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# A Comparison of Direct and Indirect Methods to Evaluate Oil Sorption Capacity of Fabrics Sorbent Materials

Zhouyang Lian<sup>1\*</sup>, Zhengwei Luo<sup>2</sup>, Hao Lu<sup>3</sup>, Wuji Wei<sup>1</sup>

<sup>1</sup>College of Environmental Sciences and Engineering, Nanjing Tech University, Nanjing 210009, China

<sup>2</sup>College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 210009, China

<sup>3</sup>College of Energy Science and Engineering, Nanjing Tech University, Nanjing 210009, China

Email: lianzy@njtech.edu.cn, luozw1989@163.com, 2844833657@qq.com, wjwei@njtech.edu.cn

Tel: +86-25-58139382

**Abstract:** Although an indirect method is widely used to evaluate oil sorption capacity of fiber materials for remediating oily water, a direct method has recently been proposed. To compare two methods, we first studied the effect of extraction time, the accuracy and precision for the direct method. Similarly, precision of the indirect method and the underlying sources of error were also investigated. The minimal extraction time required for the direct method was found to be 180 min. The relative error of direct method was less than 2.61 %, its standard deviation was less than 1.60 %, and its coefficient of variation was less than 0.313 %. The standard deviation of the indirect method was more than 55.1 %, and its coefficient of variation was more than 16 %. The error in the indirect method mainly came from the heterogeneity of oily water, which led to large, random differences between samples that could not be eliminated.

## 1. Introduction

Fiber oil sorbent materials (FOSM) can not only quickly adsorb the oil organics from water and land surfaces, but also later release the oil for use [1, 2]. In a wide range of large, oily wastewaters, oil exists in a dissolved, dispersed, or emulsified form. This is a major threat to public health, wildlife conservation, and environmental sustainability [3]. The evaluation of modified FOSM is currently a major research area, due to the possibility of improving technologies for collecting and completely removing oil from impacted water [4-7]. An ideal FOSM must include high sorption capacity, adequate oil retention and reusability. Among these, oil sorption capacity plays a key role [8-10]. Oil sorption capacity has been traditionally evaluated with an indirect method, which focuses on quantifying oil in impacted water. In this method, oil sorption capacity is calculated based on the difference in oil concentration and oil volume in the water before and after the sorption procedure [11-13]. A recent patent has disclosed a direct method to evaluate oil sorption capacity from impacted water [14]. This focuses on the FOSM as the object of research. After the sorption procedure, the oil in sorbent material is extracted in carbon tetrachloride (CCl<sub>4</sub>), and the oil sorption capacity is calculated by the volume and concentration of oil in the extraction solvent. However, few investigation of error



analysis for the evaluation methods of oil sorption capacity was reported.

Overall, this study aimed to provide empirical support for selecting an evaluation method for measuring oil sorption capacity and an understanding of the sources of error in each evaluation method. In particular, the accuracy of procedures that apply to both direct and indirect methods of evaluating oil sorption capacity was determined. For the portion of the direct method involving hot extraction of oil from sorbent materials using  $\text{CCl}_4$ , we determined the relationship between extraction time and oil content in the material, the systematic error, accuracy, and precision. The accuracy and precision of the indirect method were also investigated. Finally, the two evaluation methods were compared.

## 2. Material and Methods

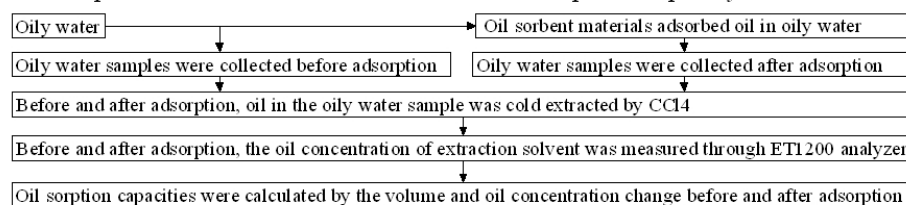
### 2.1 Materials

FOSM were PP fiber materials modified by polyethylene wax (PEW), which was described by our previous publication [15]. Atmospheric pressure diesel and coking diesel were provided by Sinopec Yangzi Petrochemical Co. China.  $\text{CCl}_4$ ,  $\text{C}_{18}\text{H}_{29}\text{NaO}_3\text{S}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$  and  $\text{HCl}$  were analytical grade.

