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# Oil Adsorption and Reuse Performance of Multi-Walled Carbon Nanotubes

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**Abstract**

Multi-walled carbon nanotubes (MWCNTs) have aroused widespread attention as a new type of adsorbents due to their outstanding ability for oil adsorption. In this work, the effects of recycling method, different types oil, metal ions and surfactants on the adsorption capacity and reuse performance of MWCNTs were investigated. The results showed that with the increase of the number of reuse, oil adsorption ability of MWCNTs decreased and stabilized gradually. Through the study on the methods of oil removing from MWCNTs and re-adsorption performance of MWCNTs, it was found that the re-adsorption capacity of incinerated MWCNTs is higher than those extruded ones. This may due to the destruction of the gap between carbon nanotubes during the extrusion process, which leading to lower oil adsorption capacity. The oil adsorption capacity on the extruded MWCNTs increased with the increase of carbon chain length of the oil, while that on the incinerated ones decreased. With the existing of mental ions and surfactant, it was found that the oil adsorption capacity increased with the increasing of ions and surfactant concentration.


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*Keywords*: Multi-walled carbon nanotubes; Oil adsorption performance; reuse performance

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## 1. Introduction

Water plays an important role in oil and gas production, particularly in aging oil fields and unconventional tight-gas, shale-gas, and coal-bed fields where the injection of high pressure water is needed to improve productivity. When the injected water, together with water already in the geological formation, flows back to the surface, it is contaminated with oil droplets and dissolved hydrocarbons from the contact with oil and gas reservoirs [1]. Moreover, the rapidly growing refining, transportation and exploitation of crude oil have led to an increasing risk of oil contamination for water. Oil-contaminated water can cause widespread contamination and severe ecological problems, including nearly irreversible damage to ecological systems, and also represents a great loss of energy resources[2]. Treatment of oil-contaminated water remains a challenge to environmental scientists and technologists. Various techniques have been proposed and used for oil-contaminated water recovery, including physical sorption by porous sorbent materials, mechanical recovery by oil skimmers, in situ burning, physical diffusion (aided by dispersants), and biodegradation[3,4],. Among all the existing techniques used for oil-contaminated water treatment physical sorption is a popular technique because it is cheap, simple and effective [1]. Therefore, much attention has been paid to developing inexpensive, practical sorbents with potential applications in spilled oil clean up. An ideal sorbent material working in water environment should be hydrophobic and oleophilic to render selectivity, and has a high oil sorption rate and capacity [5]. The sorbent materials used for oil-contaminated water clean-up can be classified into three typical groups: synthetic polymers, natural fiber materials and inorganic minerals. Synthetic polymers, such as polyurethane [6], polypropylene and butylrubber [7] have been widely used due to their hydrophobic and oleophilic characteristics. However, their very slow degradability is a major disadvantage. Natural fiber materials usually show relatively low sorption capacities and are mostly hydrophilic, e.g. corn stalk [8], pith bagasse [9], nonwoven wool[10,11] and cotton fibers. The inorganic minerals include vermiculite, exfoliated graphite, sepiolite, zeolites, etc. [2]. Carbon nanotubes (CNTs) have a unique one-dimensional structure, large specific surface area, and are oleophilic and hydrophobic. As sorbent material, carbon nanotubes exhibit excellent adsorption capacity and cyclic compression property [12–17].

However, despite the various mentioned applications of CNTs, there are few reports focusing on using CNTs in the oil-contaminated water recovery. In this paper, the multi-walled carbon nanotubes (MWCNTs), which were synthesized in a fluidized bed reactor, were used as adsorbent. The influence of different types of oil, metal ions and surfactants on the adsorption capacity and reuse performance of the MWCNTs were investigated in this work.

## 2. Experimental and Materials

### *2.1. Materials*

MWCNTs, supplied by Fluidization Laboratory of Tsinghua University, with purity being more than 95%, ID<20nm, the detail preparation method and performance of which were reported by Yu et al. [18] Gasoline, with distillation range of 78-106$^{o}$C;kerosene, with distillation range of 170-240$^{o}$C; diesel oil NO.1, with distillation range of 186-318 $^{o}$C ; diesel oil NO.2, with distillation range of 141-335 $^{o}$C.

