements for the composite of diatomite/*dispersed*-MWCNTs was found to be 210.3 m<sup>2</sup>/g; which is almost identical to that for the as-received MWCNTs (211.5 m<sup>2</sup>/g). In addition, changes in the adsorption/desorption behaviors for nitrogen were not observed (data not shown). These analytical data suggest that packing of the *dispersed*-MWCNTs into the cavity of the diatomite did not change the nature of the MWCNTs. In other words, the diatomite functioned only as a cage or container of micro-sizes for packing the MWCNTs.

### **3.3. Creation of foam-like CNT-based adsorbents**

Polyurethane pre-polymers were used as the binders to immobilize the diatomite/*dispersed*-MWCNTs. The diatomite used in this study has an average particle diameter of about 13 μm; this size is suitable for immobilizing on cell walls, namely the PUF backbones, by simply adding the diatomite/*dispersed*-MWCNTs during the course of PUF formation. Fig. 6 shows typical SEM observations; diatomite/*dispersed*-MWCNTs successfully immobilized on the cell walls of PUF were observed. As these SEM observations indicate, diatomite was immobilized tightly on the PUF cell walls while the MWCNTs in their cavities were protected from being covered (overlapped) by the polymers. The resultant material is a macro-sized, flexible, foam-like CNT-based material (Fig. 7). MWCNTs involved in this ternary composite were found to be 7.2 wt%, calculated from the TG-A data for the diatomite/*dispersed*-CNT/PUF ternary material (TG-A graph not shown).

### 3.4. Adsorption of the organic, water-soluble dyes

Acridine orange, ethidium bromide, and methylene blue (the cationic type) and eosin B and eosin Y (the anionic type) were used to represent the typical aromatic-backboned, water-soluble, organic dyes for studying the adsorptive capacity of the foam-like, ternary MWCNT-based adsorbent. For comparisons, the adsorption experiments were also performed using (i) the as-received MWCNTs, namely the MWCNT agglomerates; (ii) the MWCNT agglomerates directly immobilized onto the PUF cell walls (PUF/*agglomerated*-MWCNTs, without dispersion and neither the protection using diatomite); and (iii) the *dispersed*-MWCNTs directly immobilized onto PUF cell walls (PUF/*dispersed*-MWCNTs, without protection using diatomite), respectively, as the adsorbents. The net values for MWCNTs for each of these three materials were identical at 7.2 mg, by adjusting the overall weights of the adsorbents. The entire diatomite and PUF (both without containing MWCNTs) were used as the positive controls.

Fig. 8 shows the experimental data on the capacity for adsorption of these five dyes by using the foam-like ternary (PUF/diatomite/*dispersed*-MWCNTs) materials as the adsorbents. The capacities for dye adsorptions were plotted against the time for adsorptions for each dye. Adsorptions reached the adsorption/desorption equilibrium within 30 min for the cationic dyes (acridine orange, ethidium bromide, and methylene blue), while it was about 60 min for the anionic dyes (eosin B and eosin Y). The capacities for dye adsorptions were represented as  $\mu\text{mol}$  of the adsorbed dye per gram of MWCNTs in the foam-like ternary adsorbents, or  $\mu\text{mol-dye/g-CNT}$  (the y axis).

Table 2 summarizes the capacities for dye adsorption for the other types of foam-like adsorbents (the PUF/*agglomerated*-MWCNTs and the PUF/*dispersed*-MWCNTs)

and for the positive controls, together with the data for the ternary adsorbents (PUF/diatomite/*dispersed*-MWCNTs).

Among these three foam-like CNT-based adsorbents, the ternary material, namely, the PUF/diatomite/*dispersed*-MWCNTs, gave the highest capacities for adsorption of these dyes, followed by PUF/*agglomerated*-MWCNTs, and then PUF/*dispersed*-MWCNTs. In other words, insertion of *dispersed*-MWCNTs into the cavities of the diatomite was a practicable method for preventing MWCNTs being covered/overlapped by the polyurethane binders. Furthermore, the adsorptive capacity for PUF/diatomite/*dispersed*-MWCNTs was even higher than that for the entire CNT agglomerates, indicating the PUF/diatomite/*dispersed*-MWCNTs owning a higher adsorptive area than that of the CNT agglomerates.

### **3.5. Reusability of the PUF/diatomite/*dispersed*-MWCNTs**

The PUF/diatomite/*dispersed*-MWCNTs were found to be reusable by regeneration using aqueous ethanol solution (ethanol/water, 50/50) as the regeneration solution in an ultrasonic generator. Fig. 9 shows typical results for methylene blue for three adsorption/regeneration cycles; the adsorbed dye was mostly released after the regeneration, and the capacity for the dye absorption remained unchanged. Similar results were also obtained for the other four dyes.

