Using Solid Phase Micro Extraction Method to Separate the Trace Elements from Crude Oil Samples by Nano Graphene Oxide as a Sorbent

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Abstract

The separation method of trace elements from crude oil samples is a very important, samples collected from oil fields in Maysan province- Iraq, digested by dry ashing method (ASTM-D5863-00a). Nano graphene oxide (NGO) synthesized by modified Hummer's method and characterization by Fourier transform infrared spectrophotometer (FT-IR), ultraviolet-visible spectrophotometer (UV-vis), X-ray diffraction spectroscopy (XRD), Zeta potential analyzer and field emission scanning electronic microscopy (FESEM). Solid phase micro extraction method (SPME) used the synthesized nano sheets of GO to separate the trace elements (Mg, Co, Ni, Cu, Cd and Pb) from crude oil samples at the optimum conditions. Average concentrations of the analyte elements in crude oil samples Mg, Co, Ni, Cu, Cd and Pb, (6.013 µg/mL), (0.654 µg/mL), (23.685 µg/mL), (0.509µg/mL), (0.317 µg /mL) and (5.665 µg/mL) respectively, determined directly by flame atomic absorption spectroscopy. The average residual concentrations of the analyte elements by SPME method by using nano sheets of (GO) as a sorbent decreased due to the adsorption of the analyte ions on the nano sheets of GO , Mg, Co, Ni, Cu, Cd and Pb, (1.044 µg/mL), (0.078 µg/mL), (5.266 µg/mL), (0.091µg/mL), (0.038 µg/mL), and (1.042 µg/mL) respectively.

Key words: Trace elements, SPME, Nano sheets of graphene oxide, Crude oil, ASTM, and FESEM.

1. Introduction

Solid phase micro extraction (SPME) is a popular method for the separation and pre-concentration of metal ions, commonly used before atomic absorption spectrometry (AAS)(1), nano graphene oxide used as a sorbent in solid phase micro extraction method (SPME)(2). Direct dispersion of hydrophobic graphene oxide sheets in water has generally been considered to be an insurmountable challenge because of its high specific surface area and very strong van der Waals interactions of layer to layer. This could lead to irreversible agglomerates or even restack to form graphite and thus interrupt the further evolution of graphene oxide for analytes pre-concentration(3), using surface-active agents(4) or polar solvents as solubilizing or dispersing agents(5).

Nano graphene oxide is a flat monolayer of carbon atoms with a carbon-carbon distance 0.142 nm is the first truly two-dimensional (2D) crystalline material(6), high theoretical specific surface area (2630 m²/g⁻¹), suggesting a high sorption capacity(7), consists of a hexagonal carbon network with carboxyl, carbonyl, hydroxyl and epoxy functional groups(8). These oxygen-containing functional groups can bind with metal ions, especially the multivalent metal ions through both electrostatic and coordinate approaches, which makes nano graphene oxide an ideal sorbent for metal ions(9). Nano Graphene oxide (NGO) represents a novel type of carbon adsorbents, has great features which make it an excellent sorbent for the pre-concentration of trace metal ions, the main advantage of this sorbent is the large surface area which responsible for its high adsorption capacity and high chemical activity, because of the both sides of the planar sheets of graphene oxide are available for molecule adsorption unlike carbon nanotubes (CNTs) and fullerenes(10).

Many metals are present in crude oil as Al, Mg, Ti, Cr, Mn, Fe, Co, Cu, Zn, Ga, As, Cd, Sn, Pb, Mo, Sb, Ag, and Ba, but V(II) and Ni(II) metals are present in a high concentrations in crude oil, inorganic salts mainly as chloride and sulphate of Na, Mg, K and Ca(11). The aim of this study was using SPME
method, synthesized nano sheets of (GO) used as a sorbent to separate trace elements from crude oil samples, the application is the novelty of this study.

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2. Methodology

2.1 Instruments

Flame atomic absorption spectroscopy (FAAS) AI-1200, Aurora used for determination (Mg, Co, Ni, Cu, Cd and Pb) analytes, the operating condition for FAAS were shown in Table-1.

UV-vis spectrophotometer (double beam, UV-1800, Shimadzu), Fourier transform infra-red (FTIR-8400S, Shimadzu), Zeta potential analyzer (ELS type, zeta plus, Brookhaven), X-ray diffraction (XRD, LabX-XRD-6000, Shimadzu), Field emission scanning electronic microscopy (FESEM, 5KV, Zeiss), probe sonicator (FSFJY92-IIN, Sino Sonics), stirring water bath (KBLEE 2010) and muffle furnace (CWF1100).

