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Synthesis Of Carboxylic Acid Functionalized Reduced Graphene Oxide (RGO) With Enhanced Heavy Metals Adsorption Capability.

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ABSTRACT

Reduced Graphene Oxide(RGO) and its composites have attracted widespread attentions as novel adsorbents for the adsorption of various heavy metal contaminants. Because of the unique physicochemicalcharacte- ristics, they might become an excellent and most potential adsorbent. in this study summarizes the application of (RGO) and its composites as a superior adsorbent for the removal of heavy metal ions from water and we discusses the applications of organo-functionalized (RGO) composites for the adsorption of heavy metals(Co(II), Ni(II),Cu(II)) , the organo-functionalized (RGO) in this study its agraphene functionalized with 1,2,4 triazol Schiff base(RGO-TSB),The structures of this compound are confirmed by using FTIR spectroscopy, X-Ray diffraction, scanning electron micro- scopy (SEM), Atomic Force Micro-scopy(AFM) and TGA,DCS.

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

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INTRODUCTION

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 m^2/g) [1]. thermal conductivity, flexibility and mechanical strength. All these remarkable properties make graphene a promising substitute for other nanofillers in composites[2]. 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[3]. These aspects stem mostly from the surface properties of graphene, which can be chemically modified for specific purposes[4].

The removal of heavy metals from contaminated waters has become a major environmental concern. Many metals are essential nutrients in trace amounts, but become significant threats to environmental and human health at high concentrations. Heavy metals are non-biodegradable and can accumulate in the environment and living organisms[5]. Neurological, mental, and other various adverse effects are caused by exposure to, transportation of, and accumulation of heavy metals, especially Hg(II), Pb(II), Cr(VI), Cd(II), and As(III)/(V)[6]. Carbon nanomaterials, with their high specific surface areas and large pore volumes, have remained at the forefront of nanotechnology. Many forms, especially graphene, have been widely used to remove aqueous Hg(II), Pb(II), Cr(VI), Cd(II), As(III)/(V), Co(II), U(VI), and other metal ions[7].

Triazoles are heterocyclic compounds including five-member ring of two carbon atoms and three nitrogen atoms as part of the aromatic five-member ring. According to the position of nitrogen atoms the triazoles are exist in tow isomeric forms with molecular formula $C_2H_3N_3$. Two structural isomeric triazoles are known, the 1,2,3-(1,2,5) and the 1,2,4-(1,3,4), each exists in two dissimilar tautomeric forms[8] .

In this paper, we report synthesis and characterization of 3-thiol- 4-amino -1,2,4 triazol and imine corresponding for it , the triazol prepared from 5-Hydroxyisophathalic acid and thiocarbodihiderazide the TSB functionalized Reduced Graphene Oxide(RGO).The RGO-TSB was 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 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].

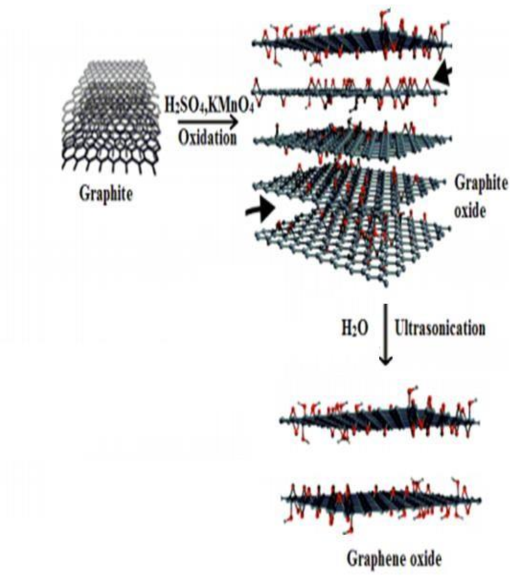
1-2 Preparation of Graphene Oxide(GO) :