### **3.6. Behaviors of adsorptions**

Adsorption isotherms were plotted and used for evaluating behaviors of adsorption of the aromatic-backboned, water-soluble, organic dyes by the PUF/diatomite/*dispersed*-MWCNTs. Parameters obtained from the adsorption isotherms give meaningful

insights into both the adsorption behaviors and the surface properties of the adsorbents. In this study, the Langmuir model was used because it fitted well with the experimental data. Expression of the Langmuir model is given in eq. (1):

$$\frac{1}{q_A} = \frac{1}{QK_A} \times \frac{1}{C_A} + \frac{1}{Q} \quad (1)$$

which was derived from the following Langmuir equation:

$$q_A = \frac{QK_A C_A}{1 + K_A C_A} \quad (2)$$

where  $q_A$  is the amount of dyes adsorbed per gram of MWCNTs of the PUF/diatomite/*dispersed*-MWCNTs ( $\mu\text{mol/g}$ );  $C_A$  is the equilibrium concentration ( $\mu\text{mol/l}$ ) of the dyes in aqueous solution;  $Q$  is the theoretical saturation capacity of the monolayer adsorption of the adsorbent ( $\mu\text{mol/g}$ ); and  $K_A$  is the Langmuir constant that reflects the affinity of the adsorptive sites, or of the MWCNTs towards the dyes. Fig. 10 shows the typical adsorption isotherms for the five targeted dyes (plotted based on eq. 2). The adsorptive experiments were carried out at room temperature.

Table 3 summarizes the values for  $K_A$  and  $Q$  together with the coefficients ( $R^2$ ) of the linear Langmuir isotherms (eq. 1) for these five dyes. All of the  $R^2$  values exceed 0.99, suggesting that PUF/diatomite/*dispersed*-MWCNTs adsorbed these dyes in the Langmuir adsorption manner.

Acridine orange showed the largest  $Q$  value, followed by methylene blue, ethidium bromide, eosin Y, and finally eosin B. This order of  $Q$  values was also found in the adsorptive experiments involving the CNT agglomerates as the adsorbent.

In general, the amount of dyes absorbed by MWCNTs will reflect the affinity between the dyes and the MWCNTs. Previous studies have found that molecular geometries and charges (or polarities) of the adsorbates (in this study, the dyes) are the key factors determining interactions and thereby the affinity between the adsorbates and MWCNTs [11 - 15]. First, in this study, the cationic dyes showed a higher propensity to be absorbed by MWCNTs than did the anionic dyes; this fact can be attributed to the electrostatic interactions between the  $\pi$ -electrons of MWCNTs and the positively charged moieties of the cationic dyes. In some cases, this phenomenon is referred to as  $\pi$ - $\pi$  electron-donor (MWCNTs)/acceptor (cationic dyes) interaction [13]. Second, among the cationic dyes, acridine orange is an ideally planar molecule and therefore can be easily absorbed by MWCNTs by  $\pi$  -  $\pi$  stacking interactions between the aromatic backbone of the dyes and hexagonal skeleton of MWCNTs [12, 13]. Methylene blue is also an ideally planar molecule but was absorbed at smaller amounts than was acridine orange; this fact may be due to the unique structure of the central ring of the methylene blue backbone. Ethidium bromide, because of the sterol-hampering effects, was absorbed at the lowest quantities among these three cationic dyes. The  $\pi$  -  $\pi$  stacking interactions led to a chemisorption but in a much weaker manner, which takes place only in a monolayer; additionally, it is reversible only at high temperature. In our study, the regeneration of the adsorbents was conducted using aqueous ethanol solution (ethanol/water, 50/50) as the regeneration solution in an ultrasonic generator; this implies the regeneration of the adsorbed CNTs is difficult.

The pH zero point of charge (pH<sub>ZPC</sub>) of the adsorbent and the pK<sub>a</sub> of the dyes are also important parameters determining the adsorptive capacity of the adsorbent for the dye adsorptions. Experimental data (Fig. 11) indicated that acridine orange and ethidium bromide were sensitive to the pH of the solutions; while methylene blue was less sensitive.

Finally, for the two anionic dyes, eosin Y and eosin B, because of both the  $\pi$ -electrons/negative-charge repulsion and the sterol-hampering effects, they were absorbed at smaller amounts than the cationic dyes. In other words, both the molecular geometry and the charge played important roles in determining the affinity and thereby the capacity for adsorption of the dyes by MWCNTs.

#### **4. Conclusion**

Through packing of the dispersed MWCNTs into the cavities of diatomite followed by the immobilization of the diatomite/*dispersed*-MWCNTs through an *in situ* PUF formation, CNT-based, foam-like, macro-sized, ternary adsorbents were created. It was capable of adsorbing the aromatic-backboned, water-soluble dyes from water, with cationic dyes exhibiting greater adsorption than anionic dyes. The capacity for dye adsorption of the PUF/diatomite/*dispersed*-MWCNTs was higher than for the CNT agglomerates because of the tubes were dispersed into tubular levels for dispersions. Moreover, the PUF/diatomite/*dispersed*-MWCNTs were highly hydrophilic; this provides a desirable yet piratical approach for eliminating dyes from the contaminated water by simply dropping the foam-like, CNT-based adsorbent into the wastewater. The PUF/diatomite/*dispersed*-MWCNTs were also reusable after de-adsorption

(regeneration) with aqueous ethanol solution. Studies are ongoing focusing on the surface properties of the PUF/diatomite/*dispersed*-MWCNTs by using XRD, FT-IR spectra and Zeta potentials.

## **Acknowledgement**

The very helpful comments provided by the reviewers of this manuscript are gratefully acknowledged. This work was supported by funding from Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 18310049).

