ATR-FTIR spectroscopy and chemometrics application for analytical and kinetics characterization of adsorption of 1-butyl mercaptan (1-butanethiol) on nickel coated carbon nanofibers (CNFS)

F. Karami, M. Khanmohammadi, A. B. Garmarudi

Chemistry Department, Faculty of Science, Imam Khomeini International University, Qazvin, Iran

Mercaptans are the main compounds in petroleum derivatives that are tried to be removed. In this work, Infrared spectroscopy and chemometrics were utilized to evaluate the analytical and kinetics characteristics of adsorption of 1-butyl mercaptan from n-hexane by Ni coated carbon nanofibers (CNFs). Electroless plating was applied for coating of Ni on CNFs. Three types of adsorbents with different amounts of coated nickel were studied and compared to investigate the effect of nickel amount on modification of the surface of the adsorbent to obtain higher capacity and rate of desulfurization. In order to obtain useful information about the adsorption process, multivariate curve resolution alternating least squares (MCR-ALS) chemometrics method was used. Information about the variations in concentration of 1-butyl mercaptan and kinetics of adsorption was achieved. This study showed that the adsorbent with higher amount of coated nickel had higher rate constant of adsorption. Also, relative concentrations of 1-butyl mercaptan were calculated in different times during adsorption process.

Keywords: ATR-FTIR spectroscopy, desulfurization, MCR-ALS, chemometrics

INTRODUCTION

Sulfur is an abundant component in petroleum and consequently in petroleum based products such as fuels. Combustion of these fuels causes the exhaust of SOx gases into atmosphere, known as one of the most important air pollutant [1]. Authorities all around the world are concerned about this problem and have made regulation to prevent production of high sulfur containing products especially fossil fuels. Euro standard is a common regulation all around the world to control and illustrate the environmental quality of fuels [2]. It is expected to attain Zero emission of SOx gases from fuel combustion in near future due to severe research interest and focus on development of effective desulfurization approaches. There are several types of methods for desulfurization [3-5].

Desulfurization by application of adsorbents has been favorable method for researchers in petrochemical science due to its simplicity and low cost, together with effective in removal outcomes [6]. One of the valuable characteristics of adsorptive desulfurization is its potential to perform deep desulfurization of fuels which may be achieved by other methods, expensively. Thus desulfurization by application of adsorbents is going to be more and more common. The most important step in development of an adsorptive desulfurization method is to prepare high capacity

adsorbents with known properties. On the other hand it is essential to characterize the developed adsorbent. Thus application of proper tools to evaluate, characterize and comparative study of novel adsorbent are the most important requirements for researchers in this domain. Characterization and monitoring of adsorbent during the adsorption process is helpful as well. Different materials have been developed as adsorbents for desulfurization [7-12]. Nowadays, carbon nanostructures such as carbon nanofibers (CNFs) and carbon nanotubes (CNTs) have attracted the attention of the researchers [13, 14]. In some researches this structures have been used as adsorbent [15].

Among analytical characterization method, spectroscopic ones are powerful in wide range of applications in material science especially in monitoring of a chemical system (16). Infrared (IR) spectroscopy as a vibrational spectroscopic method, is attractive due to its ability in detection of chemical structures within molecular level. IR spectra regions such as finger print are unique for different analytes. This ability encourages researchers to employ IR spectroscopy as a powerful analytical method in evaluation of materials and chemical systems.

In spite of advantages for IR spectroscopy, signal overlapping is an important drawback which causes consequent difficulties to extract the spectral feature which is related to target analyte of interest. The most common solution for complicated systems is to conduct a separation procedure but

To whom all correspondence should be sent:
E-mail:mohammadkhah@guilan.ac.ir

this idea is not applicable in most cases especially in an evolutionary process. A promising route for this aim while dealing with spectroscopic data of a chemical system is to use chemometric methods [17]. Chemometrics as combination of chemistry, statistics, mathematics and computer science, tries to provide most useful knowledge from experimental data by extracting the useful information [18, 19].