### *2.2. Experimental*

In this paper, similar experimental method reported by Fan et al. [19] was used. To investigate the oil adsorption and reusing performances of the MWCNTs, about 0.2 g of MWCNTs was loaded to a 5ml injection syringe (medical equipment), to accomplish the oil adsorption process. And removing of the adsorbed oil is realized through pushing the top of the padding, with a gas pressure of 0.80MPa through a nitrogen gas cylinder or through burning the MWCNTs at 240 $^{o}$C. The oil sorption process of MWCNTs was designed as follows,

(1) 0.2 g MWCNTs were directly put into the injection syringe (5ml), then excess oil (gasoline, kerosene, diesel oil No.1or diesel oil No.2) was added and kept for 2 h.

(2) The syringe was hanged for 2 h in order to drip off the excess oil. The recovery of adsorbed oil from MWCNTs was carried out by squeezing the piston of syringe under the pressure of 0.80MPa until no oil dropped. At this point, the oil remaining in the syringe may be considered as all adsorbed on the MWCNTs. The MWCNTs

sorption capacities were calculated as $Q=m/M$, where $m$ is the weight of the oil absorbed and $M$ is the initial weight of MWCNTs. This cycle of sorption and recovery was repeated several times to determine the recycling performance of MWCNTs.

(3) To compare, heat treatment method was also used to investigate the recycling performance of MWCNTs. Repeat step (1), and then the syringe was hanged for 2 h in order to drip off the excess oil, the total weight designated as $m_1$. After that, put the saturated adsorbing MWCNTs in muffle furnace under 240 $^oC$ to reach a constant weight, $m_2$. The weight of adsorbed oil was calculated as $m_1$- $m_2$. This cycle of sorption and recovery was repeated several times..

## 3. Results and Discussion

### *3.1. Effects of different types of oil on the adsorption properties of MWCNTs*

The adsorption capacity and reuse performance of MWCNTs for gasoline, kerosene, diesel oil NO.1and diesel oil NO.2 were investigated in this work. Observations on the adsorption capacity and reuse performance of MWCNTs were conducted by machinery extrusion method and incineration method, respectively. The oil sorption capacities and recycling performance of MWCNTs are shown in Fig.1and 2.

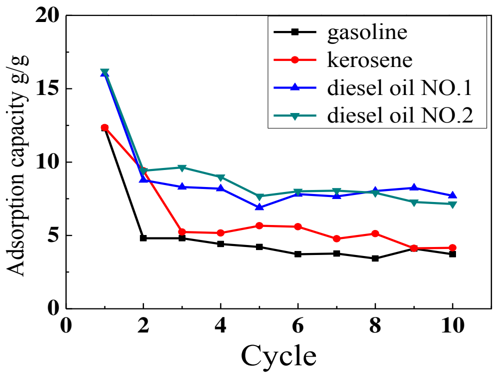


Fig. 1 Oil adsorption capacities for extruded MWCNTs

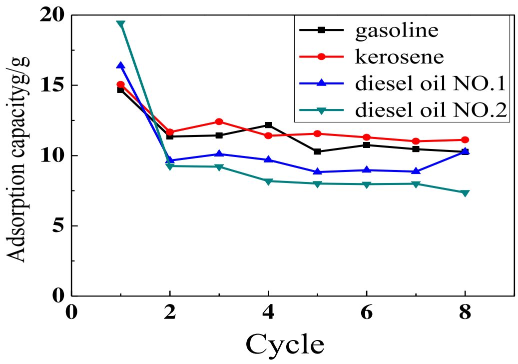


Fig. 2 Oil adsorption capacities for incinerated MWCNT

The results in Fig.1 and 2 shows that with the increase of the number of reuse, the oil adsorption ability of MWCNTs decreased and tend to stabilized gradually, for both the extrusion and incineration recovery methods. It was found that the re-adsorption capacity of incinerated MWCNTs is higher than those extruded ones. This may due to the destruction of the gap between carbon nanotubes during the extrusion process, leading to lower oil adsorption capacity. In order to observe the changes in the structure of MWCNTs before and after the process of extrusion and incineration, a scanning electron microscope (SEM) analysis has been done.

