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# Adsorptive Removal of Dibenzothiophene Using UVM-7@ZIF-8 as Nano-Adsorbent in Liquid Phase at Room Temperature

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## INTRODUCTION

Desulfurization process is one of the most important applications of the oil refining industry. Different physical, chemical and biological methods have been investigated to remove sulfur compounds from oil and gas industries, including hydrodesulfurization (HDS), biodesulfurization (BDS), absorption desulfurization (ADS), extractive desulfurization (EDS) and oxidative desulfurization (ODS) [1,2].

Among these different methods, ADS selective process is mainly considered as an appropriate approach for desulfurization, mainly due to its low energy consumption and cost and high efficiency [3,4].

In recent years, metal-organic frameworks (MOFs) and Zeolitic imidazolate frameworks (ZIFs) have shown better chemical and thermal

stability compared with other adsorbent. It introduced them as a suitable option for diverse applications such as gas storage, separation, catalyst, chemical sensors, etc. [5].

Following our studies about morphology and to improve the properties of ZIF-8 in absorbing sulfur compounds using mesoporous structures [6], in this study, the best synthesized hybrid adsorbent UVM-7@ZIF-8 is used to remove sulfur compounds from gas streams, to remove DBT in a liquid phase synthesized by the hydrothermal method. In addition, various factors such as the amount of adsorbent and absorption time have been investigated to study the efficiency and removal capacity of UVM-7@ZIF-8 adsorbent. In addition, the good selectivity of UVM-7@ZIF-8 over naphthalene (NA) indicated the absorption on non-saturation centers around Zn metal.

According to the results, the UVM-7@ZIF-8 reacted well to its excellent recycling capability to remove DBT under mild conditions.

## **METHODOLOGY**

### **MATERIAL AND METHOD**

The required materials for the synthesis of nano-adsorbents include  $Zn(NO_3)_2 \cdot 6H_2O$ , 2-methylimidazole, N-butylamine, CTAB, tetraethyl orthosilicate, triethanolamine  $TEAH_3$ , hexahydrate nitrate, dibenzothiophene, as well as naphthalene and n-octane, have all been purchased from the German Mercantile Company.

The devices used in this study included AT-500 KEM potentiometer device to determine the amount of sulfur in the tests performed by the company, X-ray diffraction device (XRD) Bruker AXS-D8 in two areas ( $0.5-10^\circ$ ) and ( $5-80^\circ$  °F), TGA analysis to check the thermal stability of the structure by Du Pont 2000 system operated under a nitrogen gas flow rate of  $10^\circ C/min$  and an FT-IR analysis to detect functional groups by the Perkin Elmer-Spectrum 65 from 500 to  $4000\text{ cm}^{-1}$ .

### **SYNTHESIS OF ZIF-8**

Preparation of ZIF-8 was done by method used at Wang et al [7] (hydrothermal method).

### **SYNTHESIS OF UVM-7**

Preparation of UVM-7 was done by method used at Abdouss et al [8].

### **SYNTHESIS OF UVM-7@ZIF-8**

In accordance with the synthesized procedure in [6], 4.53 g of  $Zn(NO_3)_2 \cdot 6H_2O$  was dissolved in 45 ml of deionized water with 2 g of UVM-7 (Solution A). Then, 5.69 g of 2-methylimidazole were dissolved in 35 ml of deionized water at  $55^\circ C$  under a magnetic stirrer. Then solution B

was added to A, and N-butylamine was dropped slowly until pH reached to 10. Finally, the entire mixture was transferred to an autoclave with a volume of 250 ml and was placed in an oven at  $120^\circ C$  for 24 hours. After cooling the autoclave at room temperature, the contents were sealed by a Buchner funnel and washed with water and ethanol using centrifuge. The precipitate was dried in a vacuum oven at  $100^\circ C$  for 12 hours.

## **ABSORPTION EXPERIMENTS IN THE DISCONTINUOUS SYSTEM**

In order to investigate the absorption properties of the synthesized samples in discontinuous experiments, 50 ml of concentrated solution was poured into a 100 ml balloon. Absorption temperature was adjusted at room temperature ( $25^\circ C$ ). Then, a certain amount of adsorbent is added to the solution. The solution was sampled at time intervals. The filtered solution was passed to separate the adsorbent particles in the sample. Finally, the sulfur content of the samples was measured using a potentiometer device.

## **INVESTIGATING THE AMOUNT OF ADSORBENT ON DBT ADSORPTION**

To study the effect of adsorbent in the adsorption process, the values of 0.2, 0.5, 0.1 and 0.2 g of ZIF-8, UVM-7 and UVM-7@ZIF-8 were added to 100-ml balloons containing 50 ml of a solution of DBT at 1000 ppm over 120 minutes.

## **Detection of time in the absorption of benzoquinone**

To investigate the effect of time in the adsorption process, 1 g of ZIF-8, UVM-7 and UVM-7@ZIF-8 adsorbents were transferred to separate balloons. Then, 50 ml of 1000 ppm of DBT

solution was added to the balloons. The solution was sampled at intervals. The sulfur content of the solution was measured by a potentiometer.