### 2.2 Adsorption procedure

The distilled water, oil, and sodium dodecylbenzenesulfonate (100 mg/L) were vigorously stirred together in a beaker for 120 min. The mixture was allowed to stand for 60 min, and then the surface oil slick was removed by FOSM. The remaining oily water was used as a source for all oily water analyses and absorption procedures. The oily water was then prepared. About 0.6000 g of FOSM was placed into the oily water and allowed to adsorb oil for 60 min before it was removed for analysis. The testing steps for the direct and indirect methods of quantifying oil sorption capacity in oily water are shown in Figure 1.

The steps of indirect method to evaluate oil sorption capacity



The steps of direct method to evaluate oil sorption capacity

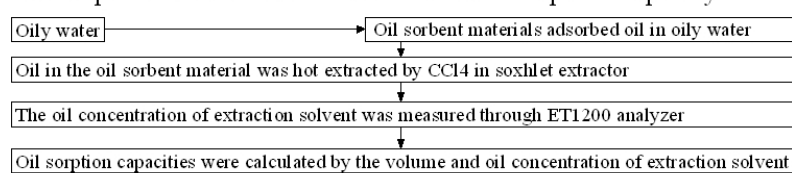


Figure 1. The comparison of testing steps of two methods

As shown in Figure 1, the two evaluation methods collect data from different materials: the indirect method uses oily water, while the direct method uses the FOSM. The extraction process also differs, with the indirect method using a cold extraction in  $\text{CCl}_4$  with a separation funnel to collect oil from the sample. The oil sorption capacity is calculated based on the changes in volume and oil concentration for the oily water before and after adsorption. In contrast, the direct method used a hot extraction in  $\text{CCl}_4$  with soxhlet extractor to collect oil from the sorbent material. In this case, the oil sorption capacity is calculated from the volume and oil concentration of the extraction solvent.

### 2.3 Analysis of oil sorption capacity evaluation methods

The ET1200 oil in water concentration analyzer, which operates based on infrared spectrophotometry, was used to measure the oil concentration in extracted samples. Each sample was scanned between  $3400\text{ cm}^{-1}$  and  $2400\text{ cm}^{-1}$  in the analyzer.  $2930\text{ cm}^{-1}$ ,  $2960\text{ cm}^{-1}$ , and  $3030\text{ cm}^{-1}$  are the absorbances of infrared light corresponding to the C-H bond stretching vibrations in the  $\text{CH}_2$  group,  $\text{CH}_3$  group, and aromatic ring, respectively. These absorbance values were used to calculate the oil content in the samples.

#### 2.4 Cold extraction of oil with $\text{CCl}_4$ and oil sorption capacity measured through the indirect method

Before and after adsorption, about  $V$  volume of oily water samples were removed by pipette. Each sample was subjected to the following cold extraction procedure. The sample was transferred to a separatory funnel, and its pH was reduced below 2 with HCl. A sample vial was washed in  $\text{CCl}_4$ , and the excess liquid was poured to the separatory funnel. This mixture was shaken for about 3 min, and then allowed to separate for about 5 min. The lower organic phase was transferred to a conical flask, to which about 3 g of anhydrous  $\text{Na}_2\text{SO}_4$  was added. The flask was shaken several times, and more  $\text{Na}_2\text{SO}_4$  was added if the material in the flask formed a crystal block. The solid-liquid phase was filtered through a filter paper in a glass funnel into a volumetric flask. The final volume was adjusted to  $V^*$  with  $\text{CCl}_4$ .

The oil concentration of the resulting cold extraction sample was determined using the ET1200 analyzer. The oil concentration of oily water sample  $C_i$  was calculated using Equation (1):

$$C_i = \frac{C \cdot V^*}{V} \quad (1)$$

Where,  $V^*$  was the volume of the extraction sample,  $V$  was the volume of oily water sample, and  $C$  was oil concentration of the extraction sample.

