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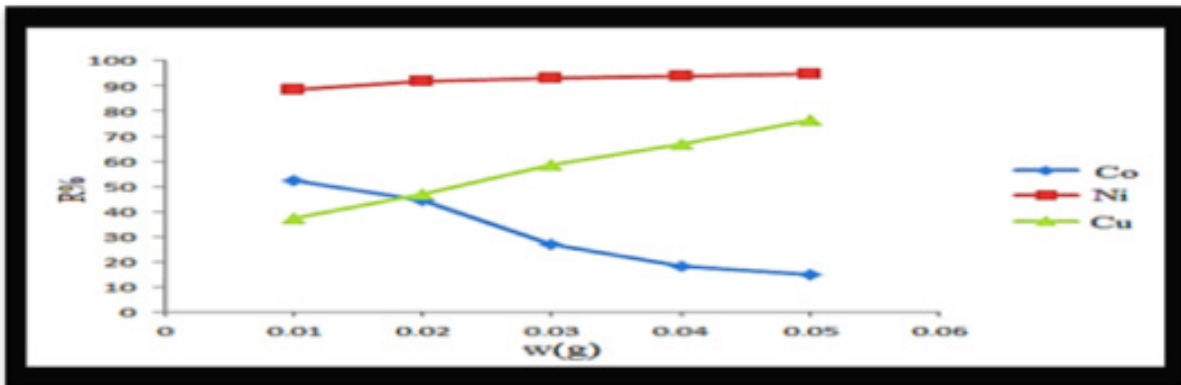