In this work, carbon nanofibers (CNFs) adsorbents were prepared by electroless coating of nickel with different amounts of metal. Electroless coating is one of the plating methods that is performed without electricity current and it makes uniform deposition and resistant structure against corrosion [20]. Prepared adsorbents were used in desulfurization of model fuel sample containing 1-butylmercatane as a well-known mercaptan in petroleum products. Variations in mercaptan concentration and adsorption kinetics were evaluated by application of MCR-ALS method on obtained infrared spectra by utilizing attenuated total reflectance (ATR) cell (21, 22). Three types of adsorbent with different nickel amount were studied. The rate and relative capacity of them were compared. Figure 1 shows the schematic diagram of the work.
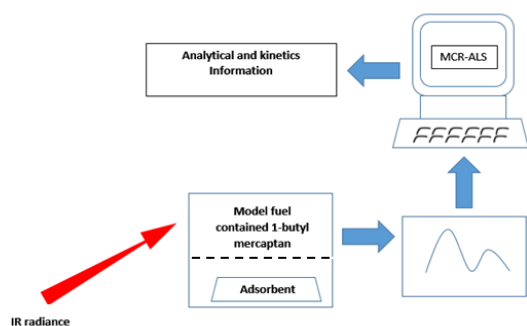

Fig. 1. Schematic diagram for characterization of adsorption process.

MATERIALS AND METHODS

Chemicals

CNFs with outer diameter of 200-600 nm and purity >95% was from neutrino Co. Hydrochloric acid (HCl), sulfuric acid (H_2SO_4 96.2%), nitric acid (HNO_3 65%), ammonia (NH_3), hexane, tin (II) chloride ($SnCl_2.2H_2O$), palladium (II) chloride ($PdCl_2$), sodium hypophosphite hydrate ($NaH_2PO_2.H_2O$) and sodium citrate ($NaHC_6H_5O_7.5.5H_2O$) were all of analytical grade from Merck. Analytical nickel sulfate ($NiSO_4$) and

1-butanethiol were from Scharlau and Acros, respectively. Double distilled water was used to prepare aqueous solutions.

Instruments

A Bomem infrared (Quebec, Canada) MB series FTIR spectrometer with DTGS mid-range detector; a KBr: Ge/Sb_2S_3, using SpectraTech (warrington, UK) in-compartment contact with sampler horizontal attenuated total reflector with a 45° ZnSe trough plate. Coated beam splitter and a SiC source, was used to record spectra. ATR cell and ultrasonic dispenser were used, too.

CNFs preparation

Known amount of HNO_3 and H_2SO_4 were mixed with CNFs in a glass flask being refluxed for 8 hours at 80°C. Oxidized CNFs were filtered to be washed with distilled water and to be dried in oven at 80°C for three hours. In order to sensitization, oxidized CNFs were added to the mixture of HCl (0.15M) and $SnCl_2$ (0.05M) being sonicated for 10 min. at 25°C. Then CNFs were separated by application of centrifuge. CNFs were washed by distilled water.

The next step was to activate the sensitized CNFs by adding them to HCl (0.15M) and $PdCl_2$ ($6×10-4M$) solution and sonicating for10 min. at 25°C. Then CNFs were separated by centrifuge being washed with distilled water.

Plating of nickel on CNFs

Activated CNFs were added to the bath including $NaHC_6H_5O_7.5.5H_2O$ as complexing agent which stabilizes the solution, $NaH_2PO_2.H_2O$ as reducing agent as source of electrons and $NiSO_4.6H_2O$ as the nickel source. Nickel salt solution with concentration of 20, 35 and 50 g/L, were used to prepare adsorbents with three different amounts of nickel.

Desulfurization process

1-Butanethiol solutions (500 ppm) were prepared to be used in evaluation of fabricated CNFs based adsorbents as model fuel. For each mercaptan removal experiment 1g of adsorbent was added to 100 mL of model fuel being sonicated for 5 minutes. And then mixture was stirred. Removal process was continued for 120 minutes and analysis samples were obtained from mixture solution with 20 minutes time intervals.

Chemometric data processing

Recorded spectra of sample solutions were provided the spectral data matrix. Which was then

processed by MCR-ALS inside MATLAB software environment.

MCR-ALS

The first step in performing MCR-ALS is singular value decomposition (SVD) [17] to determine the number of active components in the chemical process.