## Reference

- [1] M.A. Brown, S.C. De Vito, Predicating azo dye toxicity, *Crit. Rev. Environ. Sci. Technol.* 23 (1993) 249-324.
- [2] P. Pandit, S. Basu, Removal of ionic dyes from water by solvent extraction using reversed micelles, *Environ. Sci. Technol.* 38 (2004) 2435-2442.
- [3] M. Karkmaz, E. Puzenat, C. Guillard, J.M. Herrmann, Photocatalytic degradation of the alimentary azo dye amaranth mineralization of the azo group to nitrogen, *Applied Catalysis B: Environ.* 51 (2004), 183-194.
- [4] H. An, Y. Qian, X. Gu, W.Z. Tang, Biological treatment of dye wastewaters using an anaerobic-oxic system, *Chemosphere* 33 (1996) 2533-2542.
- [5] S. Iijima, Helical microtubules of graphitic carbon, *Nature (London)* 354 (1991) 56-58.
- [6] S. Iijima, T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter, *Nature (London)* 363 (1993) 603-605.
- [7] D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls, *Nature (London)* 363 (1993) 605-607.
- [8] B. Fugetsu, S. Satoh, T. Shiba, T. Mizutani, Y.-B. Lin, N. Terui, et al., Caged multiwalled carbon nanotubes as the adsorbents for affinity-based elimination of ionic dyes, *Environ. Sci. Technol.* 38 (2004) 6890-6896.
- [9] M. Al-Ghouti, M.A.M. Khraiseh, M.N.M. Ahmad, S. Allen, Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: A kinetic study, *J. Colloid and Interface Sci.* 287 (2005) 6-13.

- [10] H. Yu, X. Chen, K. Tsujii, B. Fugetsu, Use of ultra-thin cross-linked polymer films for preparation of stable mono-dispersed carbon nanotubes, *Mater. Lett.* 62 (2008), 4050-4052.
- [11] C.H. Liu, J.J. Li, H.L. Zhang, B.R. Li, Y. Guo, Structure dependent interaction between organic dyes and carbon nanotubes, *Colloids and Surfaces A* 313-314 (2008) 9-12.
- [12] W. Chen, L. Duan, D.Q. Zhu, Adsorption of polar and nonpolar organic chemicals to carbon nanotubes, *Environ. Sci. Technol.* 41 (2007) 8295-8300.
- [13] X. Wang, J. Lu, B. Xing, Sorption of organic contaminants by carbon nanotubes: influence of adsorbed organic matter, *Environ. Sci. Technol.* 42 (2008) 3207-3212.
- [14] S. Gotovac, C.M. Yang, Y. Hattori, K. Takahashi, H. Kanoh, K. Kaneko, Adsorption of polyaromatic hydrocarbons on single wall carbon nanotubes of different functionalities and diameters *J. Colloid and Interface Science*, 314 (2007) 18-24.
- [15] C. Hu, S.S. Hu, Surface design of carbon nanotubes for optimizing the adsorption and electrochemical response of analytes, *Langmir* 24 (2008) 8890-8897.
- [16] <http://www.sigmaaldrich.com/catalog/>

Table 1. Chemical structures and some other parameters of the targeted dyes [16].

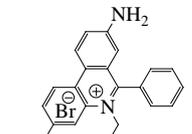
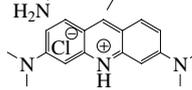
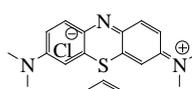
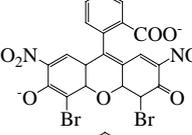
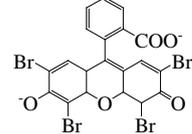
Name	Chemical structure	Molar mass (g mol <sup>-1</sup> )	Color index number	$\lambda_{\max}$ (nm)
Ethidium bromide		394.31	46065	480
Acridine orange		301.82	26115	492
Methylene blue		319.85	52015	663
Eosin B		624.06	45400	514
Eosin Y		691.85	45380	517

Table 2. Capacity ( $\mu\text{mol-dye/g-MWCNTs}$ ) of dye adsorptions for the the agglomerates of the entire MWCNTs (MWCNTs<sup>1</sup>), PUF/agglomerated-MWCNTs (PUF/MWCNTs<sup>1</sup>), PUF/dispersed-MWCNTs (PUF/MWCNTs<sup>2</sup>), PUF/diatomite/dispersed-MWCNTs (PUF/MWCNTs<sup>3</sup>), and the diatomite and PUF (the positive controls), respectively.

Dyes	MWCNTs <sup>1</sup>	PUF/MWCNTs <sup>1</sup>	PUF/MWCNTs <sup>2</sup>	PUF/MWCNTs <sup>3</sup>	Diatomite	PUFs
Acridine orange	394.41	276.13	252.65	421.73	8.45	3.75
Methylene blue	346.88	249.38	177.19	378.38	12.1	4.98
Ethidium bromide	188.4	145.09	110	296.11	2.78	1.65
Eosin Y	158.78	102.43	57.75	234.2	12.3	3.29
Eosin B	137.69	97.93	48.3	202.71	13.7	2.68

Table 3. Coefficients ( $R^2$ ) of the Langmuir isotherms and the  $K_A$  and  $Q_A$  values.