Fig (18): Effect of the adsorbent weight on metal ions removal by MRGO-Ar

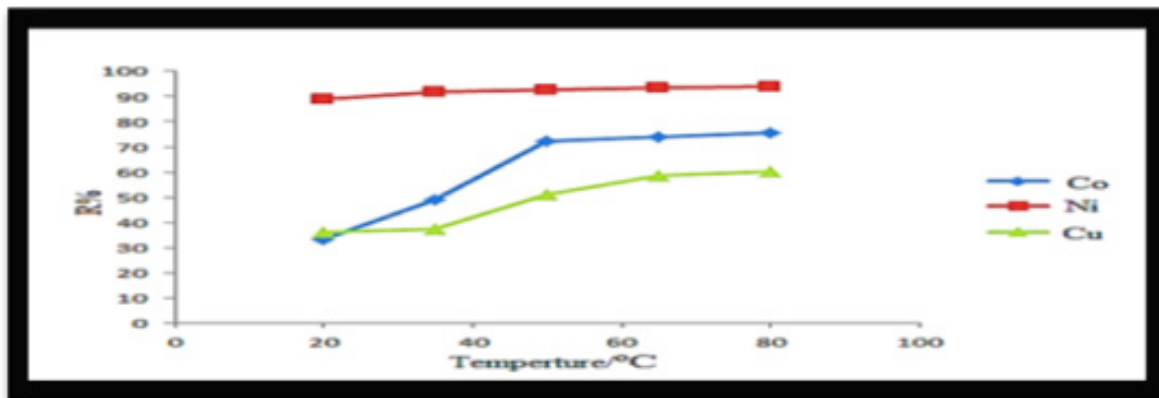


Fig (19): Effect of the Temperature on metal ions removal by MRGO-Ar

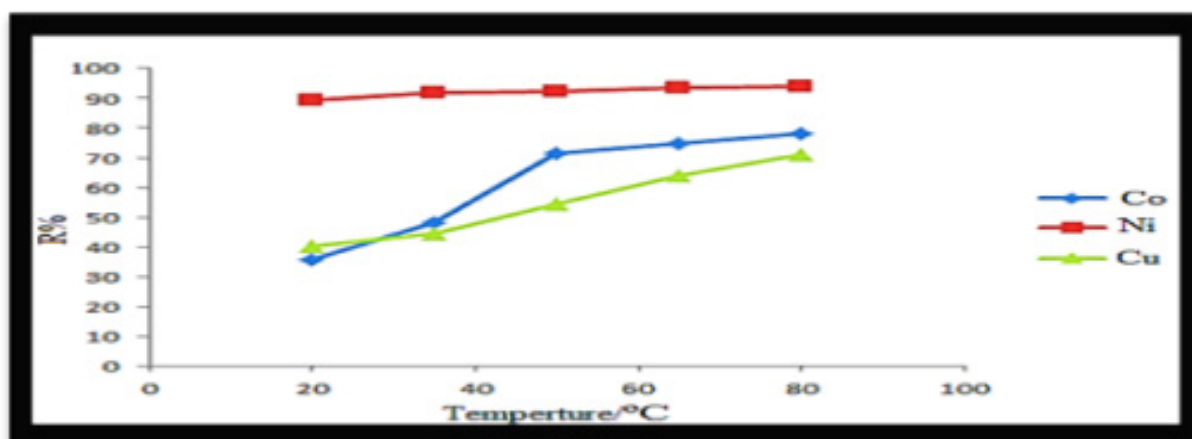


Figure (15): Effect of the Temperature on metal ions removal by RGO-Ar

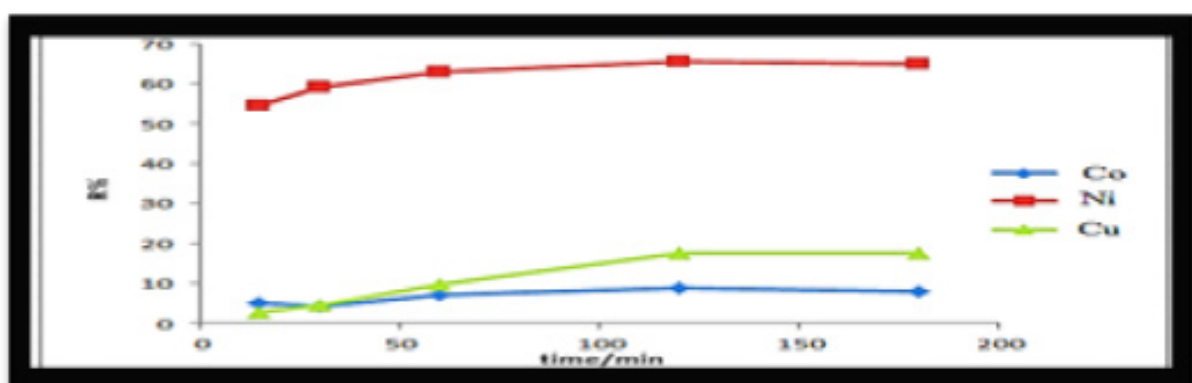


Fig (16): Effect of the contact time on metal ions removal by MRGO-Ar

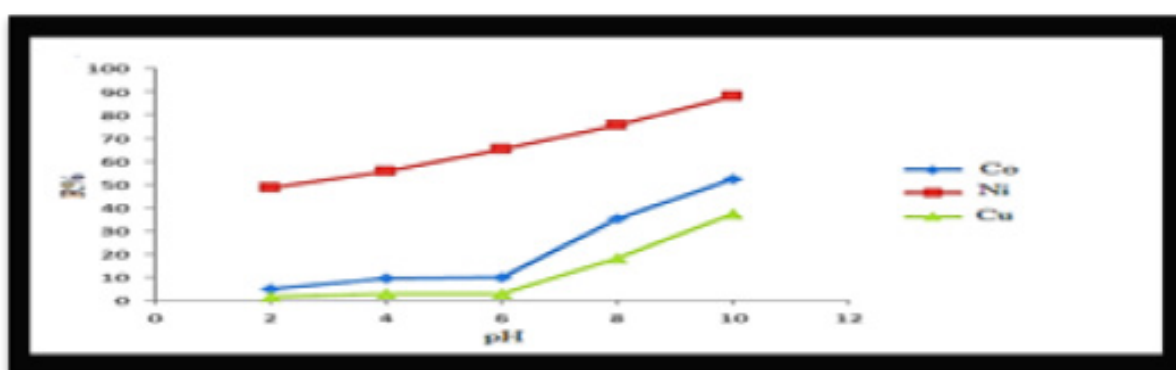


Fig (17): Effect of the pH on metal ions removal by MRGO-Ar

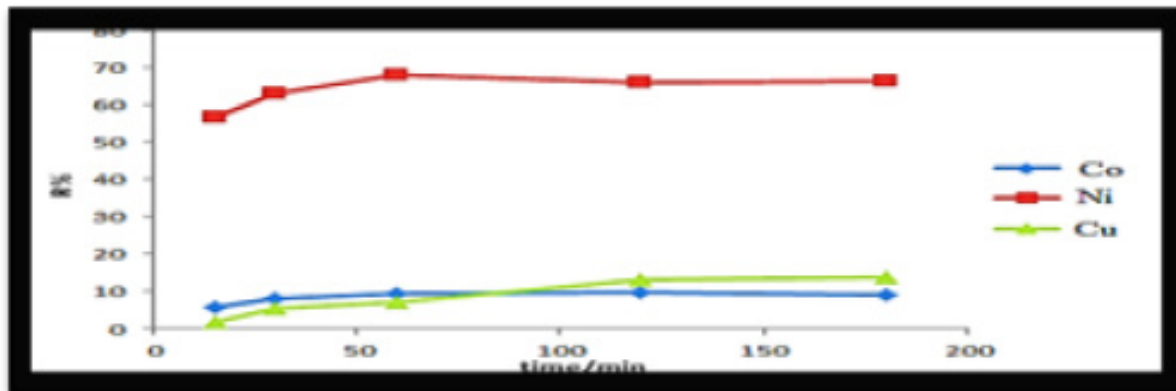


Fig (12): Effect of the contact time on metal ions removal by RGO-Ar

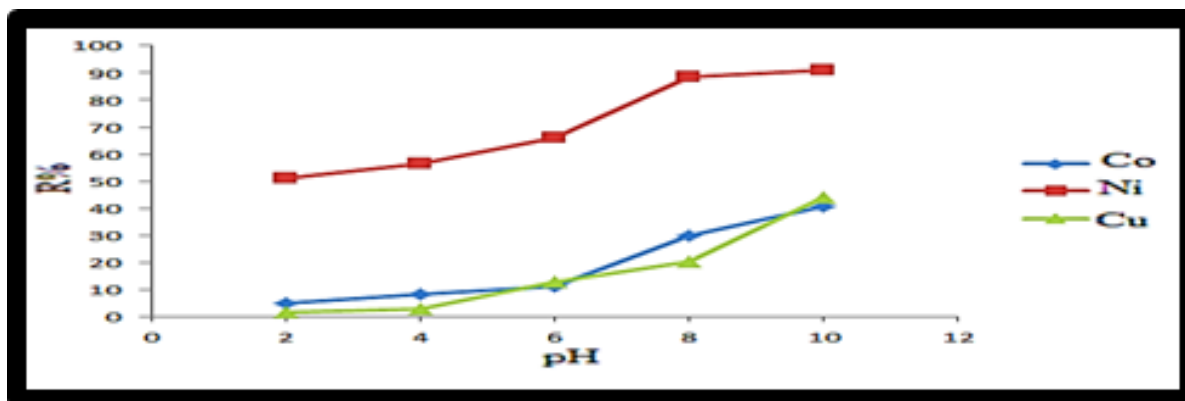


Fig (13): Effect of th pH on metal ions removal by RGO-Ar

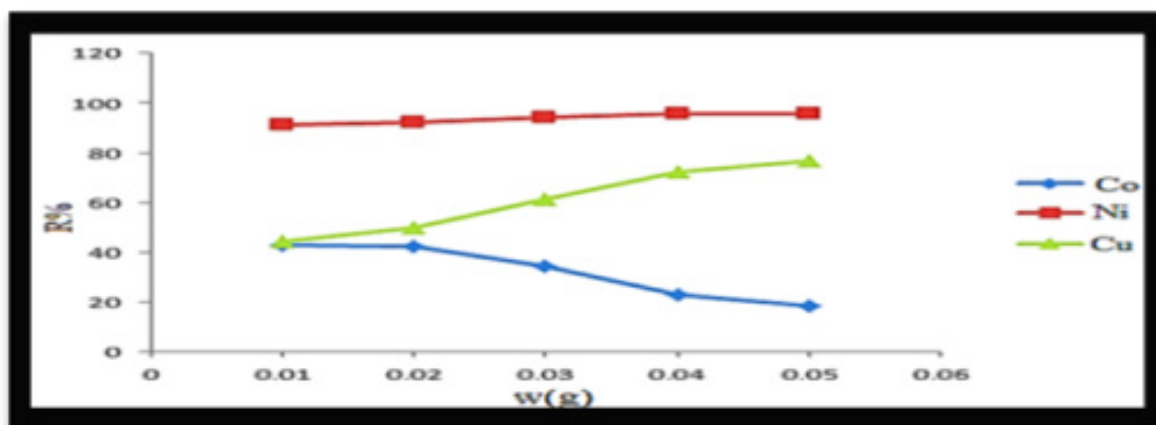


Figure (14): Effect of the absorbent wight on metal ions removal by RGO-Ar



Fig (11): Photographs of the dispersion and separation process of (MRGO-Ar) by magnetic effect: (a) at 5 minute an external magnetic field and (b) after 1 hour an external magnetic field.

In order to examine the efficiency of the functionalized graphene (RGO-Ar, MRGO-Ar) as adsorbents to various heavy metals. A series of experiments were performed. Different factors such as contact time, pH, adsorbent weight, temperature were also studied.