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

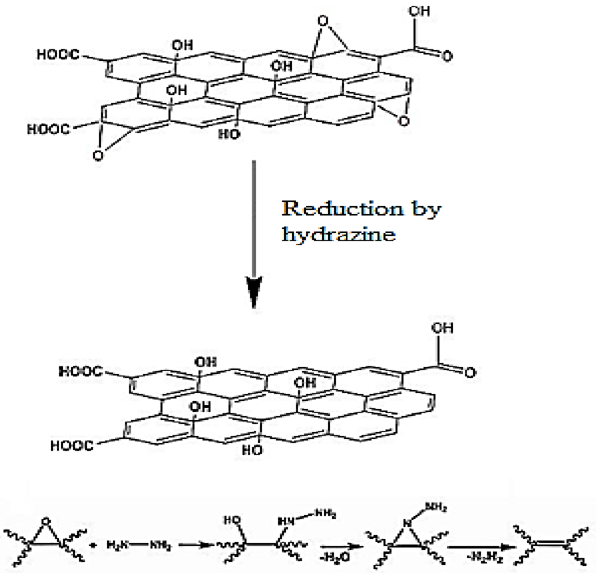
Graphite 1gm, sodium nitrate1.5 gm and of sulfuric acid 46 ml were mixed and strongly stirred at 0˚C for 15 minutes in a 500 ml reaction flask immersed in ice bath. Then potassium permanganate 6gm was added slowly to the above solution and cooled for 30minutes. After this, the suspended solution was 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 H_2O_2 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[13]. and dried in a vacuum oven at 70°C for 24 hours to obtain GO. scheme(1).

1-4 Preparation of reduced graphene oxide(RGO) by hydrazine:

Graphene oxide(100mg) 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[14]. 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 12 h .scheme(2).



scheme(1)



scheme(2)

2- Preparation of Thiocarbohydrazide (TCH):

5 ml carbon di sulfide (CS2) was added in a 100 ml round bottom flask in the ice bath.20 ml hydrazine hydrate was added drop wise with stirring. The mixture was refluxed for 30 minutes, until yellow-white precipitate was formed. The yellow- white precipitate was filtered and washed in ethanol, recrystallized from distill water and white crystals were formed, dried it in 70◦C for 4 hours[14] .

3-Preparation of(4-amino-1,2,4-triazol) for 5- Hydroxyisophathalic acid:

A mixture of 5- Hydroxyisophathalic acid(0.01mol) and thiocarbohydrazide(TCH)(0.02mol), placed in a round-bottom flask, heated until melted. The product obtained on cooling was treated with sodium bicarbonate solution . The product was then washed with water and collected by filtration. The solid product was recrystallized from a mixture of dimethylformamide and ethanol[15].

4-Preparation of (4-amino-1,2,4-triazol) for 5- Hydroxyisophathalic acid Schiff base:

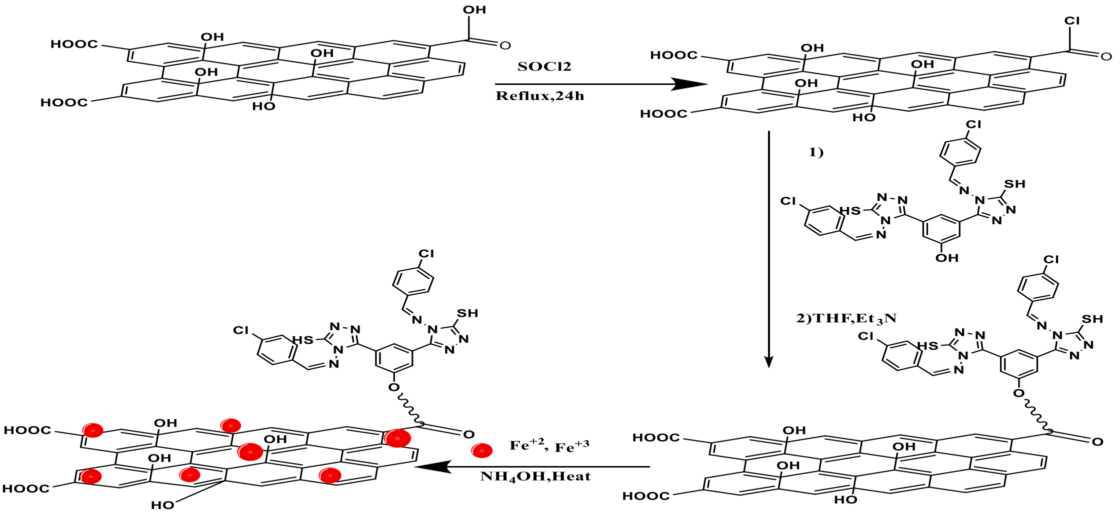
A mixture of (4-amino-1,2,4-triazol) for 5- Hydroxyisophathalic (0.001 mol) and (0.002 mol) 4-chlorobenzaldehyde with(3dropes glacial acetic acid) was placed in beaker heated until it melted[15].