Dyes	$R^2$	$K_A$ (L/ $\mu$ mol)	$Q_A$ ( $\mu$ mol/g)
Acridine orange	0.9836	0.3333	625.00
Methylene blue	0.9972	0.2143	476.19
Ethidium bromide	0.9979	0.0839	384.62
Eosin Y	0.9899	0.1072	270.27
Eosin B	0.9901	0.0937	250.00

## Figures and Captions

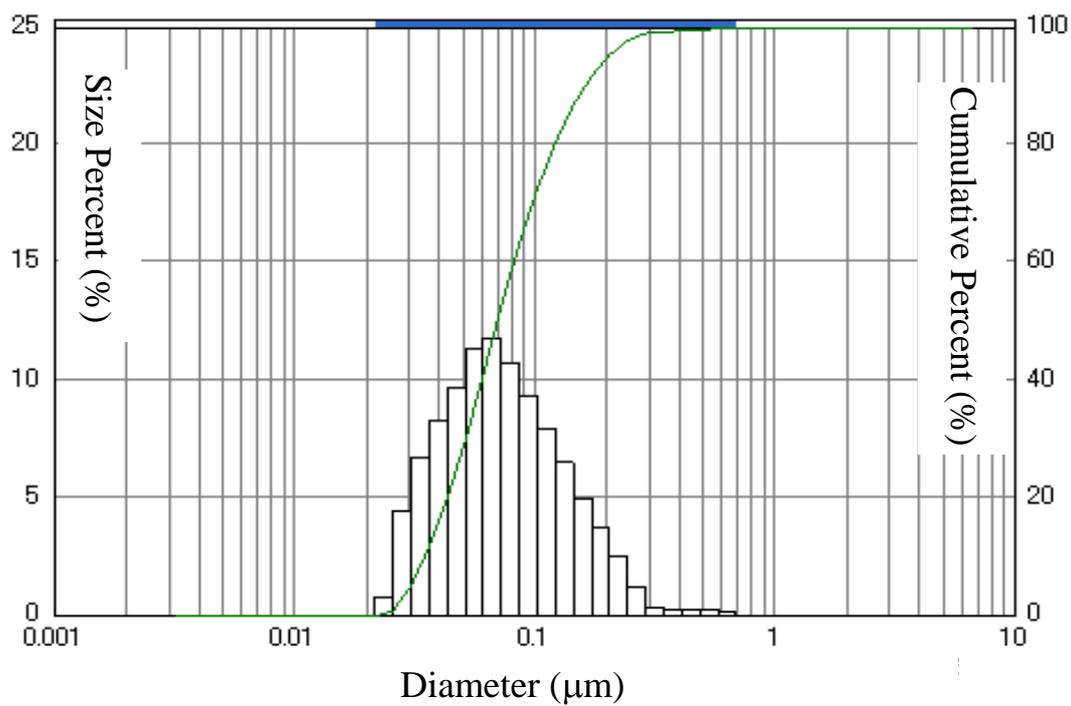


Figure 1. Dynamic light-scattering size distribution of the *dispersed*-MWCNTs in the aqueous suspensions.

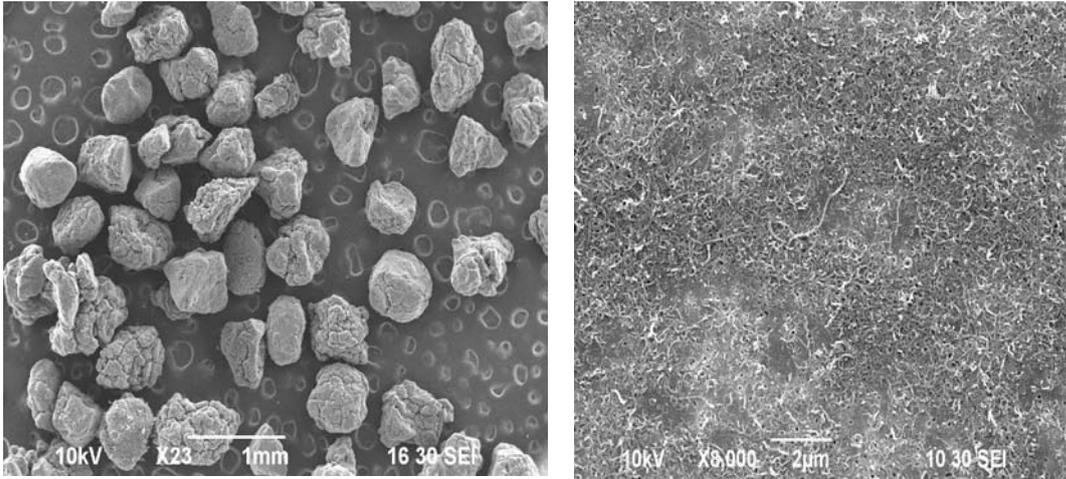


Figure 2. SEM images of the as-received agglomerates of MWCNTs (left) and the agglomerates after being dispersed into the *dispersed*-MWCNTs (right).