The metal ions Cu^{+2} , Ni^{+2} and Co^{+2} were used as examples of heavy metals. The removal process strongly depended on the ion exchange and chelating properties of adsorbents, which are linked further with the network composition and most important factor determination of adsorption capacity [18].

The metal ions concentrations were measured by atomic absorption spectroscopy. The removal efficiency $R\%$ was calculated by using the equation below :

$$R\% = \frac{C_i - C_e}{C_i} \times 100$$

Where C_i and C_e are the initial and equilibrium concentrations of ions [18, 19].

The removal percentage of mentioned metal ions were measured by using atomic adsorption technique and the results were drawn as a function of contact time. Figures (12) to (19).

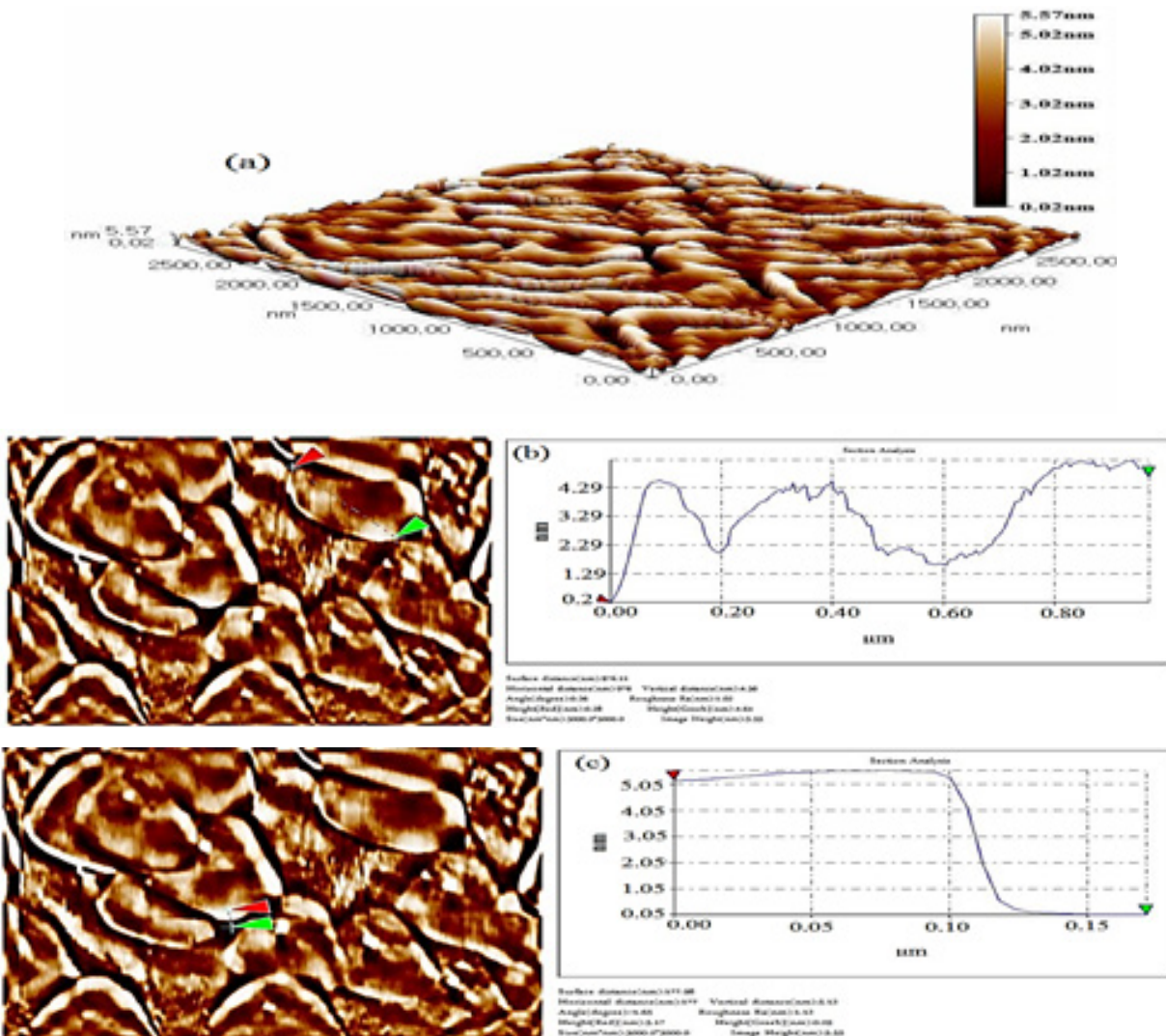


Fig.(9): AFM results of MRGO- Ar₂: (a) 3D-image, (b) the section area of length of sheet and (c) the section area of thickness of sheet.

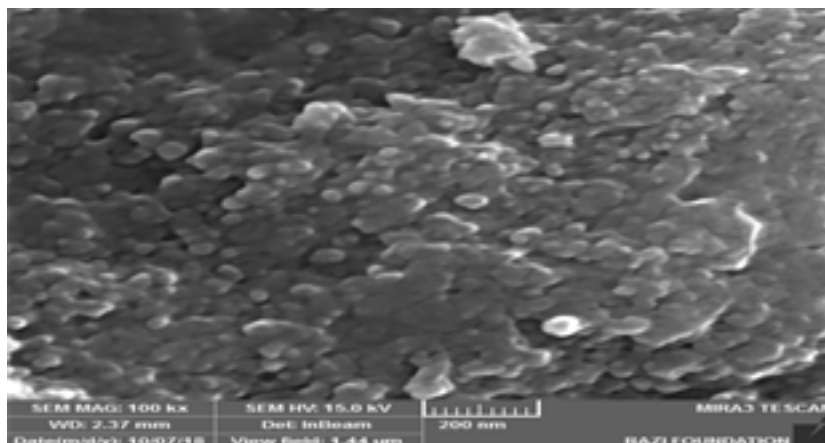


Fig. (10)
SEM image
of
(MRGO-Ar)

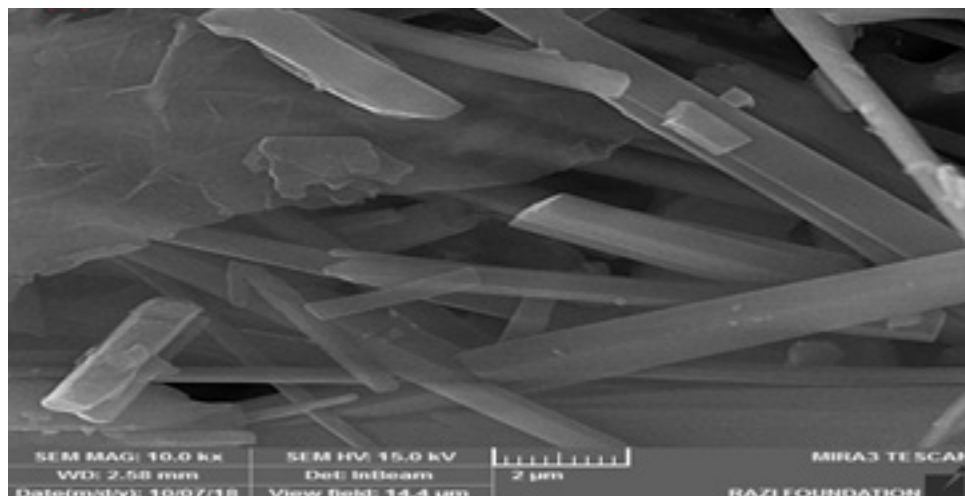


Fig.(7)
image of
SEM for
(RGO-Ar)