The SEM images, see Fig.3 (a) and (b), show that the void structure of MWCNTs was destroyed significantly, from the loose structure initially to the relatively compacted felt sheet type. However, as shown in Fig.3 (c), there is no significant change in the structure of the MWCNTs when kerosene removed through incineration, with little change of the void structure among the MWCNTs. The significant change of the void structure among carbon nanotubes after extrusion leads to the decline of oil absorption capacity.

At the same time, it can be seen from Fig. 1 that for gasoline, kerosene, diesel oil No.1 and diesel oil No.2, the adsorption capacities on the extruded MWCNTs increased with the increasing of carbon chain length of the oil. This is because the different organic molecules have different adsorption mechanism when adsorbed on MWCNTs. First, molecular size and shape determine the availability of different adsorption sites on MWCNTs. And for organic chemicals, larger molecules have higher adsorption energies [20]. Molecules, especially the larger ones, can twist themselves so that they match with the curvature surface, thus forming stable complexes with the CNTs [21-23]. So the oil adsorption capacity of MWCNTs increased with the increasing of average molecular weight of the oil, because the average molecular weight of gasoline, kerosene, diesel No. 1 and diesel No.2 increase sequentially. Furthermore, the functional groups of organic chemicals also influence the adsorption capacity of MWCNTs. Each carbon atom in a CNT has a π electron orbit perpendicular to CNT surface [24]. Therefore, organic molecules containing π electrons can form π-π bonds with CNTs, such as organic molecules with C=C double bonds or benzene rings [25, 26]. The most widely recognized influence of organic chemical functional groups on organic chemical-CNT interactions is on the electron-donor-acceptor (EDA) π-π interaction. The adsorption correlated affinity with the functional groups increased in the order of nonpolar aliphatic < nonpolar aromatics < nitroaromatics for CNTs.[27] As well known, the content of aromatic compounds and asphaltenes in gasoline, kerosene, diesel NO.1and diesel NO.2 increases sequentially. So adsorption capacities for MWCNTs increased with the increasing of carbon chain length of the oil.

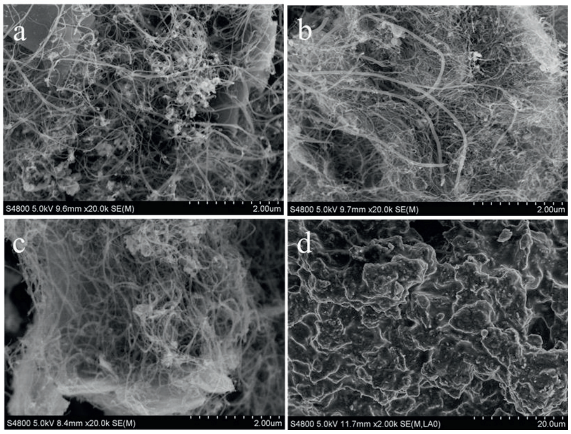


Fig. 3 The SEM of MWCNTs. (a) Primary MWCNTs (b) MWCNTs after adsorption of kerosene and extrusion (c) MWCNTs after adsorption of kerosene and incineration (d) MWCNTs after adsorption of diesel oil No.2 and incineration

It is found from Fig.2 that the incinerated MWCNTs were successfully reused for the adsorption of gasoline, kerosene, diesel No.1 and diesel No.2, showing a stabilized capacity of 10.5g/g、11g/g、9.5g/g and 8.0g/g. For the incinerated MWCNTs, the oil adsorption capacity decreased with the increase of carbon chain length of the oil. Comparing with Fig.1, it can be found that the re-adsorption capacities of the incinerated MWCNTs for gasoline, kerosene and diesel are higher than those extruded ones. However, when reused for diesel No.2 adsorption, the adsorption capacity is much lower for the incinerated MWCNTs than those extruded ones. This may because more coke was produced in the process of ignition for diesel No.2, which contains more aromatics, asphaltenes and other ingredients than other kinds of oil. (To eliminate the effects of temperature, all the oil was incinerated under 240 $^{o}$C. This incineration temperature may not fit for diesel No.2). A SEM analysis has been done for the MWCNTs after the adsorption of diesel No.2 and incineration, as shown in Fig. 3(d). Comparing Fig. 3(d) with (a) and (c), it can be obviously seen that for the MWCNTs after adsorption of kerosene and incineration, only a small part of the coking material remained on the surface of MWCNTs, with the gap structure and adsorption sites remained intact. However, from Fig3 (d), it can clearly be seen that the MWCNTs after adsorption of diesel No.2 and incineration, the void structure of carbon nanotubes was almost covered by coking materials, which lowered the adsorption capacity seriously. Analysts believe that heavier oil can contribute to more serious cocking, so the oil adsorption capacity decreased with the increase of carbon chain length of the oil.