The oil sorption capacities measured by indirect method,  $Q_{1i}$ , were calculated according to Equation (2):

$$Q_{1i} = \frac{V_{1i} C_{1i} - V_{2i} C_{2i}}{m} \quad (2)$$

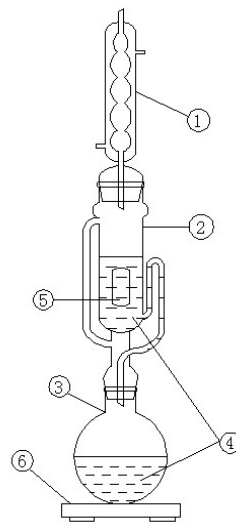
Where,  $V_{1i}$  and  $V_{2i}$  were the volume of water sample before and after adsorption,  $C_{1i}$  and  $C_{2i}$  was oil concentration of the oily water before and after adsorption, and  $m$  was the quantity of FOSM.

#### 2.5 Hot extraction of oil with $\text{CCl}_4$ and oil sorption capacity measured through the direct method

The FOSM sample was placed in an extraction tube (②, Figure 2), and about 180 mL of the extraction solvent  $\text{CCl}_4$  (④) was poured into the flat-bottomed flask (③). The solvent was brought to a boil using a heating mantle (⑥), and timing of the extraction started when the first droplet was seen dropping from the condenser. Extraction continued for  $t$  (min), with a recirculation rate (siphon 6 times/h) controlled by adjusting the temperature. The extraction solvent was then poured into a conical flask. The remaining extraction procedure followed the anhydrous  $\text{Na}_2\text{SO}_4$  and filtering steps previously described. The final volume was adjusted to  $V^*$  with  $\text{CCl}_4$ . The oil concentration of each resulting hot extraction sample was determined with ET1200 analyzer. The oil sorption capacities measured through the direct method,  $Q_{2i}$  (g/g), were calculated according to Equation (3):

$$Q_{2i} = \frac{C \cdot V^*}{m} \quad (3)$$

Where,  $V^*$  was the volume of the extraction sample,  $C$  was oil concentration of the extraction sample,  $m$  was the quantity of FOSM.



① condenser; ② extracting tube; ③ flat-bottomed flask; ④ extracting liquid( $\text{CCl}_4$ ); ⑤ oil sorbent material; ⑥ heated furnaces.

Figure 2. Soxhlet extractor.

### 3. Results and Discussion

#### 3.1 Quantification of error and factors affecting the accuracy of the direct method

##### 3.1.1 Relationship between oil content and thermal extraction time of oil-absorbing materials and determination of thermal extraction time

The amount of time necessary to extract all the oil from the sorbent material into the organic phase is likely to be essential to the accuracy of data produced using the direct method. Therefore, tests were carried out to determine the necessary extraction time. About 0.6000 g of FOSM was soaked in coking diesel for 5 min, allowed to naturally drain for 30 s, and subject to hot  $\text{CCl}_4$  extraction. The oil concentration of extraction solvent in extraction tube was measured at different times.

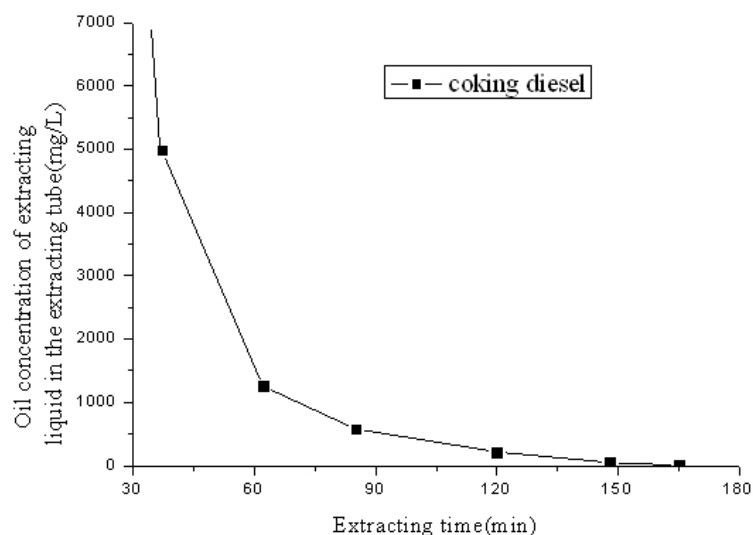


Figure 3. The relationship between the extraction time and the oil concentration.