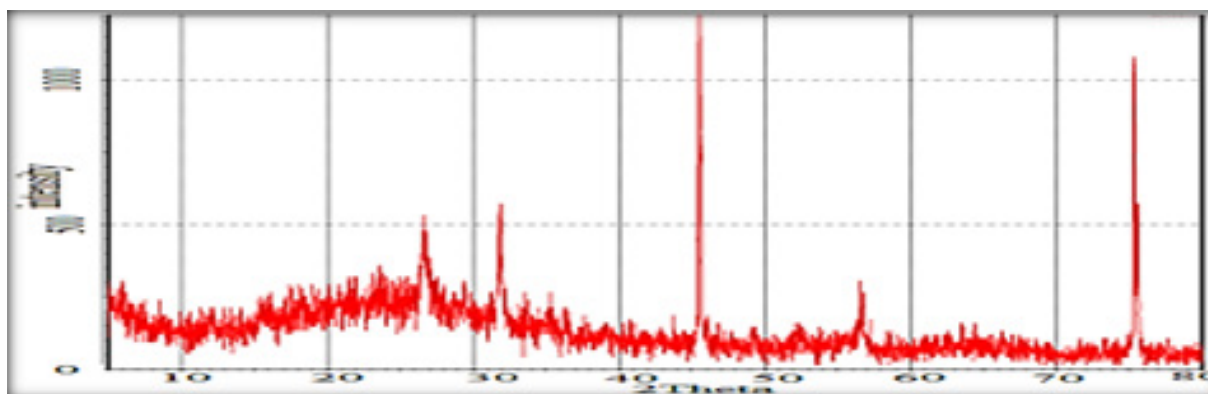


Fig. (8): shows FT-IR spectrum of (MRGO-Ar)

