Nano clay Ni/NiO nanocomposite new sorbent for separation and preconcentration dibenzothiophene from crude prior to UV—vis spectrophotometery determination

Amineh Mashkuri [a, b], Asma Saljooqi [a, b, *], Zeinab Tohidiyan [a, b]

[a] Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, PO Box 76169-133, Iran
[b] Young Research Society, Shahid Bahonar University of Kerman, Kerman, PO Box 76169-133, Iran

ABSTRACT

In this work, Ni/Ni nanoparticles were immobilized on modified nanoclay then, the resultant nano-composite was used as a sorbent for separation of dibenzothiophene. The concentration of dibenzo-thiophene was determined with UV—vis spectrophotometry at 287 nm. Different parameters affecting the separation of dibenzothiophene such as: the ratio of Ni/NiO nanoparticles to nanoclay, amounts of Ni/NiO nanoparticles and nanoclay, stirring time of dibenzothiophene solution on the sorbent, type of eluent, eluent volume, elution time, stirring time for preparing the sorbent were optimized. The obtained results were shown quantitative desorption of dibenzothiophene performed using ethanol as eluent. A linear concentration range of 0.5—15 mg/L was obtained with a detection limit of 0.047 mg/mL. The sorbent capacity was found to be 32 mg/g. Relative standard deviation was ±1.4 for six replicated determination of 5 mg/g of dibenzothiophene. The optimized procedure was successfully used for a crude oil sample.

1. Introduction

Nowadays there is an increasing environmental concern about the pollution caused by fossil fuels. Apart from fuel components, sulfur has an important role among the fuel contaminants and seems to be a big concern in environmental pollution. In most developed countries sulfur limits of less than 30 ppm for gasoline were introduced since 2006 [1,2]. During fuel combustion, mole-cules containing S form SO_x pollutants, the main responsible for acid rain [3,4] and so this organic molecules migrate in the direc-tion of ground water together with irrigation and drainage their migration can be slowed down as a consequence of their adsorption by different components of soils and sediments [5,6]. Moreover, S-contaminants poison car catalysts preventing them to remove most of the gas pollutants produced during combustion. Ever stricter legislation has been implemented all over the world to limit the content of sulfur and nitrogen in petroleum fuels. For this reason, the development of new technologies for S and N removal are necessary.

Furthermore, due to the fast change in climate, new approaches for more effective desulfurization may become more necessary in the near future. Therefore in commercial diesel or gasoline it is demanded to reduce the content of sulfur containing compounds such as thiophene, benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) to very low levels in order to prevent air pollution from SO_x and deactivation of cata-lysts. To reach this low sulfur level, various methods such as hydrodesulfurization [7—9], oxidation [10—12] and adsorption [13—16] have been investigated. Among them, adsorption has been regarded as one of the most competitive methods, especially for ultralow sulfur content, since it can operate at ambient conditions.

In addition to the common adsorbents used in SPE, clay based sorbents are potentially useful materials for the adsorption of environmental pollutants due to their unique polarity, pore-size distribution, and high surface areas [17,18] Considering their important role in the transport and retention of organic com-pounds in the soil, intercalated clays can be utilized as selective sorbents for organic pollutants. The sorbent should a cheap with adsorption properties which are specific towards a certain material.

* Corresponding author. Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, PO Box 76169-133, Iran.
E-mail address: saljooqi.a@gmail.com (A. Saljooqi).

Clay minerals are cheap adsorbing materials with high surface areas and specific basic and acidic properties which depend on the composition of the mineral [19,20]. It is, therefore, supposed that they can be used for this purpose.

Composites of metal/oxide nanoparticles supported on clay can be prepared by various techniques and their preparation is still largely based on conventional techniques such as ion exchange processes [21], γ-irradiations [22], hydrothermal synthesis [23], chemical reduction methods [24,25], polyol reduction methods [26], solvothermal methods [27], electroless plating [28] and hydrothermal synthesis [29].

Among These types of adsorbents explored, Ni-based Adsorbent exhibited better performance for removing thiophenic sulfur compounds from liquid fuels. Song and co-workers used a nickel-based Ni–Al adsorbent in an adsorption desulfurization system at a temperature range of 25–200 °C under ambient pressure without using H_2 [30]. The nickel-based adsorbents show high selectivity and sulfur adsorption capacity for the real gasoline. Landau et al. reported adsorptive desulfurization of commercial low-sulfur (22 ppm) containing gasoline on Ni/Al–SiO_2 in A fixed bed at 230 °C [31]. They found that addition of ethanol could strongly improve the performance of reduced Ni/Al–SiO_2 adsorbents.