The relationship between hot extraction time and oil concentration in the solvent is shown in Figure 3. The results indicate that the oil concentration in extraction solvent decreased as the extraction time

was lengthened. The initial downward trend was steep for the first 60 min, but decreased more slowly thereafter. This decrease in oil concentration in the solvent over time indicates a decrease in oil content of the sorbent material over time. The shift in the rate of decrease was likely due to two major physical factors. First, the fiber oil sorbent material has a capillary structure into which oil can be absorbed. Second, oil can be adsorbed on the fiber surfaces due to Van Der Waals forces. During the first 60 min, oil absorbed in the material would be quickly removed by the extraction solvent. Such a movement requires relatively little energy, and it was expressed as a curve of steep negative slope. Between 60 and 120 min of extraction, the relative importance of Van Der Waals forces between the oil and FOSM increased relative to the role of capillarity, and oil moved more slowly into the extraction solvent. This was evident in the shallow slope. From 120 to 170 min, the existence of grooves, cracks, voids, and other defects in individual fibers of the FOSM, as shown in Figure 4, the energy required to overcome the adsorption energy between oil and fibers was further increased. This is evidenced in the even smaller slope during this time period. For extraction times longer than 170 min, the measured oil concentrations were almost 0 mg/L. This indicates that essentially all the oil in the sorbent material had been removed. Therefore, an extraction time of 180 min is sufficient to completely remove oil from the FOSM.

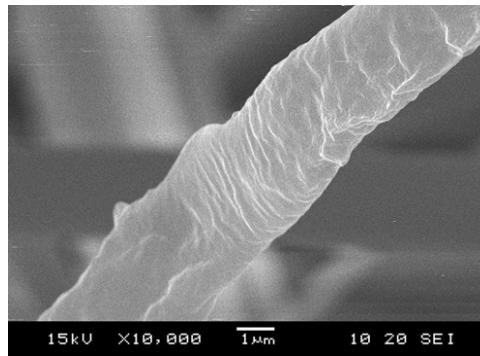


Figure 4. The morphology of the single one fiber of the FOSM.

### 3.1.2 Accuracy and precision of the direct method for evaluating oil sorption capacity

Five 0.6000 g fiber sorbent material samples were adsorbed a predetermined amount of coking diesel and its predetermined oil content was same ( $Q=0.6775$  g/g), and five 0.6000 g fiber sorbent material samples were adsorbed a predetermined amount of atmospheric pressure diesel and its predetermined oil content was same ( $Q=0.5118$  g/g). Then, ten material samples were hot extracted, and the sorption capacity of each was determined using the direct method  $Q_{2i}$  (Equation (3)), as shown in Table 1.

Table 1. Analysis data for oil sorption capacity of direct method.

Parameters		Coking diesel	Atmospheric pressure diesel
predetermined oil content $Q$		0.6775	0.5118
	1	0.6617	0.5010
The oil sorption	2	0.6605	0.4975
capacity of the direct	3	0.6600	0.4970
method $Q_{2i}(i=1\sim5)$	4	0.6608	0.4980
	5	0.6622	0.4987
Average value		0.6610	0.4984
Relative error RE		2.44%	2.61%
Standard deviation SD		0.90%	1.60%
Coefficient of variation CV		0.133%	0.313%

The data showed that the difference between measured oil sorption capacities  $Q_{2i}$  and predetermined oil content  $Q$  was relatively small, with a relative error less than 2.61 %. The corresponding standard deviation was less than 1.60 %, and the coefficient of variation was less than

0.313 %. Therefore, the direct method of evaluating oil sorption capacity has both high accuracy and high precision.

### 3.2 Quantification of error and factors affecting the accuracy of the indirect method

#### 3.2.1 Accuracy and precision of the indirect method for evaluating oil sorption capacity

Ten 0.6000 g FOSM samples were prepared, five each for coking diesel oily water and atmospheric diesel oily water, with an initial liquid volume of 2500 mL. Sorption was carried out as described in Adsorption procedure. Before and after the sorption procedure,  $V=25$  mL of oily water samples were collected, and their oil sorption capacity  $Q_{li}$  was measured using Equation (2).