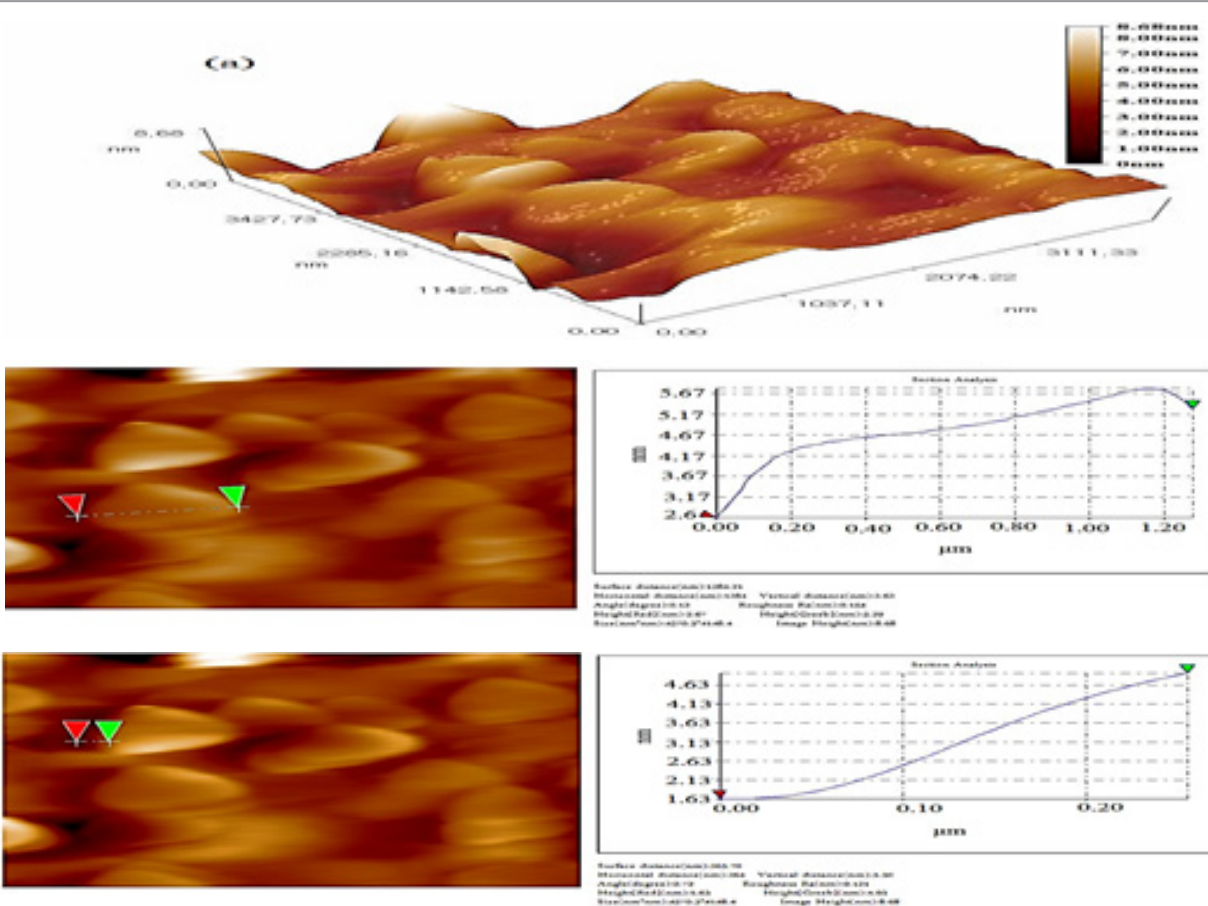
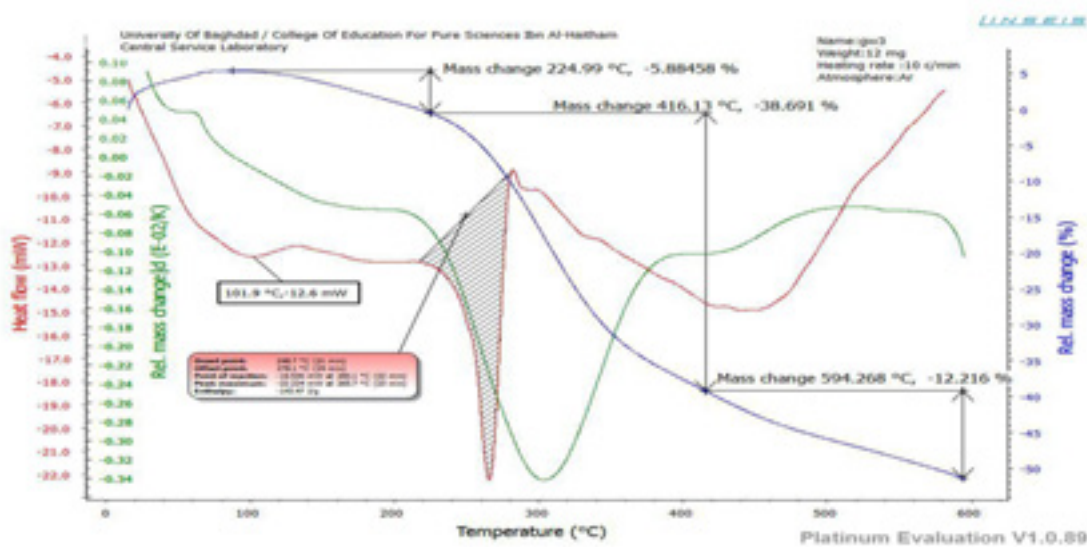
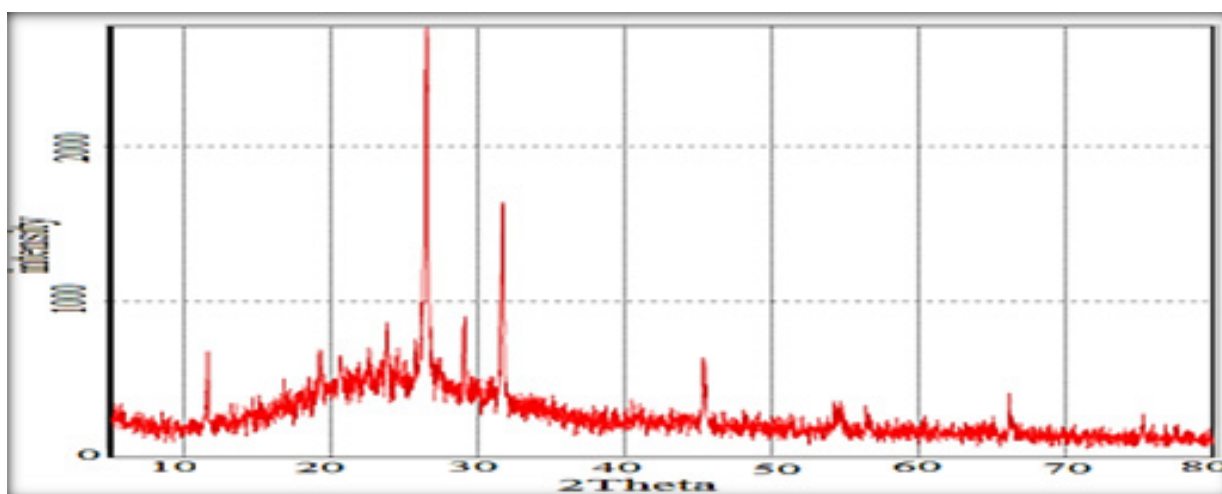
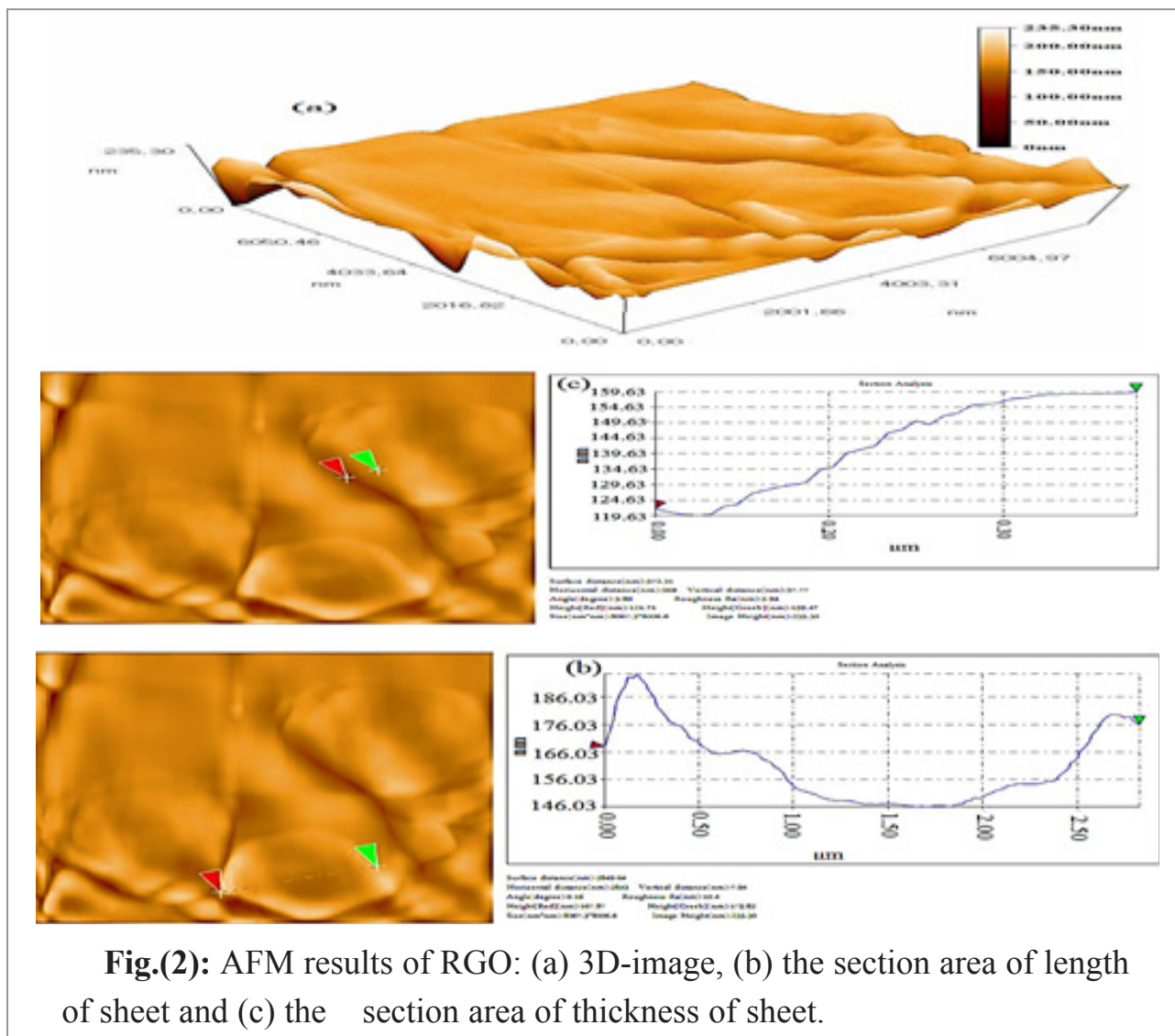


Fig.(5) : AFM results of RGO- Ar₂: (a) 3D-image, (b) the section area of length of sheet and (c) the section area of thickness of sheet.