Table-1 Operating parameters of FAAS according to manual instructions

<table>
<thead>
<tr>
<th>Elements</th>
<th>Wave length (nm)</th>
<th>Slit width (nm)</th>
<th>HCLamp (mA)</th>
<th>Range of calibration standard (µg/mL)</th>
<th>Flame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>285.2</td>
<td>0.2</td>
<td>5</td>
<td>0.5 – 2</td>
<td>Air/acetylene</td>
</tr>
<tr>
<td>Co</td>
<td>240.7</td>
<td>0.2</td>
<td>7</td>
<td>0.5 – 2</td>
<td>Air/acetylene</td>
</tr>
<tr>
<td>Ni</td>
<td>232.0</td>
<td>0.2</td>
<td>7</td>
<td>0.5 – 2</td>
<td>Air/acetylene</td>
</tr>
<tr>
<td>Cu</td>
<td>324.7</td>
<td>0.2</td>
<td>6</td>
<td>0.5 – 2</td>
<td>Air/acetylene</td>
</tr>
<tr>
<td>Cd</td>
<td>288.8</td>
<td>0.2</td>
<td>5</td>
<td>0.5 – 2</td>
<td>Air/acetylene</td>
</tr>
<tr>
<td>Pb</td>
<td>217.0</td>
<td>0.2</td>
<td>5</td>
<td>2.0 – 8</td>
<td>Air/acetylene</td>
</tr>
</tbody>
</table>

2.2 Chemicals

All solutions were prepared by using (19.5 µS/cm) deionized water, standard solutions were prepared by serial dilution of stock solutions (1000 µg/mL) Magnesium sulphate, Cobalt sulphate, Nickel sulphate, Copper sulphate, Cadmium sulphate and Lead nitrate from Sigma-Aldrich. Graphite (99.9 %), CDH company, Sulphuric acid (97%) ChemLab, Dimethyl formamide (99.5%), Potassium permanganate, Sodium nitrate/ Thomas beaker, Hydrochloric acid (37%) Applichem, Hydrogen peroxide (50%) Panreac applab.

2.3 Synthesis of nano graphene oxide

Nano graphene oxide (NGO) synthesized by modified Hummer's method\(^\text{(12,13)}\) as shown in Fig.-1. This included 0.6 g graphite and 0.5 g sodium nitrate (NaNO\(_3\)) dissolved in 23 ml of cooled (0 °C) concentrated sulfuric acid (H\(_2\)SO\(_4\)) in beaker 500 ml onto ice bath with stirring for 15 min. Potassium permanganate (KMnO\(_4\)) 3.0 g added gradually to the suspension (black color), continuous stirring to keep the reaction temperature below 20 °C onto ice bath for 30 min. The reaction beaker placed in stirring water bath at 35 °C for 2hrs. (the suspension changed to dark brown). Deionized water 50 ml added gradually (by dropper) into the suspension over a hot plate magnetic stirrer, the temperature kept below 98 °C, for 15 min, warm deionized water 100 ml added. Hydrogen peroxide (30% H\(_2\)O\(_2\)) 10 ml added gradually (by dropper) to remove the residual KMnO\(_4\) and MnO\(_2\), for 15 min. The suspension separated by centrifuge (4000 rpm for 5 min), the precipitate washed with warm hydrochloric acid (HCl) 5% to remove sulphate ions, washed with deionized water until the pH of washing solution
became 7. The product (graphene oxide) dried in oven at 60 °C for 1 hr. Graphene oxide 0.5 g added to 50 ml of N, N-di methyl formamide (DMF) solvent and sonicated by probe sonicator for 30 min, the suspension separated by centrifuge (4000 rpm for 10 min), the separated residue dried in oven at 60 °C for 1 hr.

![Graphene and Graphite](image)

Fig.-1 Hummer’s method

2.4 Optimum conditions of the solid phase micro extraction method (SPME)

The analytes (Mg, Co, Ni, Cu, Cd and Pb) determined directly in crude oil samples by FAAS. The optimum conditions of solid phase micro extraction method (SPME) by using nano sheets of graphene oxide, 20 ml digested sample volume, pH = 8, 0.5 mg of (NGO), sonicated time 2 min., stirring time 5 min. at room temperature and three droplets of 6.5 mg/mL NaCl, centrifuged for 5 min (5000 rpm) to separate the solid phase of (NGO) from the solution, analytes concentration determined in the residual solutions by FAAS.

2.5 Samples digestion

Samples digested by dry ashing digestion method according to ASTM-D5863-00a\(^{14,15}\), crude oil 1 g placed in crucible porcelain, 0.5 mL conc. sulfuric acid added, crucible porcelain placed in beaker (600mL) as an air bath on hot plate in the fume hood. The hot plate is off at this time. Heated gently from the top by the infrared lamp (2 cm above crucible porcelain), while stirring the solution with a glass rod. The temperature increased gradually of hot plate until the sample is reduced to a carbonaceous ash, the infrared lamp removed. Sample heated in the muffle furnace at 525 °C for 2 hrs. until the carbon is completely removed. The inorganic residue dissolved with 10 mL (1:1 HNO\(_3\)) for 15 min. Heated gently by a hot plate (100 °C) to dryness. Washed with 10 mL of nitric acid (5 % V/V), allow to cool, transferred quantitatively to a volumetric flask (50 mL) and diluted with nitric acid (5%) up to the mark. Samples were stored in polypropylene bottles (50 ml).