5-Preparation of acyl-chloride-functionalized Reduced Graphene Oxide(RGO-COCl):

(0.1)g of graphene was well dispersed in 10mL of dry (DMF) by sonification for 1 h and then was treated with SOCl2 (60mL, 0.82 mol) at 80 ∘C for 24h. The product was separated by centrifugation washed with anhydrous THF and dried[16].

6-Preparation of Reduced Graphene Oxide - triazol Schiff base (RGO-TSB) and magnetic nanocomposite of reduced graphene oxide (MRGO-TSB):

TSB-grafted RGO was synthesized through an esterification Reaction between RGO-COCl and TSB. Briefly, to a dispersion of (RGO- COCl) (0.05 g) in (30mL) dry THF, previously dried TSB in (2mL) THF and Et_3N (1mL) were added dropwise at 0°C. The mixture was stirred at 0°C for 1 h and at room temperature for 6 h. and refluxed for 24 h. The powder was washed with an excess amount of deionized water and ethanol. After washing, the resulting powder was dried and (0.5) g RGO-TSB was sonicated in 30 mL deionized water. later a solution of $FeCl_3.6H_2O$ (0.022 mol) and $FeCl_2.4H_2O$(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 °C for a further 4 h[17]. separated by the centurifuge and wash by deionized water scheme(3).



Scheme(3)

7-Adsorption Experiments:

The adsorption of Co^{+2},Ni^{+2} and Cu^{+2} ion has been studied sequential Steps from astandard solution of Co, Ni chloride and Copper sulfate(100ppm). 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.

8-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 $CoCl_2 .6H_2O$,and (4.05g) of $NiCl_2.6H_2O$ and (3.53) of $CuSO_4 .5H_2O$ 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-TSB was pictured and measured using AFM in Fig.(2)a-c,. The maximum height of RGO-TSB was 20.64nm with smooth sheets-shaped in appearance as illustrated in the 3D-AFM image in Fig.(2)(a). The length and thickness of the chose sheet in Fig.(2)(b-c) was calculated depends on the section area analyses, SEM image of RGO Fig(3).

The Characterization of the RGO-TSB 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-TSB sheets. The morphology of the RGO-TSB was pictured and measured using AFM in Fig.(5)a-c,. The maximum height of RGO-TSB was 20.64nm with smooth sheets-shaped in appearance as illustrated in the 3D-AFM image in Fig.(5)(a). The length and thickness of the chose sheet in Fig.(5)(b-c) was calculated depends on the section area analyses. The TGA,DTG and DSC measurements for RGO-TSB in Fig (6) shows TGA , DTG, and DSC curves of RGO-TSB,The Three DTG peaks are observed at 69, 245 and 260°C.The TGA of RGO-TSB depicts a continuous weight loss with a relatively constant rate, The curve, also shows a maximum degradation temperature and exhibits little weight loss (3.95%) occurs at (128.302) °C indicating a less amount of water absorbed by the RGO[18]. In the second step weight loss (47.16%) at 344.618 ºC that designated the loss of TSB[19]. Furthermore, a 19.25% weight loss at (595.181) °C due to the bulk pyrolysis of the carbon skeleton[20]. The DSC analysis curve proved peaks at 71.5 , and 257.9 ºC refer to an endothermic decomposition process. Peaks observed at 199.4°C were related to exothermic decomposition processes and Fig. (7) shows the SEM image of RGO-TSB.