Therefore, the objective of this paper is to investigate adsorptive desulfurization over nano particles of Ni/NiO-loaded nano clay for the separation of DBT from crude oil. Adsorptive selectivity for DBT and effects of the potentially interfering compounds as well as adsorption conditions on the adsorptive performance were studied in detail.

2. Materials and methods

2.1. Materials

All the reagents used were of the highest purity available and at least of analytical reagent grade. Nanoclay (Cloisite® 15A) was purchased from Nanocor (Aberdeen, United States). Dibenzothiophene of 98% purity was supplied from Merck F (Darmstadt, Germany). The NiO nanoparticles used was synthesized according to the procedure described in the literature (Fig. 1) [32].

2.2. Apparatus

Absorption spectra were obtained with a Varian Cary-50 UV–Vis spectrophotometer by using 1 cm path length quartz cells and the measurements were performed at 25 ± 0.1 °C (California, USA). IEC-model HN-S centrifuge (Minnesota, USA) was used to accelerate phase separation. Funnel tipped glass tubes (80 × 5 mm) were used as columns for holding the sorbent. All glassware and columns were washed with mixture of concentrated hydrochloric acid and concentrated nitric acid (1:1) before use.

2.3. Preparation of the sorbent

0.1 g of nano clay was entered to a test tube containing a magnet in it, respectively 3 ml octanol, 0.1 g benzyldimethyltetradecylammoniumchloride; 0.2 g of Ni/NiO nanoparticles was added. The resulting mixture was stirred for half an hour at high speed by a magnetic stirrer. Then, to remove impurities were washed 3 times with 2.0 ml of ethanol for 2 min was centrifuged at 3000 rpm. Then for 3 h at 75° C was dried in an oven.

2.4. Select the absorption appropriate wavelength

The solution with a concentration of 5.0 mg L^{-1} of DBT was prepared and its absorption by the UV–vis spectrophotometric measurement of the absorption spectrum was scanned from 270 to 350 nm. Referring to Fig. 2, the spectrum has a maximum at 287 nm, which was chosen as the benchmark index for the quality and quantity of this work.

2.5. General procedure

A 2.0 ml of an hexane solution containing 5.0 mg of DBT was added into prepared sorbent and was stirred for 20 min on a magnetic stirrer at high speed. Then it was centrifuged at 3000 rpm and the solution onto the sorbent was removed. Separated solution absorbance, was measured by a UV–vis spectrophotometer. It was observed that 100% of the amount of DBT in the first solution was adsorbed by the sorbent. Then, the amount of 2 ml of ethanol was added into the sorbent and then for 10 min with a magnetic stirrer was stirred at high speed. Then centrifuged at 3000 rpm and the solution onto the sorbent were removed. Absorption of amount recovered by ethanol was measured with a UV–vis spectrophotometer. Thus, it is concluded that the volume of ethanol is able to
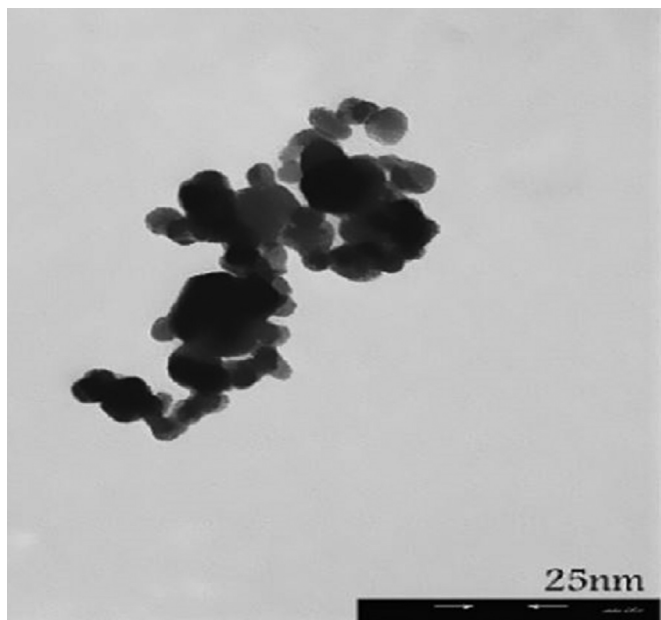