3. Results and discussion

3.1 Nano Graphene oxide NGO Characterization

The FT-IR spectrum of synthesized of (NGO) as shown in Fig. 2-a, band at 1626 cm\(^{-1}\) for C=C bond the broad band of O–H bond appeared at 3360-3460 cm\(^{-1}\), the C=O band stretching vibrations of carbonyl and carboxylic groups appeared at around 1709 cm\(^{-1}\), the bands around 1217 cm\(^{-1}\) to C–OH and 1035 cm\(^{-1}\) are attributed C–O of epoxy group stretching vibrations. The UV–Vis spectrum of the nano sheets of (GO) dispersion (0.1 mg/mL) as shown in Fig. 2-b, the maximum absorption peak \(\lambda_{\text{max}}=\)
239.5 nm and a shoulder peak 289.5 nm were the absorption bands corresponding to $\pi \rightarrow \pi^*$ electron transitions of poly aromatic C=C bonds and $n \rightarrow \pi^*$ electron transitions of C=O bonds respectively (16). FT-IR and UV–vis spectra proved the presence of large amounts of oxygen functional groups (hydroxyl, carboxyl, carbonyl, and epoxy groups) on the surface of the synthesized nano sheets of (GO). Zeta potential study the surface charge on the nano sheets of (GO), which affects the nanomaterial agglomeration and adsorption of ions onto nano surface (17), zeta potential of the synthesized nano sheets of (GO) (-17.17 mV), as shown in Fig. 2-c. The XRD spectrum of graphite, $2\theta = 26.7^\circ$ (18), the peak disappeared by the oxidation process where a new peak appeared at a lower angle ($2\theta \approx 11^\circ$) provided the presence of the synthesized (NGO) as shown in Fig. 2-d. The obtained results agree with the previous studies (19, 20). The FESEM used to study the surface morphology of (NGO) as shown in Fig. 3, the corrugation shape observed. Low wrinkled on nano sheets of (GO) surface are more sensitive and show better adsorption ability (21). The energy dispersive X-ray (EDX) (attached with the FESEM), used to identify the elements involved in the nano sheets of (GO) formation as shown in Fig. 3, the appearance of a peak at energy (0.18 keV) to carbon atoms, and another peak at energy (0.5 keV) to oxygen atoms, proved the presence carbon and oxygen atoms only in pure synthesized NGO. The obtained results agree very well with the previous studies (13, 22).

![Fig.-2: Characterization of synthesized NGO (a) FT-IR, (b) UV–vis absorption spectrum, (c) Zeta potential, (d) XRD](image-url)
3.2 Optimization of solid phase micro extraction method (SPME)

In this work, the adsorption process was carried out for (Mg$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$) ions by solid phase micro extraction (SPME) method by using nano sheets of graphene oxide, the recovery determine for the solution with SPME method, analyzed by flame atomic absorption spectroscopy (FAAS).

The recovery was evaluated by using equation $R\% = [(C_{\text{added}} - C_{\text{after}})/C_{\text{added}}] \times 100\%$, where $C_{\text{added}}$ the direct concentration of analytes directly and $C_{\text{after}}$ the concentration of analytes by the SMPE method$^{23}$. The basic pH=8 sufficiently for adsorption process of analytes ions on the nano sheets of GO surface area, where increased recovery% when the pH increased as shown in Fig. (4-a). (NGO) mass, the recovery increased 0.25-1.0 mg as shown in Fig. (4-b), the obtained recovery 0.5 mg explained the availability of more sorption sites on nano sheets of (GO) surfaces$^{23}$.

The results shows the recovery of the analyte ions remained constant within 20 – 50 mL of sample volume, but less than 20 mL the recovery of metal ions decreased under optimum conditions because the adsorption capacity independent on the sample volume$^{24}$ as shown in Fig. (4-c). Stirring time (5-120 min) does not play a significant role in SPME method as shown in Fig. (4-d), results show the adsorption process is very quick because the equilibrium reached fast the available sorption sites for metal ions. The sonication time, remained constant in the range (2-10 min), while the recovery of the metal ions without sonicated was lower than 2 min., because the solution is not dispersed (accumulated), therefore, incomplete adsorption on the nano sheets of (GO) surface as shown in Fig. (4-e). The recovery of metal ions did not change remarkably with a change of the temperature, but at 70$^\circ$C the recovery is decreased because of the weak electrostatic forces between the metal ions and the surface charge of the nano sheets of (GO) at high temperatures (the process of adsorption is exothermic)$^{25}$ as shown in Fig. (4-f). Adsorption efficiency dramatically increased with NaCl concentration (2 - 6.5 mg mL$^{-1}$) and decreased at higher concentrations of NaCl (7 - 8 mg mL$^{-1}$) as shown in Fig.(4-g), lower NaCl concentration resulted in inefficient nano sheets of (GO) aggregation and low efficiency of adsorption of analyte. Whereas higher NaCl concentrations resulted in significant elution of analyte from nano sheets of (GO) because of competition between positive sodium ions and analyte ions$^{26}$.