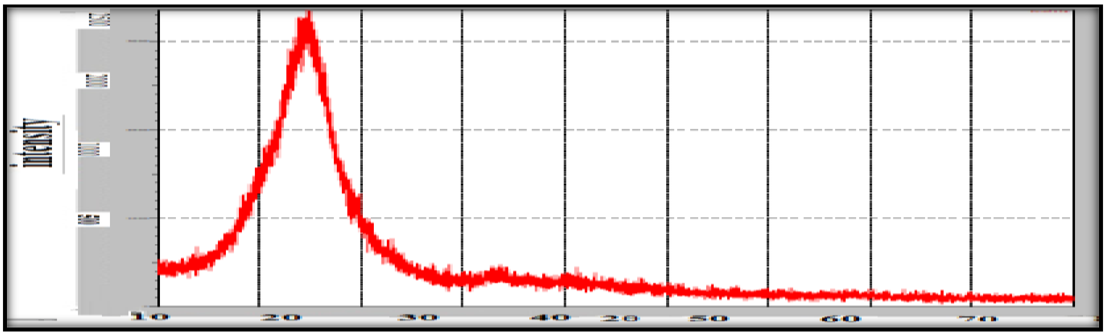
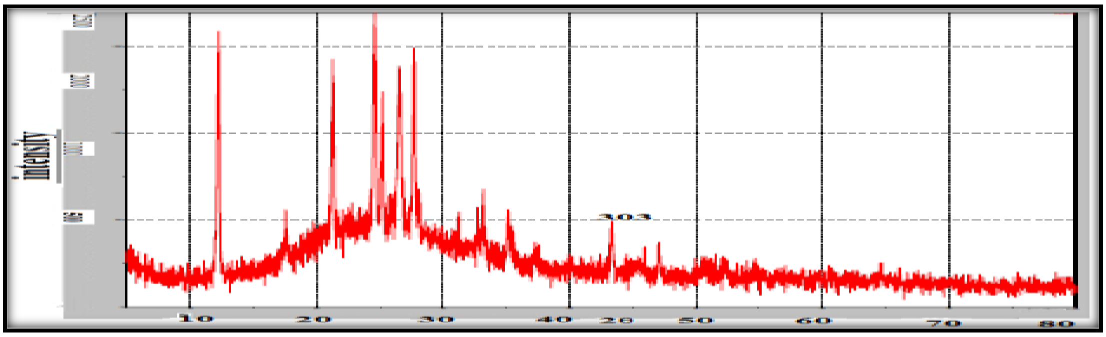


Fig (1) XRD patterns of RGO



Fig(4) XRD patterns of RGO-TSB.