### *3.2. Effects of different metal ion on the oil adsorption properties of MWCNTs*

According to the characteristic of oilfield wastewater, the effect of metal ions on the oil adsorption capacity of MWCNTs was also observed preliminarily. In this study, the calcium and magnesium ions were selected, which are the most common metal ions in oilfield wastewater.

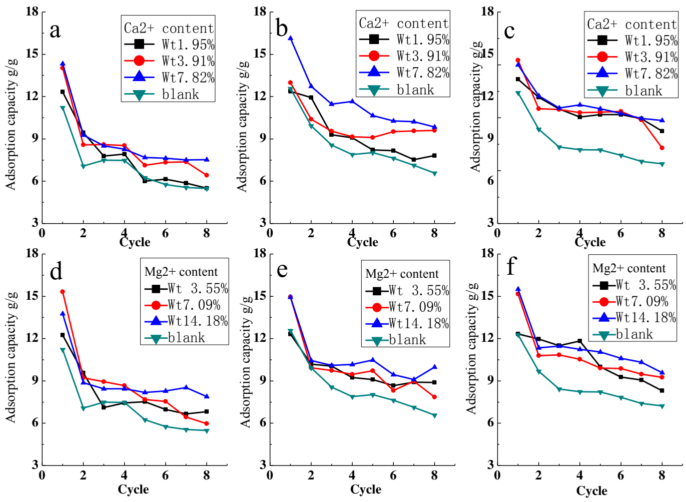


Fig.4 The influence of metal ions on different oil adsorption capacities on MWCNTs. (a), (b) and (c) the effects of calcium ion content on adsorption capacity of kerosene, diesel No.1 and diesel No.2, respectively. (d),(e) and (f) the effect of magnesium ion content on adsorption capacity of kerosene, diesel No.1 and diesel No.2 , respectively.

The effects of different ion content on the adsorption capacity for kerosene, diesel No.1 and diesel No.2 were investigated. During the experiment, the MWCNTs were soaked using a calcium chloride or magnesium chloride solution with certain metal ion content for 1h before the adsorption of oil. After the oil adsorption, the MWCNTs are extruded for de-oiling and then repeat the salt soaking and oil adsorption process. From Fig.4 it can be clearly seen that with the existing of metal ions, the oil adsorption capacity of multi-walled carbon nanotubes increased with the increasing of ion concentration. It is expected that the presence of metal ions can bridge organics and the functional groups on MWCNTs, compress the double layer and neutralize the negative charges of organics, and thus weaken the repulsion between organics molecules, and between organics and CNTs [28-30].

### *3.3. Effects of Surfactants on the oil adsorption properties of MWCNTs*

Currently, with the development of enhanced oil recovery, surfactants were widely used. Therefore, the oilfield wastewater contains a large amount of surfactants. In this paper we select petroleum sulfonate as the research object and investigate the effect of different petroleum sulfonate concentrations on the adsorption capacity of MWCNTs for kerosene and diesel NO.1.

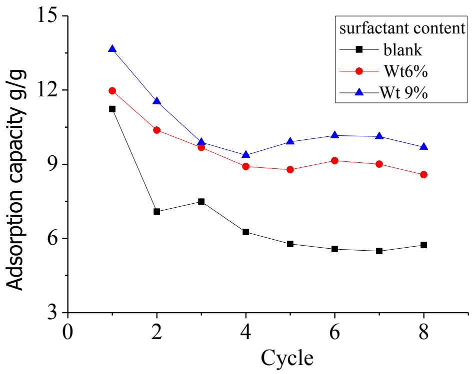


Fig.5 Influence of different surfactants content on kerosene adsorption capacity(extruded MWCNTs).