Next to SVD, initial estimation of concentration was provided by application of evolving factor analysis (EFA) [23] in which submatrices of gradually increasing size from data matrix were selected being treated by principal component analysis (PCA) [17] both from top to bottom (forward EFA) and from bottom to top (backward EFA) to study the emergence and decay of probable active components.

RESULTS AND DISCUSSION

The aim of this work was to characterize the desulfurization capability of nickel coated CNFs adsorbents with different amounts of coated nickel, prepared by electroless plating. 20, 35 and 50 g/L nickel solutions were applied and prepared adsorbents are named A-20, A-35 and A-50, respectively to be studied. Scanning Electron Microscope (SEM) was employed to admit the coating of nickel on CNFs and differences in the adsorbents prepared by different nickel concentrations as observed in Figure 2. The adsorbents prepared by more concentrated Ni solutions demonstrate more nickel nanoparticles on the surface. Also, atomic absorption measurement admitted the high amount of coated nickel on CNFs by application of nickel solution with higher concentration. Figure 3 shows the result of atomic absorption measurements.

In desulfurization process the IR spectra of the model fuel solution were recorded in increments of 20 min. The related IR spectra for each sample are illustrated in Figure 4.
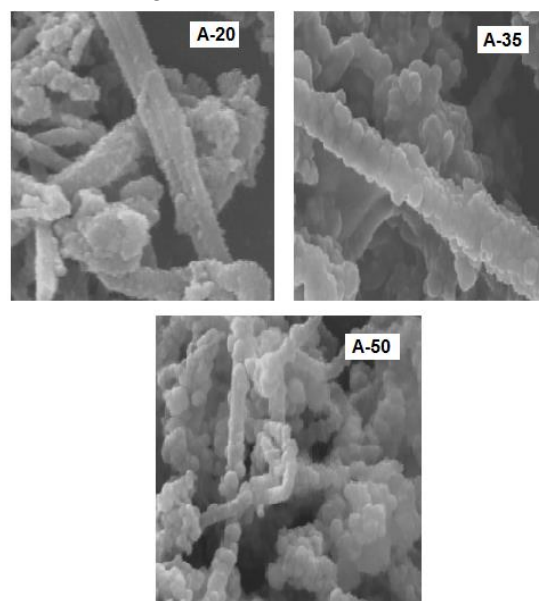

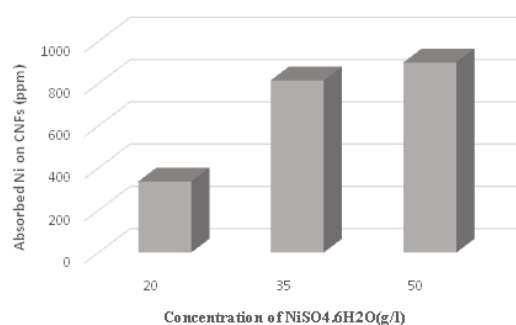
Fig. 2. SEM photos of three types of adsorbents

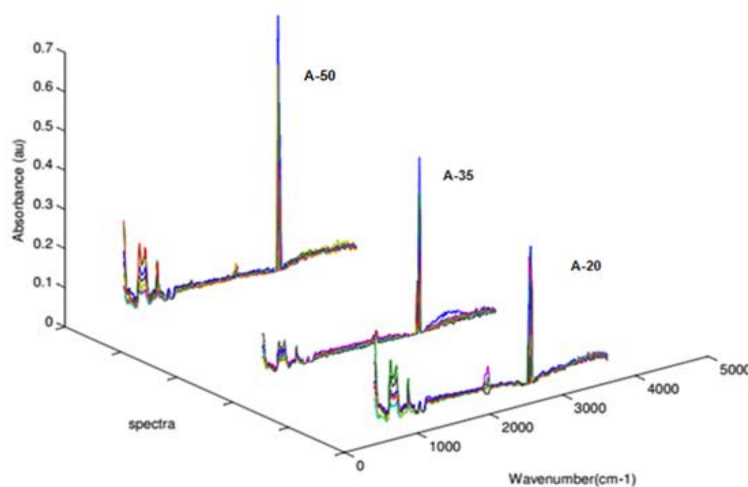**Fig. 3.** The results of atomic absorption to evaluate the coated nickel amount.