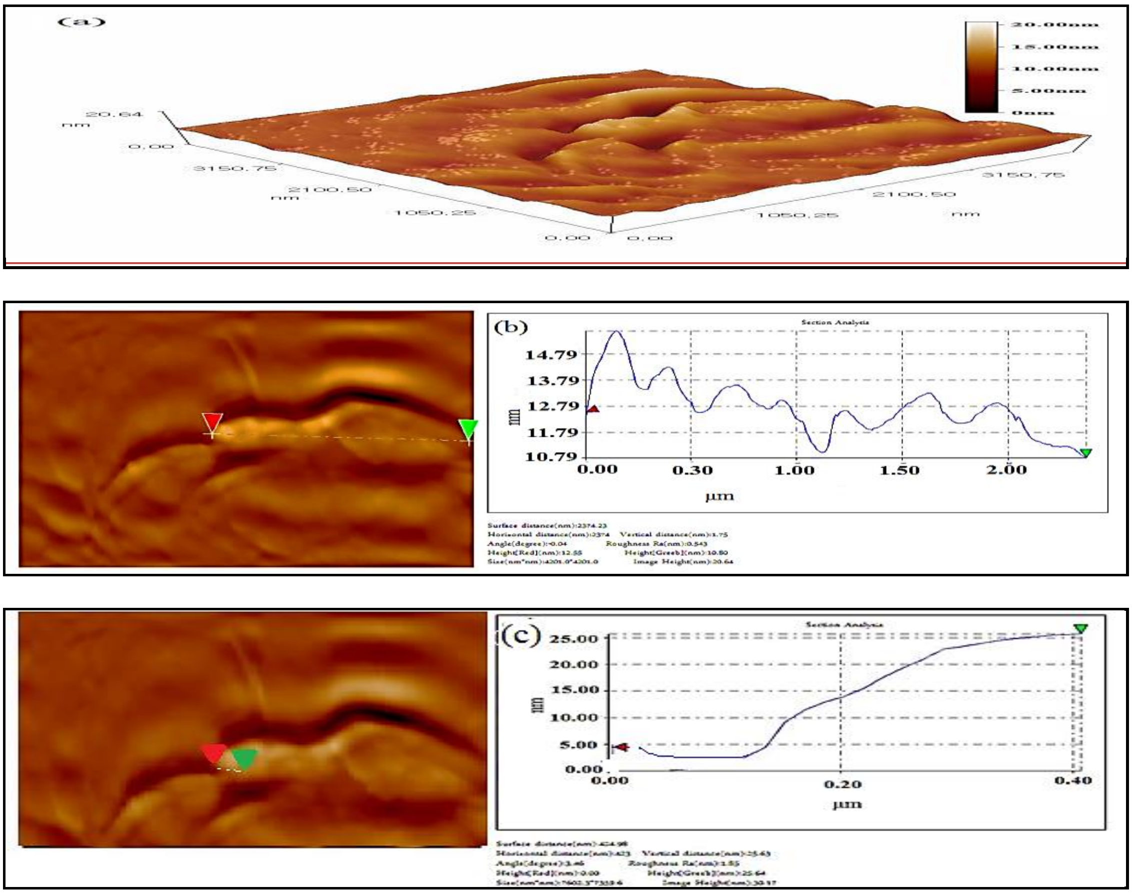


Fig.(2). AFM results of RGO- TSB: (a) 3D-image, (b) the section area of length of sheet and (c) the section area of thickness of sheet.

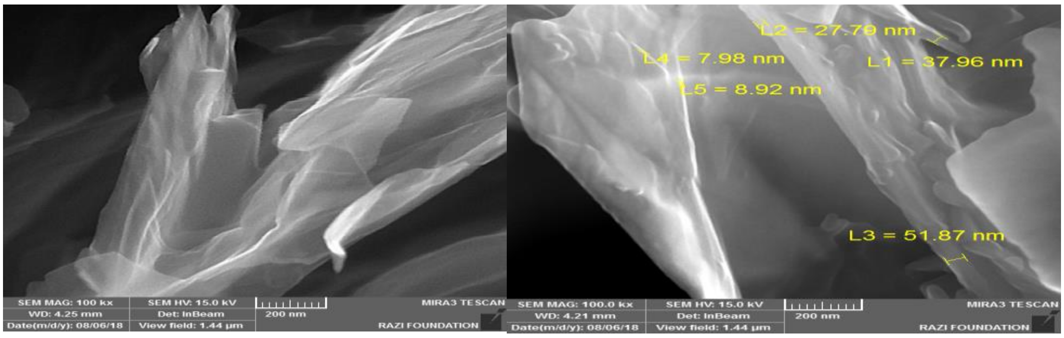
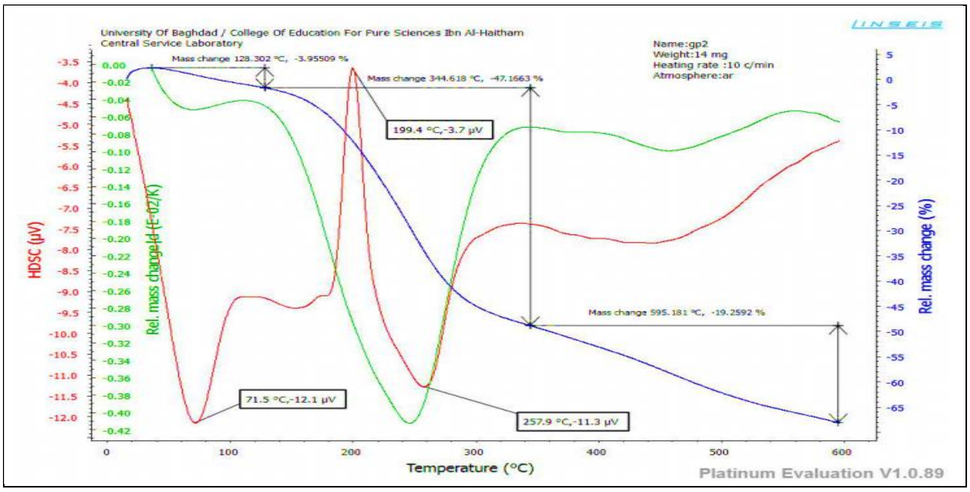