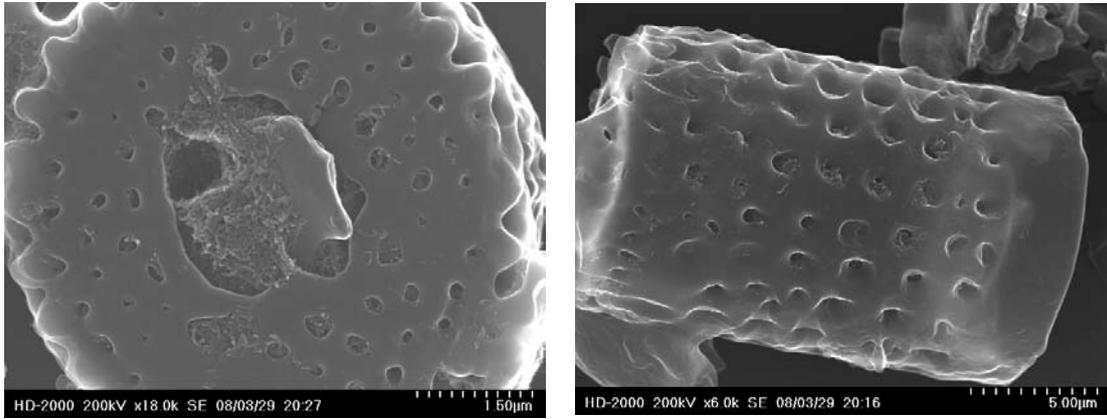


Figure 3. SEM images of the *dispersed*-MWCNTs after being packed into the cavities of the diatomite.

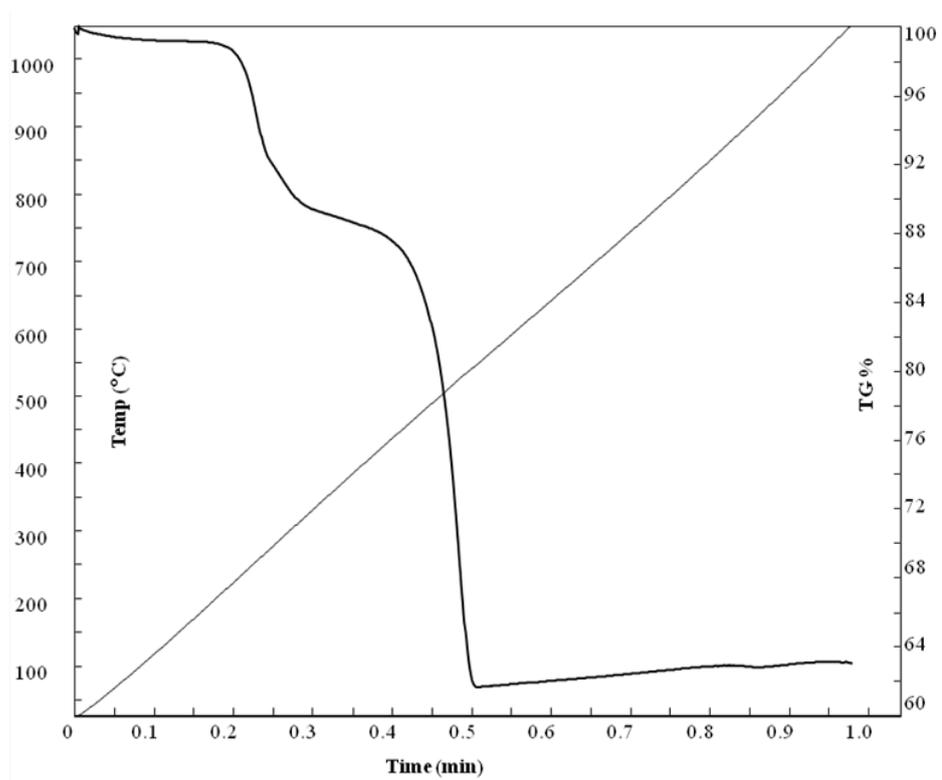


Figure 4. TG-A measurement of the contents of the MWCNTs in the diatomite/*dispersed*-MWCNTs.