Table 2. Analysis data for the oil sorption capacity of the indirect method.

Parameters		Coking diesel	Atmospheric pressure diesel
	1	0.3507	0.5405
The oil sorption	2	0.4009	0.3562
capacity of the indirect	3	0.4897	0.4004
method $Q_{li}(i=1\sim5)$	4	0.3805	0.4521
	5	0.4472	0.4128
Average value		0.4138	0.4324
Standard deviation SD		55.1‰	69.4‰
Coefficient of variation CV		13.0%	16.0%

The results shown in Table 2 reveal that oil sorption capacities evaluated by indirect method had high variability, poor reproducibility, and a high degree of dispersion. The standard deviation for the indirect method overall was more than 55.1 ‰, and its coefficient of variation was more than 16.0 %, which were 34 times and 51 times greater, respectively, than those of the direct method.

#### 3.2.2 Analysis of the role of sampling depth in the indirect method

About 2500 mL of coking diesel oily water was prepared, and  $V=25$  mL samples were collected at different depths  $h_i$  (4 cm, 6 cm, 8 cm, 10 cm, 12 cm). The oil concentration  $C_i$  was determined at each depth as previously described.

Table 3. Analysis data for the oil concentration of samples.

Parameters	The oil concentration of oily water sample $C_i$ (mg/L)
$h_1=4$ (cm)	250.75
$h_2=6$ (cm)	234.69
$h_3=8$ (cm)	157.99
$h_4=10$ (cm)	136.79
$h_5=12$ (cm)	122.87
Average value	180.62
Standard deviation SD	58.3‰
Coefficient of variation CV	32.3%

As shown in Table 3, the oil concentrations of samples collected at different depths within a single column of oily water differed notably. The standard deviation and coefficient of variation were 58.3 ‰ and 32.3 %, respectively. These results indicate that different samples from the same oily water strongly differ in oil concentration, resulting in a poor precision in sorption capacity measurements. Furthermore, the oil concentration of a given sampling point may not be representative of the overall oil concentration of oily water. The error from samples was random, and it could be eliminated only by using the entire oily water sample for extraction.

### 3.3 Comparison of results from the direct method and the indirect method using the full oily water sample for extraction

To verify the accuracy of the indirect method using the total oily water sample volume for analysis, results from this approach were compared with those produced using the direct method. About ten oily water samples were prepared, five each for coking diesel oily water and atmospheric diesel oily water, with the oil concentration  $C_{1i}$  of 500 mg/L, 600 mg/L, 700 mg/L, 800 mg/L and 900 mg/L, and the volume of each oily water was 600 mL. Ten 0.6000 g FOSM samples were also prepared. Samples were subjected to the sorption procedure as previously described.

For the indirect method, all the oily water was collected for sampling so that  $V=600$  mL. The oil concentrations  $C_{2i}$  were measured as previously described, and the sorption capacities  $Q_{1i}$  were calculated using Equation (2). For the direct method, the fiber sorbent material was subject to hot extraction, and its oil sorption capacity  $Q_{2i}$  was obtained as previously described, using Equation (3).

Table 4. The results of direct method and the total water extraction analysis using indirect method.

Atmospheric pressure diesel				Coking diesel			
No.	direct method $Q_{2i}(\text{g/g})$	indirect method $Q_{1i}(\text{g/g})$	RE	No.	direct method $Q_{2i}(\text{g/g})$	Indirect method $Q_{1i}(\text{g/g})$	RE
1	0.2135	0.2114	0.98%	1	0.2085	0.2083	0.10%
2	0.2591	0.2570	0.81%	2	0.2252	0.2208	1.95%
3	0.2745	0.2728	0.62%	3	0.2478	0.2444	1.37%
4	0.2807	0.2802	0.18%	4	0.2677	0.2634	1.61%
5	0.2972	0.2962	0.34%	5	0.2894	0.2875	0.66%

As shown in Table 4, the oil sorption capacities measured by the indirect method based on analysis of the full water volume were very similar to those measured using the direct method, with an error of less than 1.95 %. The use of all oily water after adsorption as a sample therefore prevents the errors introduced to the indirect method by collecting samples from a heterogeneous volume of oily water.