Figure (3) SEM image of RGO



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

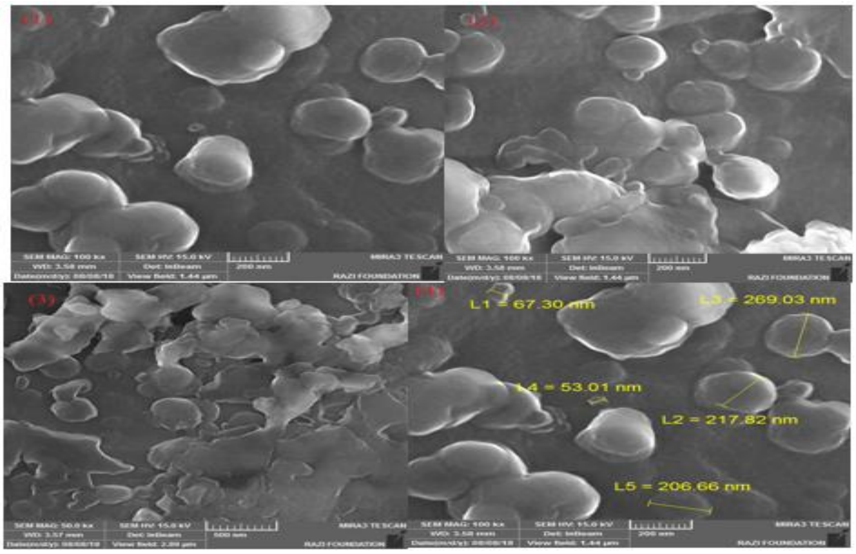
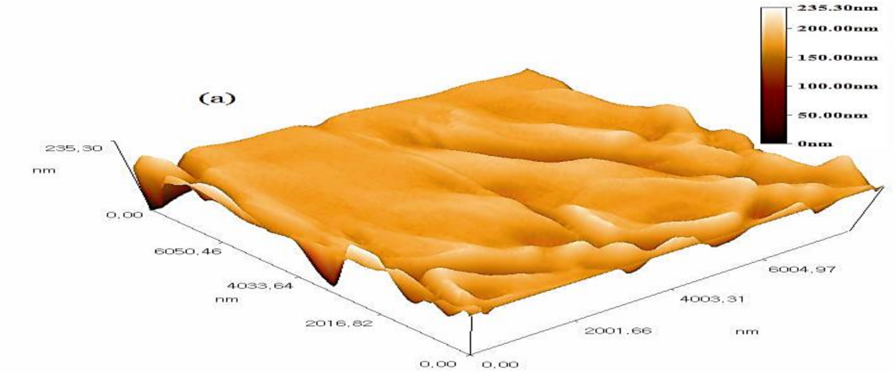