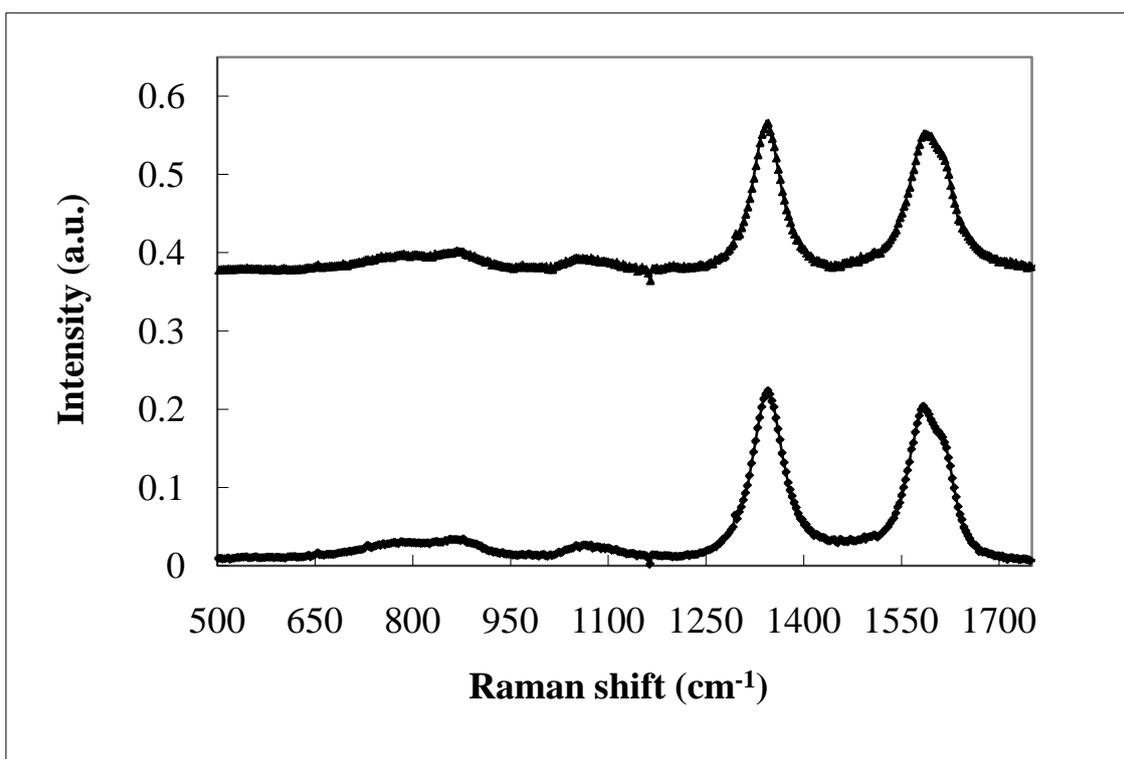


Figure 5. Raman spectroscopies for the as-received MWCNTs (the CNT-agglomerates, bottom) and the *dispersed*-MWCNTs after being packed into the cavities of the diatomite (top)).

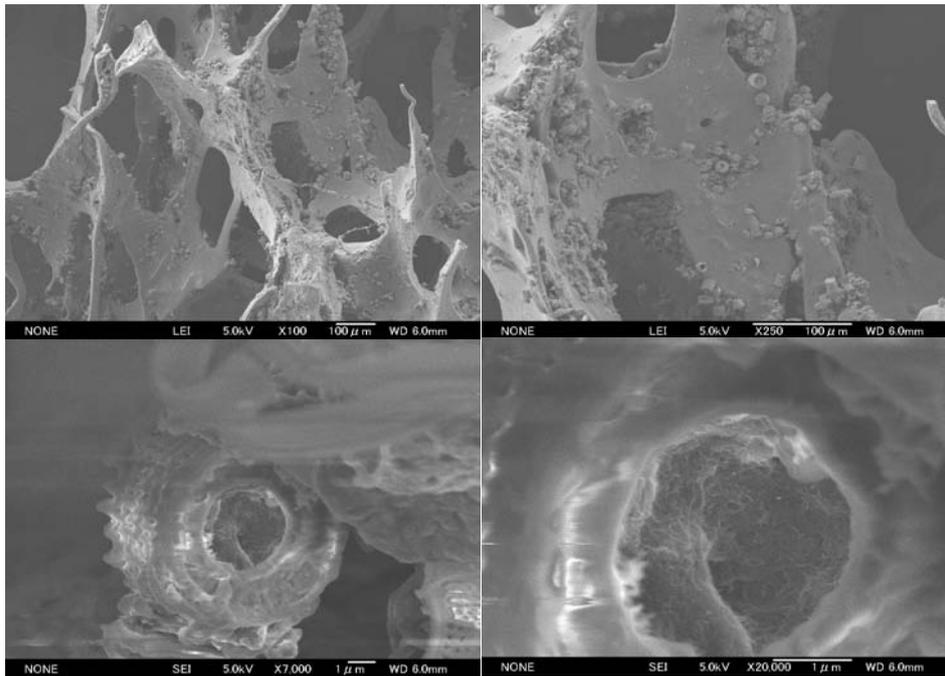


Figure 6. SEM images of diatomite/*dispersed*-MWCNTs after being immobilized on the cell walls of PUFs through *in situ* PUF formation. Scale bars: upper pictures: 100  $\mu\text{m}$ ; lower pictures: 1  $\mu\text{m}$ , respectively.

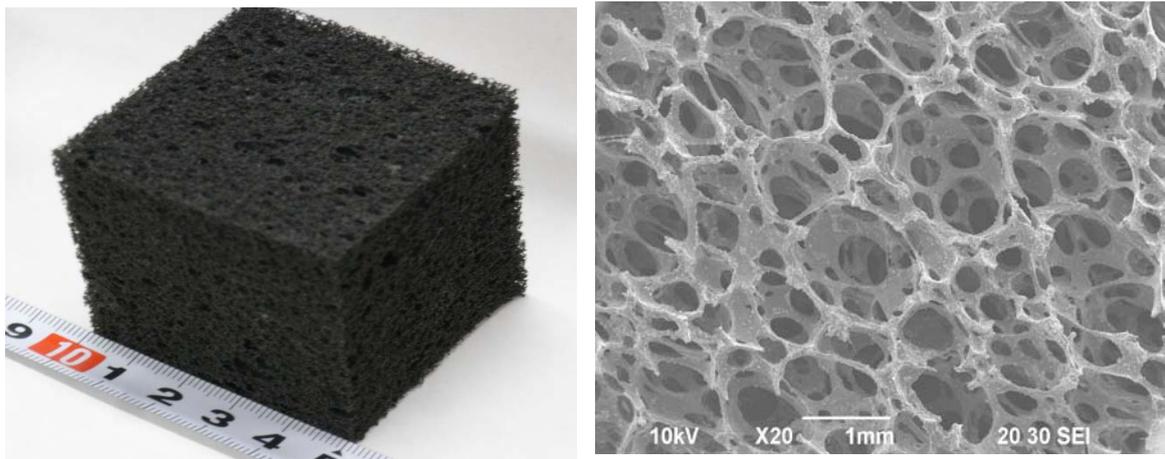


Figure 7. Photo (left) and SEM observation (right) of the macro-sized, foam-like, ternary CNT-based adsorbent.