Fig(6): The TGA ,DTG and DSC curves of RGO-Ar



calculated depends on the section area image of MRGO-Ar.
analyses and Fig. (10) shows the SEM

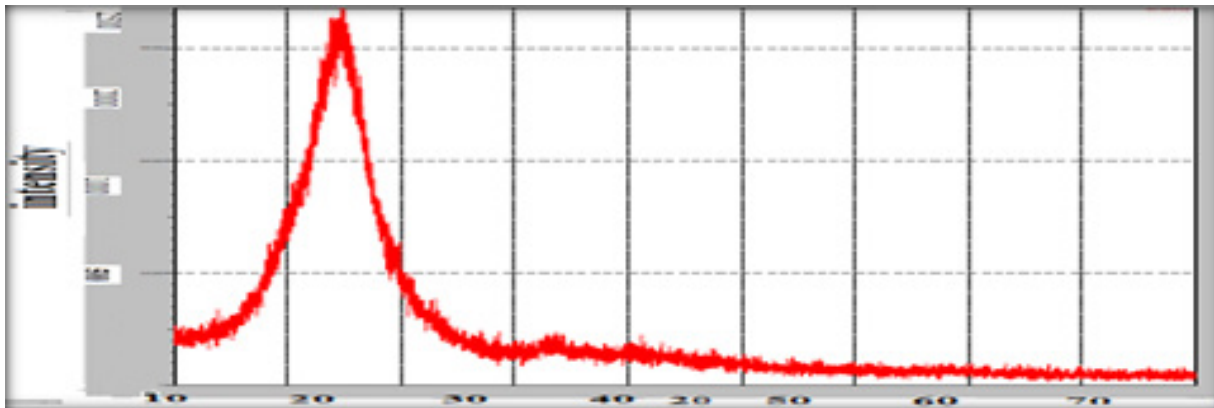


Fig (1): XRD patterns of RGO

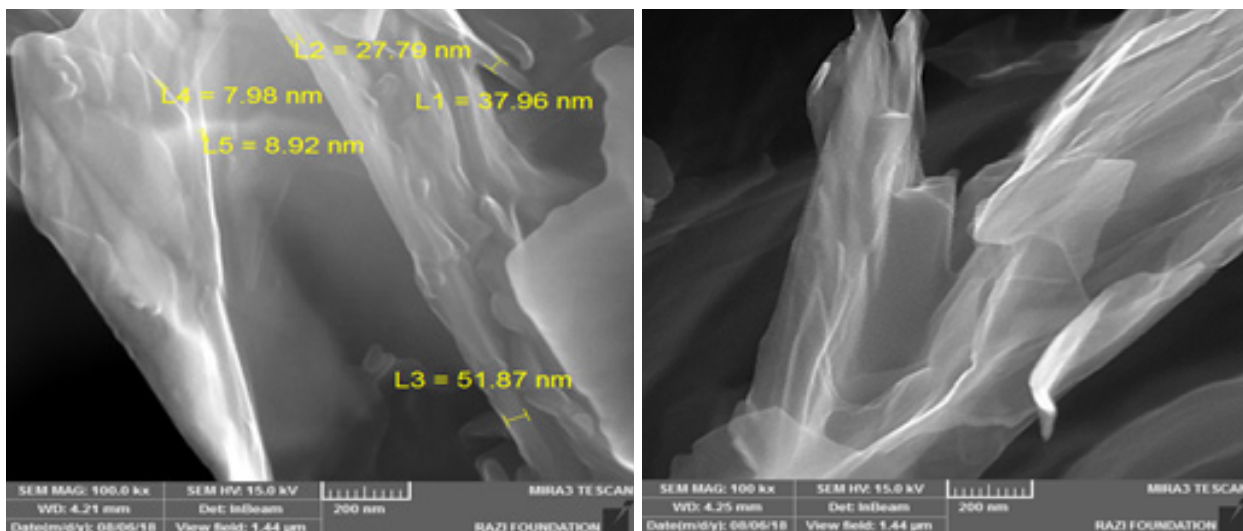


Figure (3) : SEM image of RGO

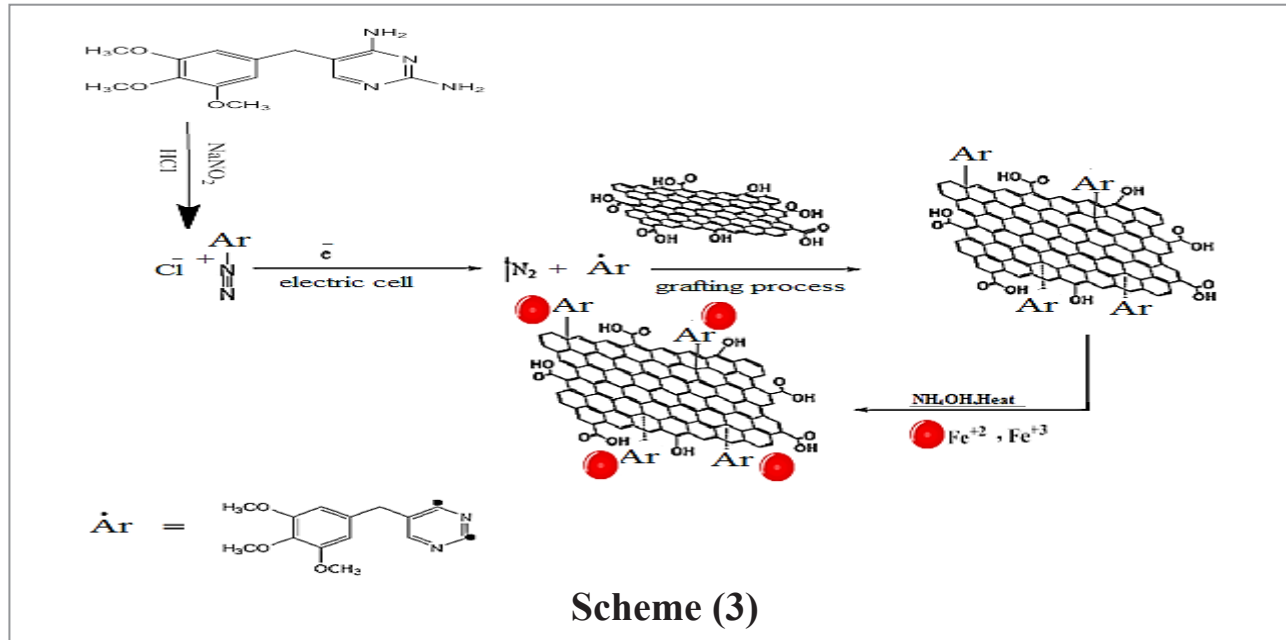
in Fig.(2a). The length and thickness of the chose sheet in Fig.(2b-c) was calculated depends on the section area analyses, SEM image of RGO Fig(3).