Fig. 4 Recorded IR spectra of mercaptan removing chemical system with adsorbents.

After constructing the spectral data matrix for each sample, preprocessing was conducted including baseline correction and noise removal. The next step was to perform MCR-ALS as a curve resolution method which would decompose the data matrix into two matrices of concentration (C) and spectral (S^T) profiles of data set for each component, utilizing least squares.
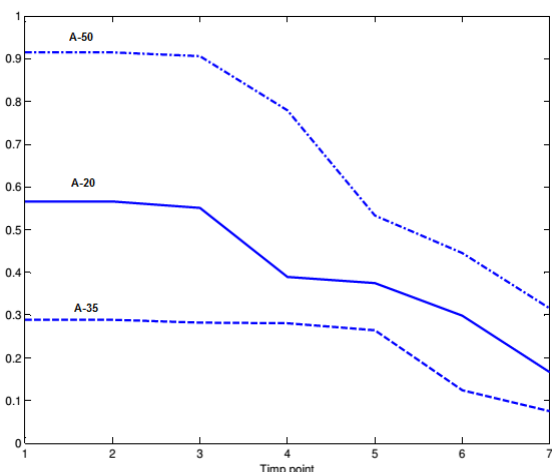

Fig. 5 Concentration profile of active component from EFA

The first step was SVD which showed only one component to be active within the system. Then EFA was performed. To obtain concentration of 1-butyl mercaptan during the removal process. Figure 5 shows the concentration profiles of active component in desulfurization process for studied samples.

The concentration profile provided by EFA was applied to start the optimization process in MCR-ALS, obtaining the spectral profile to screen the structure of active component and concentration profile to monitor its concentration variations. In some of the usual constraints of MCR-ALS were applied during optimization process to attain assured results. Non-negativity is a constraint which proposes the calculation so that spectral profile of the active components and their related concentrations cannot have negative values. On the other hand, unimodality constraint would affect the resolved concentration profiles to obtain only one maximum in resolved profile. Figure 6 and Figure 7 show the spectral and concentration profiles of the systems, respectively.

The spectral features of the profile confirm the similarity between the active component detected in the system and 1-butyl mercaptan while concentration profiles shows gradual decrement in concentration of this component in all the samples.

Table 1 shows the relative concentration of 1-butyl mercaptan during the adsorption process determined by MCR-ALS output. The results show that the adsorbent with higher amount of nickel adsorbs higher amount of mercaptan.

Adsorption kinetics

Another role of chemometric data processing methods was to aid in calculation of kinetics model of chemical process [24, 25]. Quantitative results provided by concentration profile of the MCR-ALS model were applied to conduct a kinetics study for the adsorption process calculating the kinetics constant. For this aim, at first a predefined kinetics model was selected trying to fit the concentration data to the proposed model. Considering the initial estimation of concentration profile, first order kinetics model was selected. The equation of first order kinetics model is:

$$[A]= [A]_0 e^{-kt} \qquad (1)$$

Where [A] is momentary concentration of 1-butyl mercaptan, $[A]_0$ is the initial concentration, k is the kinetics constant and t is time. The calculated kinetics constant and validation parameters of MCR-ALS are shown in Table 2 for all samples.