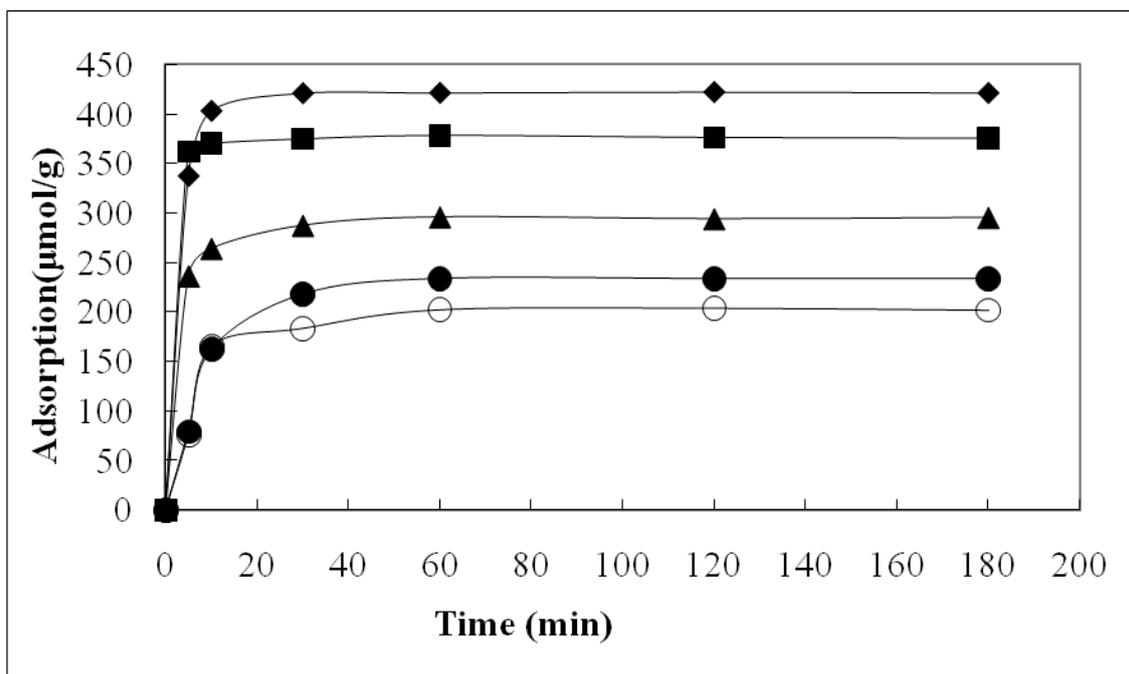


Figure 8. Capacities of the PUF/diatomite/*dispersed*-MWCNTs for adsorption of the targeted dyes of acridine orange (◆), methylene blue (■), ethidium bromide (▲), eosin Y (●), and eosin B (○), respectively.

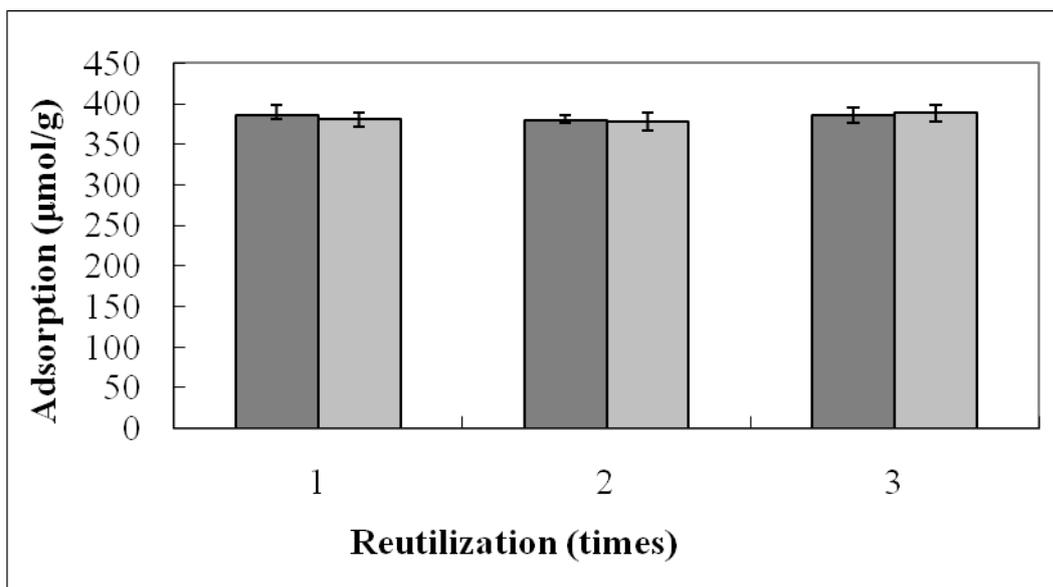


Figure 9. Three cycles of adsorption/desorption for methylene blue using PUF/diatomite/*dispersed*-MWCNTs as the adsorbent.