The Characterization of the RGO-Ar by XRD patterns have a different diffraction intensity from RGO as shown in Fig(4), Atomic Force Microscope (AFM) was also used to examine the morphology and the thickness of the RGO-Ar sheets. The morphology of the RGO-Ar was pictured and measured using AFM in Fig.(5a-c). The maximum hight of RGO-Ar was 8.68nm with smooth sheets-shaped in appearance as illustrated in the 3D-AFM image in Fig.(5a). The length and thickness of the chose sheet in Fig. (5b-c) was calculated depends on the section area analyses. The TGA,DTG and DSC measurements for RGO-Ar in Figure (6) shows TGA , DTG, and DSC curves of RGO-Ar,The Three DTG peaks are observed at 63, 305 and 447°C.The TGA of RGO-Ar depicts a continuous weight loss with a relatively constant rate, The curve, also shows a maximum degradation temperature and exhibits little weight loss (5.88%) occurs at (224.99) °C indicating a less amount of water absorbed by the RGO and unmodified exfoliated RGO sheets. This weight

loss is related to the departure of the hydroxyl groups remaining on the surface of RGO sheets after thermal annealing[15]. The significant weight loss(38.69%) observed around(416.13) °C is attributed to the decomposition of functional of organic functional groups covalently attached onto RGO sheets[16]. Furthermore, a 12.21% weight loss at(594.26) °C due to the bulk pyrolysis of the carbon skeleton[17]. The DSC analysis curve proved peaks at 101.9 , and 278.5 °C refer to an endothermic decomposition process. Peaks observed at 291.4 °C were related to exothermic decomposition processes. and Fig. (7) shows the SEM image of RGO-Ar.

The Characterization of the MRGO-Ar by XRD patterns have a different diffraction intensity from RGO as shown in Fig(8). Atomic Force Microscope (AFM) was also used to examine the morphology and the thickness of the MRGO-Ar sheets. The morphology of the MRGO-Ar was pictured and measured using AFM in Fig. (9a-c). The maximum height of MRGO-Ar was 5.57 nm with smooth sheets-shaped in appearance as illustrated in the 3D-AFM image in Fig.(9a). The length and thickness of the chose sheet in Fig.(9b-c) was

°C for a further 4 h[14] . separated by the centrifuge and wash by deionized water scheme (3).



3- Adsorption Experiments:

The adsorption of Co^{+2} , Ni^{+2} and Cu^{+2} ion has been studied sequential Steps from a standard solution of Co, Ni chloride and Copper sulfate (100 ppm). The adsorption of Co, Ni and Cu ion on the studied functionalization of graphene and magnetic functionalization of graphene was analyzed using atomic absorption spectroscopy.

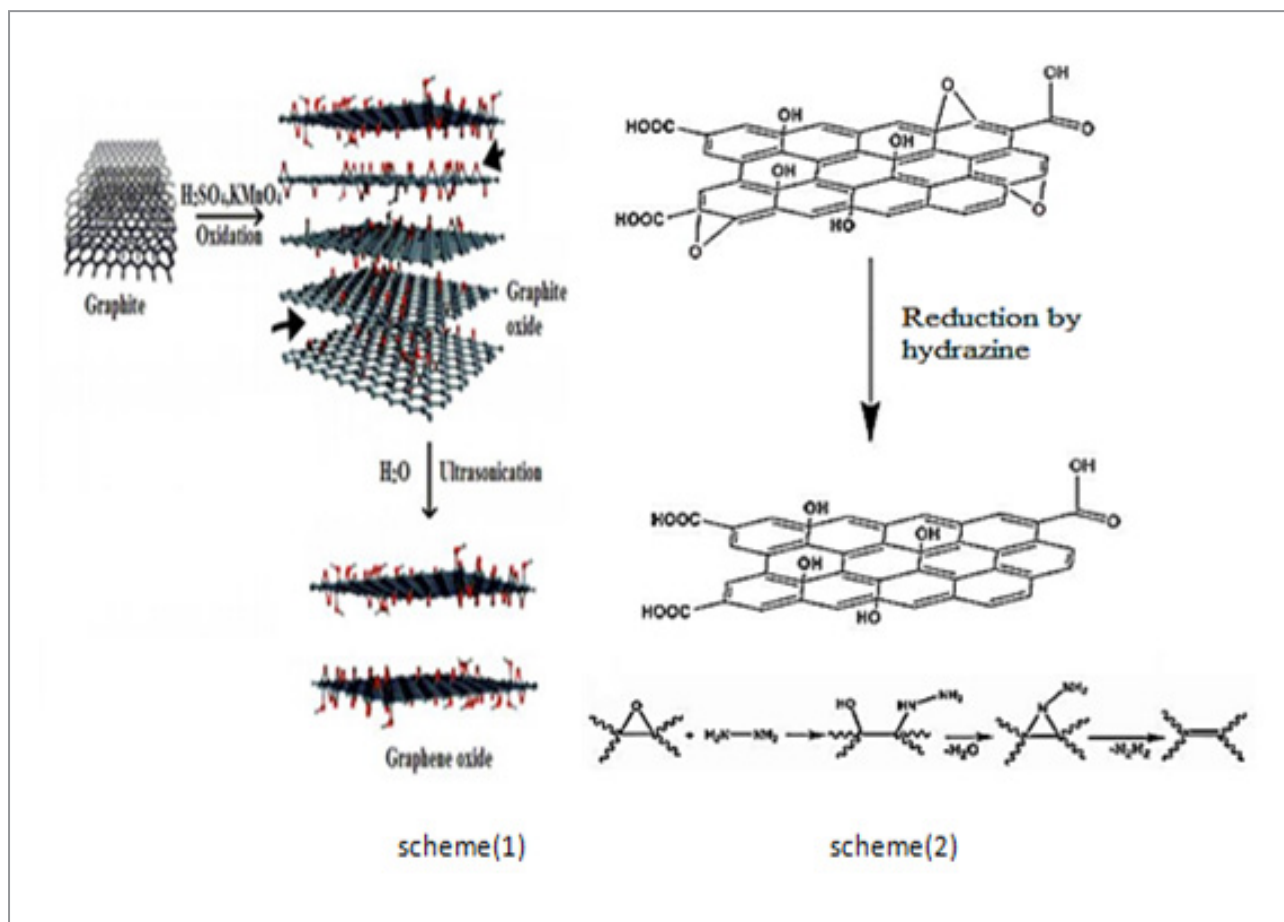
4- Preparation of the Stock Solutions of Heavy Metal Ions:

Stock solutions of Co^{+2} , Ni^{+2} and Cu^{+2} ions (1000 ppm) were prepared by dissolving (4.64g) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and (4.05g) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and (3.53) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in (1000ml) of

deionized water. The stock solutions were stored at room temperature. The data for RGO-TSB and MRGO-TSB at different conditions of contact time, adsorbent weight, pH, and temperature.