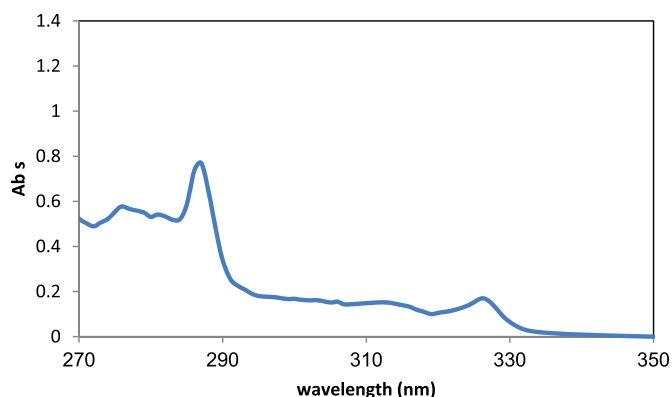**Fig. 1.** TEM image of the NiO nanoparticles.

Fig. 2. Select the appropriate wavelength.

recover 100% of the amount of DBT adsorbed by the nanoclay, respectively.

3. Results and discussion

In order to achieve the best performance, the separation procedure was optimized for various analytical parameters, such as the ratio of Ni/NiO nanoparticles to nanoclay, amounts of Ni/NiO nanoparticles and nanoclay, stirring time of DBT solution on the sorbent, type of eluent, eluent volume, elution time, stirring time for preparing the sorbent. The effects of various potentially interfering ions were also investigated. In all experiments, the recovery percentage (R%) was calculated as the product of CeVe/CiVi to 100; where C and V represent DBT concentration and volume and suffixes e and i correspond to the elute and initial solutions, respectively.

3.1. Choosing appropriate sorbent

The three sorbent for the extraction of DBT were studied. These adsorbents are: nanoclay, nanoclay modified with nickel oxide nanoparticles and nanoclay modified with nanoparticles of nickel/nickel oxide. According to the results reported in Table 1 were observed nanoclay modified with nanoparticles of Ni/NiO sorbent for the extraction of DBT from the other two sorbent is better, therefore nanoclay modified with nanoparticles of NiO/NiO was selected as the best sorbent.

3.2. The ratio and amounts of nano Ni/NiO to nanoclay

For the effective Adsorption of DBT, sorbent was prepared with three different ratios of nano clay and nanoparticle of Ni/NiO. Then the extraction of DBT was carried out. The results are reported in Table 2. The results show that when the ratio of nano Ni/NiO and nano clay is 2 to 1, the recovery of DBT is 100%. Three adsorbent each with the ratio of 2 to 1, but with different amounts of nano clay were prepared. The results in Table 3 show that the amount of 0.2 g of nano Ni/NiO and 0.1 g of nano clay show the best recovery for DBT.

The result show that increasing the amount of Ni/NiO nanoparticles stabilized on nano clay is associated with increased adsorptive capacity of the sorbent to adsorb the DBT, and this effect is due to the tendency of Ni/NiO nanoparticles is to adsorb DBT.

3.3. Effect of time of stirring, solution of DBT on the sorbent

The retention of a compound on an adsorbent depends on the contact time of the sample solution. The effects of stirring time on the DBT adsorption over nanoclay were examined. Table 4 shows that most recovery of DBT is at the stirring times 20, 30 and 40 min. By increasing the stirring time from 10 to 40 min, the recovery increases. First, by increasing the stirring time from 10 to 20 min DBT molecules have more time to contact with increase stirring time more than 20 min, the percentage of adsorption remains constant. Thus, to prevent the long time of the process, the stirring time 20 min for the DBT (see Table 4).

Table 1
Choosing appropriate sorbent.

Sorbent	% Recovery
Nanoclay	22.1
Nanoclay modified with NiO nanoparticles	43.3
Nanoclay modified with Ni/NiO nanoparticles	68.9

Table 2
The ratio of nano Ni/NiO to nanoclay.

Ratio of nano Ni/NiO to nanoclay	Recovery %
1:0	22.1
1:1	78.4
1:2	68.9
2:1	100.0

Table 3
The amounts of nano Ni/NiO to nanoclay.

Nanoclay (g)	Nano Ni/NiO (g)	Recovery %
0.05	0.1	61
0.1	0.2	100
0.15	0.3	64

Table 4
Effect of time of stirring, solution of DBT on the sorbent.