Interfering ions may affect the adsorption efficiencies of analytes because of the competitive adsorption between the interfering ions and analyte ions. The recovery of the determined analyte ions was studied
in the solutions containing interfering metal ions, the tolerance limits defined as the largest concentrations of ions resulting in less than ±5% of recovery values, by comparing the recovery value before and after adding the interfering ions (23) as shown in Table 2.

3.3 Adsorption capacity

The adsorption capacity of analytes calculated by using equation, $q \text{ (µg/mg)} = \frac{(C_o-C)V}{W}$ Where q is the amount of analyte adsorbed per unit weight of (GO), $C_o$ and C are the analyte concentrations related to initial and residual respectively, V is the sample volume and W is weight of (NGO) (24). Adsorption capacity of Mg$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ (1µg/mL) calculated at optimum conditions of SPME method as shown in table 3.

![Fig. 4: Optimum conditions of SPME, (a) pH, (b) Nano sheets of GO mass, (c) Sample volume, (d) Stirring time, (e) Sonicated time, (f) Temperature, (g) NaCl Concentration](image)

Table. 2: Tolerance limit of interfering ions on the analytes

<table>
<thead>
<tr>
<th></th>
<th>Mg$^{2+}$</th>
<th>Co$^{2+}$</th>
<th>Ni$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Cd$^{2+}$</th>
<th>Pb$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(III) (µg/mL)</td>
<td>0.8</td>
<td>0.8</td>
<td>0.4</td>
<td>0.8</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Mn(IV) (µg/mL)</td>
<td>1.0</td>
<td>0.8</td>
<td>0.4</td>
<td>0.8</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe(II) (µg/mL)</td>
<td>5.0</td>
<td>3.0</td>
<td>4.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe(III) (µg/mL)</td>
<td>3.0</td>
<td>2.0</td>
<td>3.0</td>
<td>4.0</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Zn(II) (µg/mL)</td>
<td>5.0</td>
<td>4.0</td>
<td>2.0</td>
<td>4.0</td>
<td>1.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>
Table 3: Adsorption Capacity of analyte ions

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Recovery %</th>
<th>Adsorption Capacity (µg/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg²⁺</td>
<td>85.1</td>
<td>34.04</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>85.1</td>
<td>34.04</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>82.2</td>
<td>32.88</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>71.9</td>
<td>28.76</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>83.3</td>
<td>33.32</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>84.9</td>
<td>33.96</td>
</tr>
</tbody>
</table>

3.4 Analytical performance

The analytes determined directly by FAAS, with SPME method according to the optimum conditions, as shown in Table 4 and Fig. 5. The concentrations of the analytes in crude oil samples decreased by using SPME method because of the adsorption of the analyte metals ions on the nano sheets of (GO) surface. The average recovery% (78%, 82.3% and 82.9%) of the analytes in crude oil samples deceased than the recovery% (82.2%, 84.9% and 85.1%, and) of the analytes (1 µg/mL), at the optimum conditions for (Ni, Pb and Mg) respectively, because the mass of NGO (0.5 mg) was insufficient for adsorption of the analytes on the nano sheets of (GO) surface.

Table 4: Concentration of analytes by direct, SPME methods and recovery in crude oil samples
Conclusion

The abundant oxygen-containing functional groups (anionic nature) on nano sheets of (GO), the adsorption mechanism of the analyte ions (cation nature) as shown in Fig.-6 can be fast and efficiently adsorbed on the nano sheets of (GO) surface at the base pH=8, after the ionization of hydrogen ions from the (-COOH) and (-OH) groups, the anionic groups will attract the cationic analytes through the electrostatic attraction forces. The proposed method is a cationic ion exchange chromatography, where the nano sheets of (GO) (anionic nature) acts a sorbent of stationary phase and the analyte solution (cationic nature) acts a mobile phase. The advantage of this method is cheap, time efficient and economic consumption, only 0.5mg NGO as a sorbent. SPME is a novel method applied to separate metal ions from crude oil samples. The proposed method is capable of
analyzing samples with high content of salts because the interfering ions do not have a significant effect on recovery of analytes and adsorption efficiency.

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References