#### 4. Conclusions

The indirect method requires two measurements of oil concentration compared with the single measurement required by the direct method, and we found that the latter requires a much longer extraction period. To ensure oil was completely extracted from the FOSM, a hot extraction must be carried out for 180 min using the direct method. The relative error of direct method was less than 2.61 %, its standard deviation was less than 1.60 %, and its coefficient of variation was less than 0.313 %. The standard deviation of the indirect method was more than 55.1 %, and its coefficient of variation was more than 16 %. The main source of error for the indirect method was due to the heterogeneity of samples collected from oily water. This error source was random and could not be eliminated. The direct method was therefore far more accurate and precise than the indirect method. However, using the total water sample for extraction and analysis in the indirect method greatly reduced errors introduced via sample collection, making it comparable to the direct method.

#### References

- [1] Abdul A. A., Abdulrauf R. A. & M. Enamul Hossain. (2012) A sustainable approach to controlling oil spills. *Journal of environmental management*, 113: 213-227.
- [2] Qi X., Jia Z., Yang Y. & Liu H. (2011) Sorption Capacity of New Type Oil Absorption Felt for Potential Application to Ocean Oil Spill. *Procedia Environmental Sciences*, 10: 849-853.
- [3] Danish E. Y. (2010) Ecological impact from chemicals in the Arabian Gulf due to Gulf oil spill. *Water Environment Journal*, 24: 65-73.
- [4] Ji F., Li C., Dong X., Li Y. & Wang D. (2009) Separation of oil from oily wastewater by sorption and coalescence technique using ethanol grafted polyacrylonitrile. *Journal of hazardous*



- materials, 164: 1346-1351.
- [5] Hiroshi M., Shiori K., Masahiro K., Ayaka H., Kazuma H., Koji S., Rensuke K & Kenji K. (2009) Utilization of silkworm cocoon waste as a sorbent for the removal of oil from water. *Journal of hazardous materials*, 165: 266-270.
  - [6] Zhou Y. B., Chen L., Hu X. M & Lu J. (2009) Separation of oil from oily wastewater by modified resin. *Water Science & Technology*, 59: 957-963.
  - [7] Li X., He L., Zhou H., Li W & Zha W. (2012) Influence of silicone oil modification on properties of ramie fiber reinforced polypropylene composites. *Carbohydrate Polymers*, 87: 2000-2004.
  - [8] Gerald D., Herve C., Marie-Elisabeth B., Christophe B & Christian V. (2003) Oil removal from water by selective sorption on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents. *Environment Science Technology*, 37: 1013-1015.
  - [9] Maja R., Vesna I., Darinka R., Robert M., Dragan J & Petar J. (2008) Efficiency of recycled wool-based nonwoven material for the removal of oils from water. *Chemosphere*, 70: 525-530.
  - [10] Zhu H., Qiu S., Jiang W., Wu D & Zhang C. (2011) Evaluation of electrospun polyvinyl chloride/polystyrene fibers as sorbent materials for oil spill cleanup. *Environment Science Technology*, 45: 4527-4531.
  - [11] Rajakovic V., Aleksic G., Radetic M & Rajakovic L. (2007) Efficiency of oil removal from real wastewater with different sorbent materials. *Journal of hazardous materials*, 143: 494-499.
  - [12] Rajakovic-Ognjanovic V., Aleksic G & Rajakovic L. (2008) Governing factors for motor oil removal from water with different sorption materials. *Journal of hazardous materials*, 154: 558-563.
  - [13] Zhang J., Hou Y., Zhou H & Li C. (2010) Study on oil removal from oilfield wastewater using activated semicoke. *Chinese Journal of Environmental Engineering*, 4: 355-359.
  - [14] Liu Y. & Wei W. (2012) A direct method to evaluate oil sorption capacity in oily water, CN201110278214.1 [P] (in Chinese)
  - [15] Wei W., Huang J, Chen Qiguo. (2011) A preparation of the PP fiber materials modified by PEW. CN201010581144.2 [P] (in Chinese)