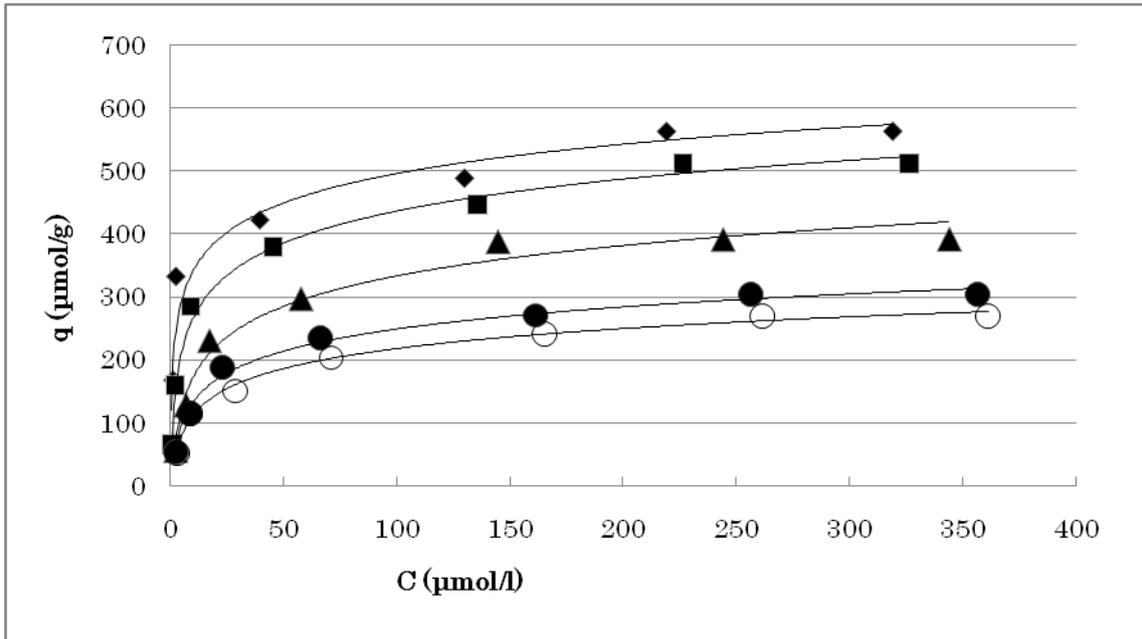


Figure 10. Langmuir isotherms for sorption of the model dyes by the PUF/diatomite/dispersed-MWCNTs. Dyes are acridine orange (◆), methylene blue (■), ethidium bromide (▲), eosin Y (●), and eosin B (○), respectively.

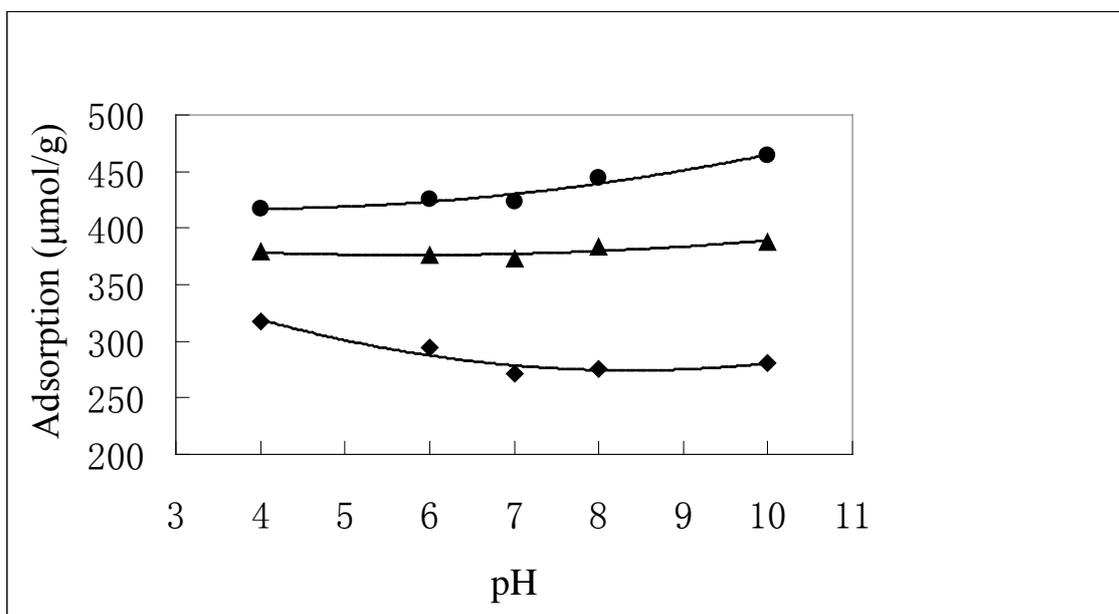


Fig. 11 Effects of solution pH on adsorptive capacity for absorbing the model dyes by the PUF/diatomite/*dispersed*-MWCNTs. Dyes are acridine orange (◆), methylene blue (■), ethidium bromide (▲), respectively.