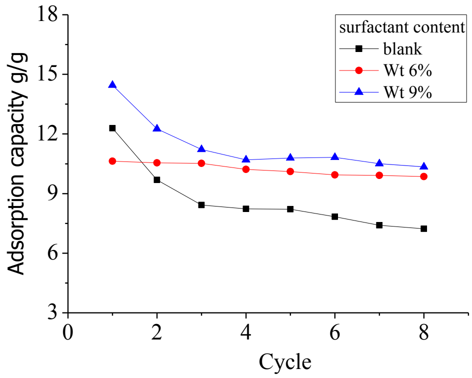


Fig.6Influence of different surfactants content on diesel NO.1 adsorption capacity(extruded MWCNTs).

During the experiment, the MWCNTs were soaked using a petroleum sulfonate solution with certain surfactants content for 1h before the adsorption of oil. After the oil adsorption, the MWCNTs are extruded for de-oiling and then repeat the surfactants soaking and oil adsorption process. Fig.5and 6 shows the effects of different surfactants concentration on kerosene and diesel NO.1 adsorption under the extrusion method. From the two figures, it can be seen that with the existing of petroleum sulfonate, the oil adsorption capacity of MWCNTs increased with the increasing of surfactants concentration. This may because the organic chemical-CNT interactions could be remarkably altered by the surfactants solution.Surfactants can disperse CNT bundles and make more adsorption sites available for adsorbates, and thus organic chemicals were able to interact more strongly with CNT surfaces in the presence of surfactants than without surfactants [31].

## 4. Conclusion

(1) The re-adsorption capacity of incinerated MWCNTs is higher than those extruded ones. The oil adsorption capacity on the extruded MWCNTs increased with the increasing of carbon chain length of the oil, while that on the incinerated ones decreased.
(2) The oil adsorption capacity of MWCNTs increased with the increasing of metal ions and petroleum sulfonate content.

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## References

[1] Wang H, Lin K Y, Jing B, et al. Removal of oil droplets from contaminated water using magnetic carbon nanotubes[J]. Water research, 2013, 47(12): 4198-4205.
[2] Gui X, Li H, Wang K, et al. Recyclable carbon nanotube sponges for oil absorption[J]. Acta Materialia, 2011, 59(12): 4798-4804.
[3] Cheng M, Gao Y, Guo X, et al. A functionally integrated device for effective and facile oil spill cleanup[J]. Langmuir, 2011, 27(12): 7371-7375.
[4] Deng D, Prendergast D P, MacFarlane J, et al. Hydrophobic meshes for oil spill recovery devices[J]. ACS applied materials & interfaces, 2013, 5(3): 774-781.
[5] Gui X, Zeng Z, Lin Z, et al. Magnetic and highly recyclable macroporous carbon nanotubes for spilled oil sorption and separation[J]. ACS applied materials & interfaces, 2013, 5(12): 5845-5850.