Time (min)	Recovery %
10	97.0
20	100.0
30	99.9
40	99.6

3.4. Choice of eluent

One important factor that affects the extraction efficiency is the type, volume, and concentration of the eluent used for the elution of metal ions from the sorbent [33]. A series of selected eluents, including carbon tetrachloride, dimethyl formaldehyde, ethanol, dichloromethane and acetonitrile were used for elution of DBT from the modified nanoclay. As shown in supporting information Table 5, ethanol and dichloromethane provides the best effective elution of DBT but Due to the toxicity of dichloromethane, ethanol was chosen as eluent solvent. Also check the amount of recovery by acetonitrile, in addition to having a lot of noise, there is no peak; acetonitrile thus cannot act as an eluent.

The effect of the volume of ethanol on the recovery of DBT also was studied. The results obtained showed (Fig. 3) that the extraction recovery increased with increase of the eluent in the range of 1–4 mL, then remained constant when the amount was
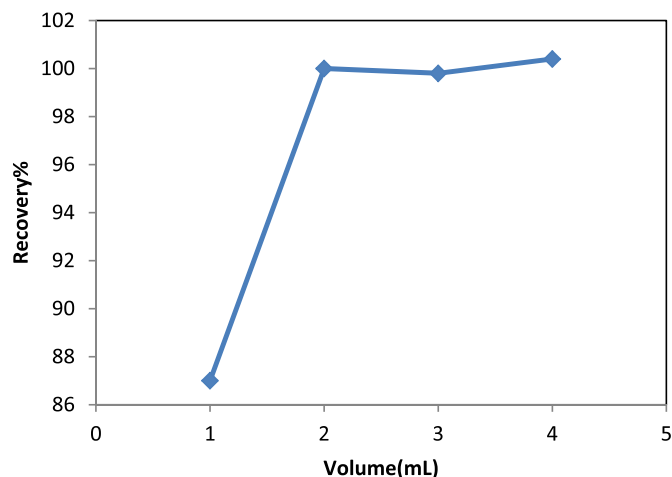

Fig. 3. Eluent volume.

Table 5
Choice of eluent.

Type of Eluent	Recovery %
Carbon tetrachloride	69.0
Dimethyl formaldehyde	79.0
Ethanol	100.0
Dichloromethane	100.3
Acetonitrile	−

Table 7
Stirring time for preparing the sorbent.

Time (min)	Recovery %
5	80.0
10	86.0
15	86.1
20	86.4
30	100.0
60	100.4

continuously increased. Therefore, 2.0 mL of ethanol was used for the desorption of DBT from the sorbent in the subsequent experiments.

3.5. Effect of stirring time of eluent

The effect of different stirring time on the recovery of the analyte was studied from 5.0 to 40.0 min. According results, initially with increased stirring time, due to increased contact time the adsorbent with eluent, recovery of DBT increases until at 10 min, becomes one hundred percent recovery. With increasing of time more than 10 min, the percent recovery does not change and remains constant, resulting stirring time 10 min, is the best stirring time of ethanol on the sorbent for recover DBT (Table 6).

3.6. Stirring time for preparing the sorbent

For the preparation of sorbent, 0.1 g clay was transferred to a test tube and the order of 3 ml octanol, 0.1 g benzyldimethylte-tradecylammoniumchloride, and 0.2 g of nano Ni/NiO was added. The mixture was stirred at high speed at various times. Then, to remove impurities were washed 3 times with 2 ml of ethanol for 2 min each time it was centrifuged at 3000 rpm. Sorbent for 3 h at 75° C in an oven was dried. Then DBT extraction was performed according to the procedure. According to the results, time 30 min to prepare the adsorbent was the best of times. The results are shown in Table 7.

3.7. Analytical performance

Under the optimized conditions, the calibration curve for DBT was obtained by extraction a series of DBT standards according to the procedure outlined above. The curve was linear from 0.5 to 15.0 mg/L for DBT. The calibration equation was $A = 0.0457C + 0.279$ with a correlation coefficient of 0.9967, where A is the absorbance, and C is the concentration of DBT in the first solution (mg/L). The LOD defined as $3s_b/m$ (where s_b is SD of the blank and m is the slope of the calibration cure) were obtained to be 4.7×10^{-2} mg/g. Relative standard deviation was ±1.4 for six replicated determination of 5.0 mg/g of DBT. The enrichment factor was 4. Because of this, the aim of this work is extraction of DBT and not preconcenteration, the enrichment factor obtained for this work is acceptable. The optimized procedure was successfully used for a crude oil sample.