Table 1.- Relative concentration of 1-butyl mercaptan during adsorption process

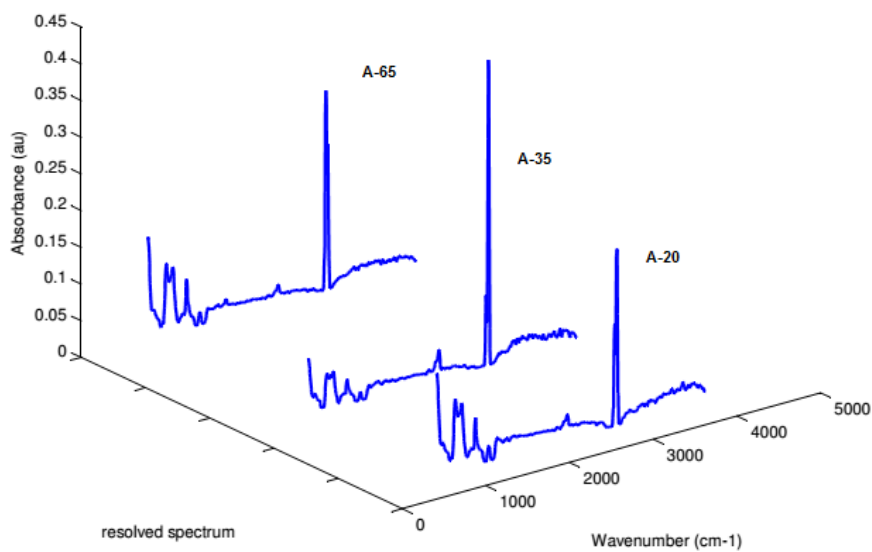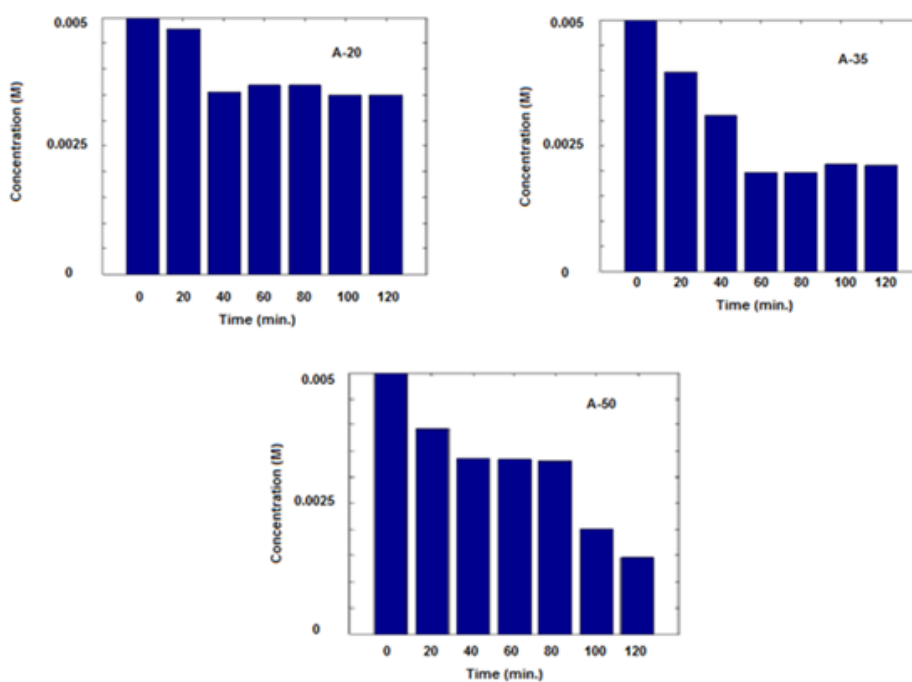| Time (min.)	A-20 (%)	A-35 (%)	A-50 (%)
0	100	100	100
20	95.54089	79.38959	78.53602
40	71.06656	62.01267	67.15535
60	73.86979	39.36603	66.86252
80	73.86979	39.36603	66.29031
100	69.96974	42.63515	40.26428
120	69.96974	42.17822	29.03991

Fig. 6. Spectral profiles of mercptan.

Fig. 7. Concentration profiles of A-20 (A), A-35(B) and A-50 (C).

Table 2. Kinetics and validation parameters

	A-20	A-35	A-50
k	0.7	1.2	2.3
Sum of Squares for k calculation	0.04	0.03	0.05
Standard deviation of residual vs. experimental data for MCR-ALS	0.002	0.005	0.002
R^2 for MCR-ALS	0.98	0.99	0.99

It is obvious that with increasing of the amount of nickel coated on CNFs the rate constants of the adsorption have increased. The main reason for increasing the relative capacity and rate constant of adsorption for adsorbent with higher amount of metal, can be related to the making connection between the non-bonding electron pairs in sulfur and metal on the surface.