[6] Duong H T T, Burford R P. Effect of foam density, oil viscosity, and temperature on oil sorption behavior of polyurethane[J]. Journal of applied polymer science, 2006, 99(1): 360-367.
[7] Ceylan D, Dogu S, Karacik B, et al. Evaluation of butyl rubber as sorbent material for the removal of oil and polycyclic aromatic hydrocarbons from seawater[J]. Environmental science & technology, 2009, 43(10): 3846-3852.
[8] Husseien M, Amer A A, El-Maghraby A, et al. A comprehensive characterization of corn stalk and study of carbonized corn stalk in dye and gas oil sorption[J]. Journal of Analytical and Applied Pyrolysis, 2009, 86(2): 360-363.
[9] Hussein M, Amer A A, Sawsan I I. Oil spill sorption using carbonized pith bagasse: 1. Preparation and characterization of carbonized pith bagasse[J]. Journal of Analytical and Applied Pyrolysis, 2008, 82(2): 205-211.
[10] Radetic M, Ilic V, Radojevic D, et al. Efficiency of recycled wool-based nonwoven material for the removal of oils from water[J]. Chemosphere, 2008, 70(3): 525-530.
[11] Radetic M M, Jocic D M, Jovancic P M, et al. Recycled wool-based nonwoven material as an oil sorbent[J]. Environmental science & technology, 2003, 37(5): 1008-1012.
[12] Zhang Q, Zhao M Q, Tang D M, et al. Carbon -Nanotube -Array Double Helices[J]. Angewandte Chemie, 2010, 122(21): 3724-3727.
[13] Futaba D N, Miyake K, Murata K, et al. Dual porosity single-walled carbon nanotube material[J]. Nano letters, 2009, 9(9): 3302-3307.
[14] Lee C, Baik S. Vertically-aligned carbon nano-tube membrane filters with superhydrophobicity and superoleophilicity[J]. Carbon, 2010, 48(8): 2192-2197.
[15] Gui X, Wei J, Wang K, et al. Carbon nanotube sponges[J]. Advanced Materials, 2010, 22(5): 617-621.
[16] Li B, Cao X, Huang X, et al. Facile "Needle -Scratching" Method for Fast Catalyst Patterns Used for Large -Scale Growth of Densely Aligned Single -Walled Carbon -Nanotube Arrays[J]. Small, 2009, 5(18): 2061-2065.
[17] Li B, Goh C F, Zhou X, et al. Patterning colloidal metal nanoparticles for controlled growth of carbon nanotubes[J]. Advanced Materials, 2008, 20(24): 4873-4878.
[18] Hao Y, Qunfeng Z, Fei W, et al. Agglomerated CNTs synthesized in a fluidized bed reactor: agglomerate structure and formation mechanism[J]. Carbon, 2003, 41(14): 2855-2863..
[19] Fan Z, Yan J, Ning G, et al. Oil sorption and recovery by using vertically aligned carbon nanotubes[J]. Carbon, 2010, 48(14): 4197-4200.
[20] Mao Z, Sinnott S B. A computational study of molecular diffusion and dynamic flow through carbon nanotubes[J]. The Journal of Physical Chemistry B, 2000, 104(19): 4618-4624.
[21] Karajanagi S S, Vertegel A A, Kane R S, et al. Structure and function of enzymes adsorbed onto single-walled carbon nanotubes[J]. Langmuir, 2004, 20(26): 11594-11599.
[22] Richard C, Balavoine F, Schultz P, et al. Supramolecular self-assembly of lipid derivatives on carbon nanotubes[J]. Science, 2003, 300(5620): 775-778.
[23] Gurevitch I, Srebnik S. Conformational behavior of polymers adsorbed on nanotubes[J]. The Journal of chemical physics, 2008, 128(14): 144901.
[24] Zhou G, Duan W, Gu B. First-principles study on morphology and mechanical properties of single-walled carbon nanotube[J]. Chemical Physics Letters, 2001, 333(5): 344-349.
[25] Lin D, Xing B. Adsorption of phenolic compounds by carbon nanotubes: role of aromaticity and substitution of hydroxyl groups[J]. Environmental science & technology, 2008, 42(19): 7254-7259.
[26] Chen W, Duan L, Wang L, et al. Adsorption of hydroxyl-and amino-substituted aromatics to carbon nanotubes[J]. Environmental science & technology, 2008, 42(18): 6862-6868.
[27] Ren X, Chen C, Nagatsu M, et al. Carbon nanotubes as adsorbents in environmental pollution management: a review[J]. Chemical Engineering Journal, 2011, 170(2): 395-410.
[28] Wang S G, Liu X W, Gong W X, et al. Adsorption of fulvic acids from aqueous solutions by carbon nanotubes[J]. Journal of Chemical Technology and Biotechnology, 2007, 82(8): 698-704.
[29] Biesaga M, Pyrzynska K. The evaluation of carbon nanotubes as a sorbent for dicamba herbicide[J]. Journal of separation science, 2006, 29(14): 2241-2244.
[30] Hyung H, Kim J H. Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: Effect of NOM characteristics and water quality parameters[J]. Environmental science & technology, 2008, 42(12): 4416-4421.
[31] Carrillo-Carrión C, Lucena R, Cárdenas S, et al. Surfactant-coated carbon nanotubes as pseudophases in liquid–liquid extraction[J]. Analyst, 2007, 132(6): 551-559.