RESULTS AND DISCUSSION

The Characterization of the RGO shown in XRD patterns Fig(1) , Atomic Force Microscope (AFM) was also used to examine the morphology and the thickness of the RGO sheets Fig(2), The morphology of the RGO was pictured and measured using AFM in Fig.(2a-c),. The maximum height of RGO was 235.30nm with smooth sheets-shaped in appearance as illustrated in the 3D-AFM image



2- Preparation of graphene nanosheets with 5-(3,4,5-trimethoxybenzyl) pyrimidine-2,4-yl (RGO-Ar) and magnetic nanocomposite of reduced graphene oxide (MRGO-Ar):

0.002 mol (0.58g) from 5-(3,4,5-trimethoxybenzyl) pyrimidine-2,4-diamine put in beaker contains acidic solution its proportions 1:1 water and HCl (37%) and in another beaker dissolve 0.002 mol from NaNO₂ With a quantity of distilled water it was gradually added to the first step solution while maintaining

temperature of less than 5°C in the dark remains on stirring for half an hour. on the same solution connected to an electric cell with platinum electrodes for both anode and cathode (10 V) add a homogeneous solution of graphene 0.1g. after 24h separated by the centrifuge and wash three times with deionized water and dried. later a solution of FeCl₃·6H₂O (0.022 mol) and FeCl₂·4H₂O (0.011 mol) in (20 mL) water was added to it. The mixture was stirred at 70 °C for 15 min. Then 2ml from ammonium hydroxide was added. The mixture was kept stirring at 70

as both the anode and cathode[9]. Electrolyte(1000mL distilled water, 10g sodium bicarbonate)[10] , and power supply 15V for 24h making yield 0.5g graphite[11].

1- 2 Preparation of Graphene Oxide(GO) :

Hummer method was used [12] to oxidize the graphite's for the synthesis of GO as follows:

Graphite 1gm, sodium nitrate 1.5 gm and of sulfuric acid 46 mL were mixed and strongly stirred at 0°C for 15 minutes in a 500 ml reaction flask immersed in ice bath. Then potassium permanganate 6gm was added slowly to the above solution and cooled for 30minutes. After this, the suspended solution was stirred continuously for 2 hour at 35°C, and water 46 ml was added slowly to the suspension for 10 minutes and raised the temperature to 98 °C. The solution was left with stirring for 20 minutes. Subsequently, the suspension was diluted by warm water 140ml and stirring for 10minutes. After that, The solution was maintained at room temperature, treated with H₂O₂ 15 mL (30%) to reduce residual permanganate to soluble manganese ions. Finally, the resulting suspension was filtered by centrifugation, washed with 10% HCl and distilled water and

dried in a vacuum oven at 70°C for 24 hours to obtain GO. Scheme(1).

1-3 Preparation of reduced graphene oxide (RGO) by hydrazine:

Graphene oxide (100 mg) was dispersed in (1mL) HCl solution. Then (1 mL) of hydrazine monohydrate (80%) was added, and the mixture was heated at 95°C for 2 h. Then RGO was collected by filtration[13]. The obtained product was washed with water several times to remove the excess hydrazine, and was dried in a vacuum oven at 100°C for 12h.Scheme(2).

INTRODUCTION

Water pollution caused by heavy metal ions has become one of the most hazardous environmental issues in the world [1]. Heavy metal ions such as Cu(II), Co(II), Pb(II), Hg(II), etc generated by human economic activities diffuses into river, surrounding soil, and ground water system, threatening the ecosystem and human health due to their toxicity, non-biodegradability and carcinogenicity[2]. Conventional separation technologies for heavy metal removal from aqueous solution include chemical precipitation [3], electrochemical deposition, membrane treatment ion exchange and adsorption technologies[4].

For developing high performance of graphene-based nanocomposites, dispersibility of graphene sheets in matrices and interfacial interaction are challenging due to the strong tendency of agglomeration and surface inertia of graphene and it a two-dimensional material, possesses high specific surface area (2630 m²/g)[5]. thermal conductivity, flexibility and mechanical strength. All these remarkable properties make graphene a promising substitute for other nanofillers in composites[6]. As

for graphene based nanocomposites, delicate morphological organization, local interfacial properties uniform dispersion, and ease of processing are essential to the performance of the resulting composites[7]. These aspects stem mostly from the surface properties of graphene, which can be chemically modified for specific purposes[8].

In this study, we report synthesis and characterization of graphene nanosheets with 5-(3,4,5-trimethoxybenzyl) pyrimidine-2,4-yl and decoration with iron II /III ions and used to remove Heavy Metal Ions, Atomic absorption spectrophotometry techniques have been used to produce quantitative adsorption data for some prepared sample at different conditions of contact time, adsorbent weight, pH, and temperature.

EXPERIMENTAL

All the chemicals and solvents were purchased of A.R. Grade quality obtained from (Aldrich and BDH) were used without further purification.

1- Preparation of Nano Materials:

1 - 1 Preparation of exfoliated nano Graphite From carbon Rods:

The electrochemical setup that is used to exfoliate graphite normally contains the following elements: graphite rod

Magnetic Reduced Graphene Oxide- 5-(3,4,5 trimethoxybenzyl) pyrimidine- 2,4-yl(MRGO- Ar) for the removal of Co(II), Ni(II) and Cu(II) ions from aqueous solution: Synthesis and Adsorption.

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Baghdad University

ABSTRACT:

For developing high performance of graphene-based nanocomposites, dispersibility of graphene sheets in matrices and interfacial interaction are challenging due to the strong tendency of agglomeration and surface inertia of graphene. Here we report an efficient way to functionalize graphene nanosheets with 5-(3,4,5 trimethoxybenzyl)pyrimidine- 2,4-yl groups on their surfaces and magnetic nanocomposite iron II /III reduced graphene oxide -5-(3,4,5 trimethoxybenzyl)pyrimidine- 2,4-yl(MRGO-Ar) in this study summarizes the application of (RGO) and its composites as a superior adsorbent for the removal of heavy metal ions(Co(II), Ni(II),Cu(II)) The structures of this compound are confirmed by using X-Ray diffraction, scanning electron microscopy (SEM), Atomic Force Micro-scropy(AFM) and TGA,DCS .

Keywords: Reduced Graphene Oxide (RGO),(MRGO-Ar), adsorption, heavy metal ions .