## DISCUSSION AND RESULTS

The nanoparticles of UVM-7@ZIF-8 adsorbent was synthesized according to the experimental method. The synthesis of adsorbents was tested to evaluate the adsorption of DBT by a discontinuous adsorption system. The results are as follows. According to the results of the BET analysis presented in [6], absorption-desorption isotherms of N<sub>2</sub> in UVM-7, ZIF-8 samples were of type IV, I, respectively. In UVM-7@ZIF-8 sample, the isotherm is type I at higher P/P<sub>0</sub> and type IV at lower P/P<sub>0</sub> ratio.

### EFFECT OF ADSORBENT LOADING ON DBT ABSORPTION PERFORMANCE

In order to find the optimal amount of adsorbent in DBT removal process, adsorption experiments were performed with different adsorbent contents. The amount of 1 g was chosen as the most suitable amount of adsorbents in all of the elimination experiments.

#### Effect of time on DBT absorption performance

In order to compare the efficiency of DBT adsorption on ZIF-8, UVM-7 and UVM-7@ZIF-8, absorption efficiency was investigated at different times. The absorption efficiency of DBT on UVM-7@ZIF-8 is higher than other adsorbents. In addition, 98.4% of the DBT was absorbed over UVM-7@ZIF-8 over 90 minutes, indicating that UVM-7@ZIF-8 was able to absorb DBT in a shorter relative duration with high absorption efficiency. The absorption capacity of ZIF-8, UVM-7 and UVM-7@ZIF-8 is 115.8 mgS/g, 90.8 mgS/g, and 299.2 mgS/g respectively.

## RECYCLABILITY OF UVM-7@ZIF-8

To optimize the recovery temperature, TGA was performed on UVM-7@ZIF-8 adsorbent. The weight loss of about 8% in the first stage is mainly due to the loss of moisture (about 100 °C). As well as weight loss of about 52% in the second stage related to remove organic matter (about 350 °C), namely, the 2-methylimidazole linker at ZIF-8 structure. To evaluate the adsorbent recovery function, the adsorption reaction cycle was repeated to three stages and the sulfur capacity was obtained after about three cycles of reaction of about 96.5%, indicating the stability and recoverability of the synthesized adsorbent.

## SELECTIVITY TESTS

To evaluate the adsorbability selectivity of DBT, different concentrations of aromatics of naphthalene in the range of 500-1000 ppm to normal octane solvent have been added under optimal absorption conditions. The results showed a slight decrease (about 2.5%) in adsorbent adsorption capacity by adding NA. These results indicate that the  $\pi$ - $\pi$  interactions between the adsorbent organic linker and the aromatic ring DBT are not responsible for the absorption process.

## ABSORPTION MECHANISM

As shown in Figure 1, the XRD patterns did not change significantly after first cycle which shows the adsorbed protective structure with respect to the physical absorption of DBT, and the relative reduction observed in peak intensity in samples after absorption, the occurrence of lower chemical interactions in the DBT absorption mechanism. Figure 2 investigates FT-IR results before and after absorption of DBT.

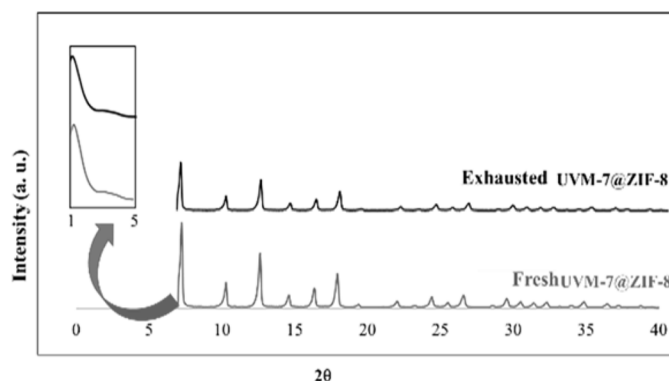


Figure 1: XRD patterns.

The new vibration peak of Metal-Sulfur, which appeared in the region about  $1110\text{ cm}^{-1}$  after absorption, [9] shows the interactions of unsaturated metals with DBT molecules through the electron lone pair on the sulfur atom [10]. Also, the C-S vibrating peak at wavelengths of about  $700\text{ cm}^{-1}$  shows the presence of DBT molecules after absorption.

Based on the results of adsorbent recovery and

the absence of  $\pi$ - $\pi$  chemical interactions due to the selectivity of adsorbent to naphthalene and the investigation of FT-IR spectra after absorption and also the probability of sulfur trapped in the UVM-7@ZIF-8 hybrid adsorbent structure [6], the proposed mechanism based on two types of coordination and hydrogen interactions for DBT removal using UVM-7@ZIF-8 has been considered, as shown in Figure 3.