Table 6
Effect of stirring time of eluent.

Time (min)	Recovery %
5	96.8
8	98.9
10	100.0
20	100.0
30	100.1
40	99.6

3.8. Adsorption capacity

The adsorption capacity is the maximum compound quantity taken up by 1 g of solid phase and given by milligram compound per gram sorbent [34]. To assess the absorption capacity of the adsorbent for the DBT, the continuous extraction method was used. In this work, 2.0 ml of DBT with a known concentration was transferred to 0.3 g sorbent and then percent extraction of DBT was measured using UV−vis spectrophotometry. The transferred DBT concentration was gradually increased to the sorbent and then percent extraction of DBT was measured. The gradual increase in concentration until the percent of extraction does not decrease was continued. Finally in the concentration of 4800 mg/L was the extraction of DBT is 100% percent. At concentrations greater than 4800 mg/L, extraction percent is less than one hundred. The maximum capacity of the sorbent for DBT was found to be 32 mg/g.

3.9. Interference effect

With a gradual increase in the amount of interference compounds during subsequent analysis and evaluation of recovery values obtained at each step, limit of interference for interfering compounds the determination of analyte compounds, are obtained. The tolerance limit was defined as the highest amount of interfering compounds that produced an error no >±5% in the determination of investigated DBT. The results show (Table 8) that the proposed method is of good selectivity and can be used for determination of DBT in various real samples without interference.

4. Applications

4.1. Determination of DBT in crude oil

To determine the concentration of DBT in crude oil, 1 μL of crude oil was dissolved in 22 mL of dichloromethane, Then equal volumes (2 ml) of this solution was transferred into a 5 mL volumetric flask and by solutions containing different and certain amounts of DBT in dichloromethane, was brought to volume. Then 2 ml of the resulting solution was transferred onto the prepared sorbents and according to procedure, extraction was performed. Absorption intensity was measured by a UV−vis spectrophotometer. Results in Fig. 4 have been reported. With using extrapolation of the line in Fig. 4, DBT concentration in crude oil is equal to: 7.183×10^4 mg/L.

Table 8
Interference effect.

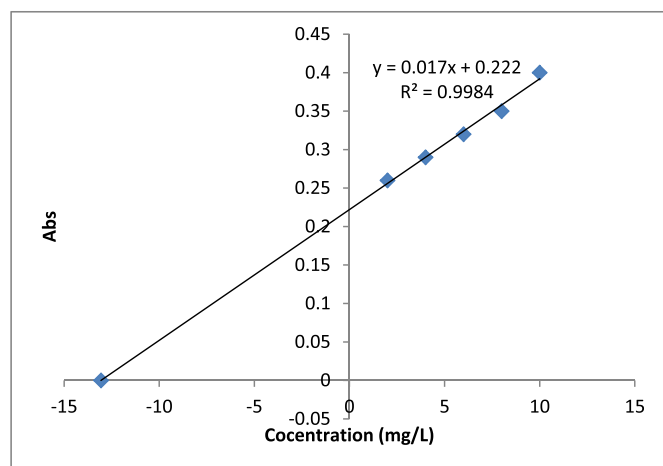| Foreign compound	Foreign compound/Dibenzothiophene	Recovery %
Carbon disulfide	1	100.0
Carbon disulfide	100	100.0
Hexadecanthiol	1	100.0
Hexadecanthiol	100	100.0

Fig. 4. Determination of DBT in crude oil.

5. Conclusion

High sulfur content in petroleum products may cause environmental pollution and other negative consequences. Thiophene compounds, a significant portion of the organic sulfur compounds in oil form. The thiophene compounds, DBT has the highest frequency. Due to these reasons, the separation DBT of fossil fuel important.

In this work, for the first time nano clays modified with nanoparticles of Ni/NiO is used to remove the DBT. In order to evaluate the performance of these adsorbents for the separation of DBT, DBT concentration washed with ethanol by a UV–vis spectrophotometer was measured. A crude oil sample to evaluate the usability of the proposed method for real samples, were analyzed.

In the present work, the first of Ni/NiO nanoparticles stabilized on clay was used to separation the DBT. Ability of the adsorbent to remove DBT is very good so that its absorbing capacity has very high. The proposed method is cheap, easy, fast and has industrial capability.

Acknowledgements

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