CONCLUSION

Adsorption is one of the main strategies in desulfurization of petroleum products as simple and low cost way. Improvement of this strategy needs to develop well characterized adsorbents. One of the essential needs for specialist in petrochemical science is ability to characterize the adsorbent and adsorption process in a proper way. This work applied ATR-FTIR spectroscopy with ability to detect a wide range of compounds to evaluate the adsorption of 1-butyl mercaptan as pollutant in fuel by nickel coated carbon nanofibers as new adsorbent. Evaluation was performed for three types of adsorbents with different coated nickel amount. Also MCR-ALS chemometrics method was used to obtain the concentrations variations of 1-butyl mercaptan and Kinetics constant during the adsorption process. This exploratory study showed that the adsorption of 1-butyl mercaptan has higher amount and rate for adsorbents with higher amounts of coated nickel.

REFERENCES

1. K.K Sarda., A. Bhandari, K.K. Pant, S. Jain, *Fuel., 93*, 86 (2012).
2. S. Brunet, D. Mey, G. Pérot, C. Bouchy, F. Diehl, *Applied Catalysis A General, 278*, 143 (2005).
3. M. Rashtchi, G.H. Mohebali, M.M. Akbarnejad, J. Towfighi, B. Rasekh, A. Keytash, *Biochemical Engineering Journal*, 29, 169 (2006).
4. Z. Jiang, H. Lü, Y. Zhang, C. Li, *Chinese Journal of Catalysis*, 32, 707 (2011).
5. Y. Fan, G. Shi, H. Liu, X. Bao, *Fuel, 90*(5), 1717 (2011).
6. A.H.M.S. Hussain, B.J. Tatarchuk. *Fuel, 107*, 465 (2013).
7. Y. Wang, F.H. Yang, R.T. Yang, J.M. Heinzel, A.D.Nickens, *Industrial & Engineering Chemistry Research, 45*, 7649 (2006).
8. F. Subhan, B.S..Liu, *Chemical Engineering Journal, 178*, 69 (2011).
9. C. Sentorun-Shalaby, S.K. Saha, X. ,Ma C. Song *Applied Catalysis B: Environmental, 101,* 718 (2011).
10. X. Ma, M. Sprague, C. Song, *Industrial & Engineering Chemistry Research*, **44,** 5768 (2005).
11. M.V. Landau, M. Herskowitz, R. Agnihotri, JE. Kegerreis, *Industrial & Engineering Chemistry Research*, **47(18),** 6904 (2008).
12. A.J. Hernández-Maldonado, G. Qi, RT. Yang *Applied Catalysis B: Environmental, 61*, 212 (2005).
13. N.M..Rodriguez, *Journal of Materials Research, 8(12),* 3233 (199).
14. R.H. Baughman, A.A. Zakhidov, W.A. de Heer *Science*, **297,** 787 (2002).
15. V.K. Gupta, R. Kumar, A. Nayak, T.A. Saleh, M.A. Barakat*, Advances in Colloid and Interface Science.* **193–194,** 24 (2013).
16. T. Schadle B. Pejcic B. Mizaikoff, *Analytical Methods*, **8**, 756 (2016).
17. R.G. Brereton, Chemometrics: Data Analysis for the Laboratory and Chemical Plant: Wiley; 2003.
18. M. Maeder, Y.M. Neuhold, Practical Data Analysis in Chemistry, Elsevier Science; 2007.
19. P. Gemperline, Practical Guide To Chemometrics, Second Edition, CRC Press; 2006.
20. C-Y. Huang, J-F. Pai, *European Polymer Journal*, **34**, 261 (1998).
21. J. Jaumot, R.A. Gargallo de Juan Tauler *Chemometrics and Intelligent Laboratory Systems.* **76**(1), 101 (2005).
22. K.H. Esbensen, D. Guyot, F. Westad, L.P. Houmoller, Multivariate Data Analysis - in Practice: An Introduction to Multivariate Data Analysis and Experimental Design: Camo Process AS; 2002.
23. H.R. Keller, D,L. Massart, *Chemometrics and Intelligent Laboratory Systems.* **12**, 209 (1991).
24. Y. Guo, Y. Ni, J. Chen, S. Kokot, *Analytical Methods.* **8**, 197 (201).
25. A. de Juan, M. Maeder, M. Martínez, R. Tauler *Chemometrics and Intelligent Laboratory Systems, 54*, 123 (2000).