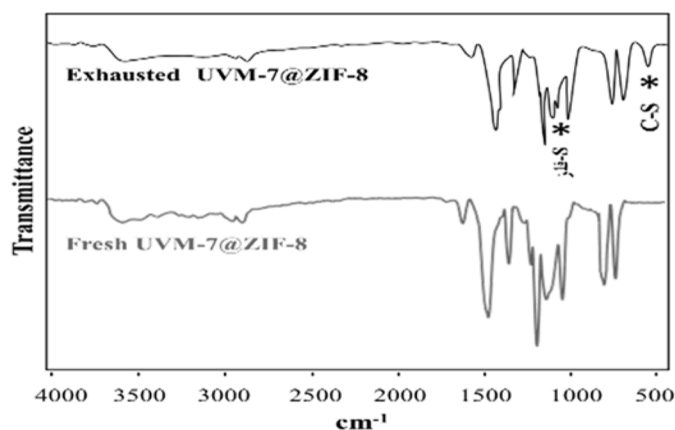


Figure 2: FT-IR spectra.

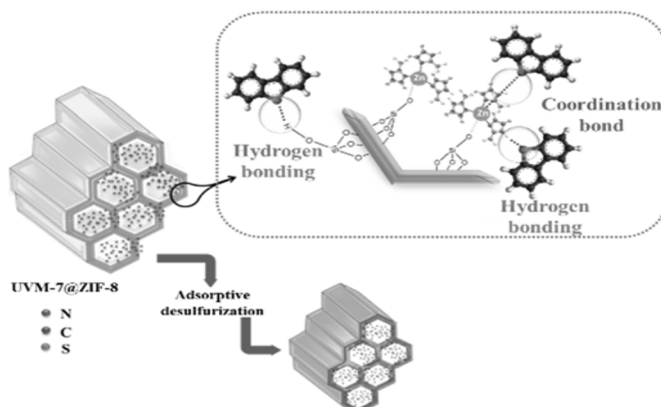


Figure3: Reaction mechanism.

## CONCLUSIONS

Hydrothermal synthesized hybrid UVM-7@ZIF-8 was used to remove DBT in a discontinuous adsorption system. Based on the results, UVM-7@ZIF-8 had the highest capacity for DBT (mg 299.2 mgS/g) compared to ZIF-8 (115.8 mgS/g) and UVM-7 (90.8 mgS/g). Recycling of 96% in adsorption of DBT for UVM-7@ZIF-8 represents a structural and recycling ability of this compound. According to these results, synthesized nano hybrids are a good adsorbent for DBT removal.

## REFERENCES

- [1]. Tang W., Gu J., Huang H., Liu D. and Zhong C., "Metal-organic frameworks for highly efficient adsorption of dibenzothiophene from liquid fuels," *AIChE J.*, Vol. 62, No. 12, pp. 4491-4496, 2016.
- [2]. Ania CO. and Bandosz T. J., "Importance of structural and chemical heterogeneity of activated carbon surfaces for adsorption of dibenzothiophene," *Langmuir*, Vol. 21, No. 17, pp. 7752-7759, 2005.
- [3]. Rivoira L., Juárez J., Falcón H., Costa MG., Anunziata O. and Beltramone A., "Vanadium and titanium oxide supported on mesoporous CMK-3 as new catalysts for oxidative desulfurization," *Catal. Today*, Vol. 282, pp. 123-132, 2017.
- [4]. Tang M., Zhou L., Du M., Lyu Z., Wen X-D., Li X. and Hui G., "A novel reactive adsorption desulfurization Ni/MnO adsorbent and its hydrodesulfurization ability compared with Ni/ZnO," *Catal. Commun.*, Vol. 61, pp. 37-40, 2015.
- [5]. Bao Q., Lou Y., Xing T. and Chen J., "Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) in aqueous solution via microwave irradiation," *Inorg. Chem. Commun.*, Vol. 37, pp. 170-173, 2013.
- [6]. Saeedirad R., Ganjali S. T., Bazmi M. and Rashidi A., "Effective mesoporous silica-ZIF-8 nano-adsorbents for adsorptive desulfurization of gas stream," *J. Taiwan Inst. Chem. Eng.*, Vol. 82, pp. 10-22, 2018.
- [7]. Wang S., Fan Y. and Jia X., "Sodium dodecyl sulfate-assisted synthesis of hierarchically porous ZIF-8 particles for removing mercaptan from gasoline," *Chem. Eng. J.*, Vol. 256, pp. 14-22, 2014.
- [8]. Abdouss M., Hazrati N., Beigi A. A. M., Vahid A. and Mohammadalizadeh A., "Effect of the structure of the support and the aminosilane type on the adsorption of H<sub>2</sub>S from model gas," *RSC Adv.*, Vol. 4, No. 12, pp. 6337-6345, 2014.
- [9]. Roy P. and Srivastava S. K., "Hydrothermal growth of CuS nanowires from Cu-dithiooxamide, a novel single-source precursor," *Cryst. Growth Des.*, Vol. 6, No. 8, pp. 1921-1926, 2006.
- [10]. Wu L., Xiao J., Wu Y., Xian S., Miao G., Wang H. and Zhong L., "A combined experimental/computational study on the adsorption of organosulfur compounds over metal-organic frameworks from fuels," *Langmuir*, Vol. 30, No. 4, pp. 1080-1088, 2014.