Fig (7) SEM image of RGO-TSB



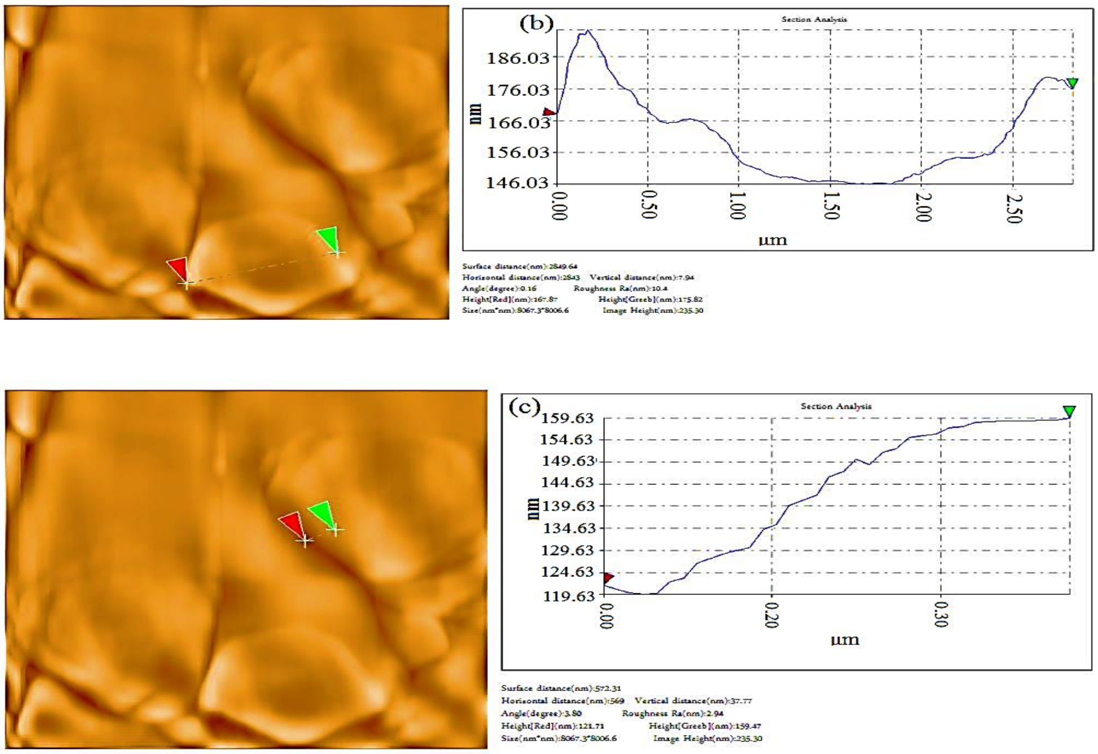


Fig.(5). AFM results of RGO: (a) 3D-image, (b) the section area of length of sheet and (c) the section area of thickness of sheet.

And the Characterization of the MRGO-TSB 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-TSB sheets. The morphology of the MRGO-TSB was pictured and measured using AFM in Fig.(9)a-c,. The maximum height of MRGO-TSB was 30.17 nm with smooth sheets-shaped in appearance as illustrated in the 3D-AFM image in Fig.(6)(a). The length and thickness of the chose sheet in Fig.(9)(b-c) was calculated depends on the section area analyses and Fig. (10) shows the SEM image of MRGO-TSB

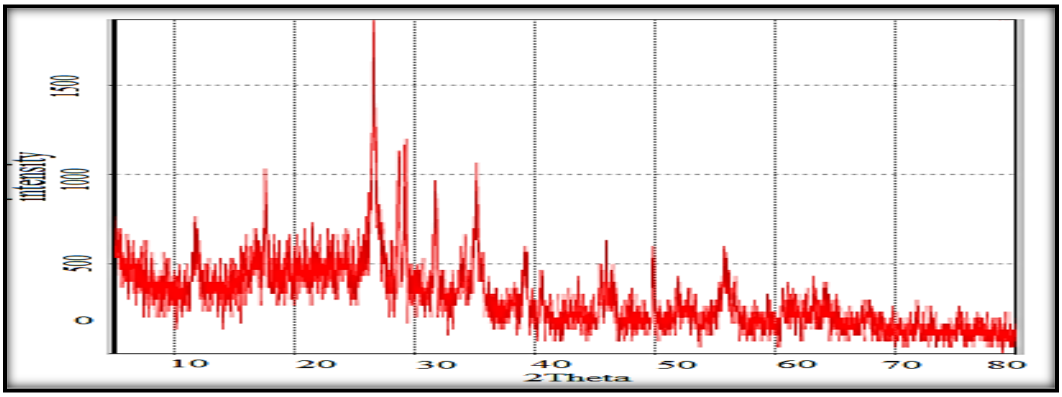


Fig (8) XRD patterns of MRGO- TSB

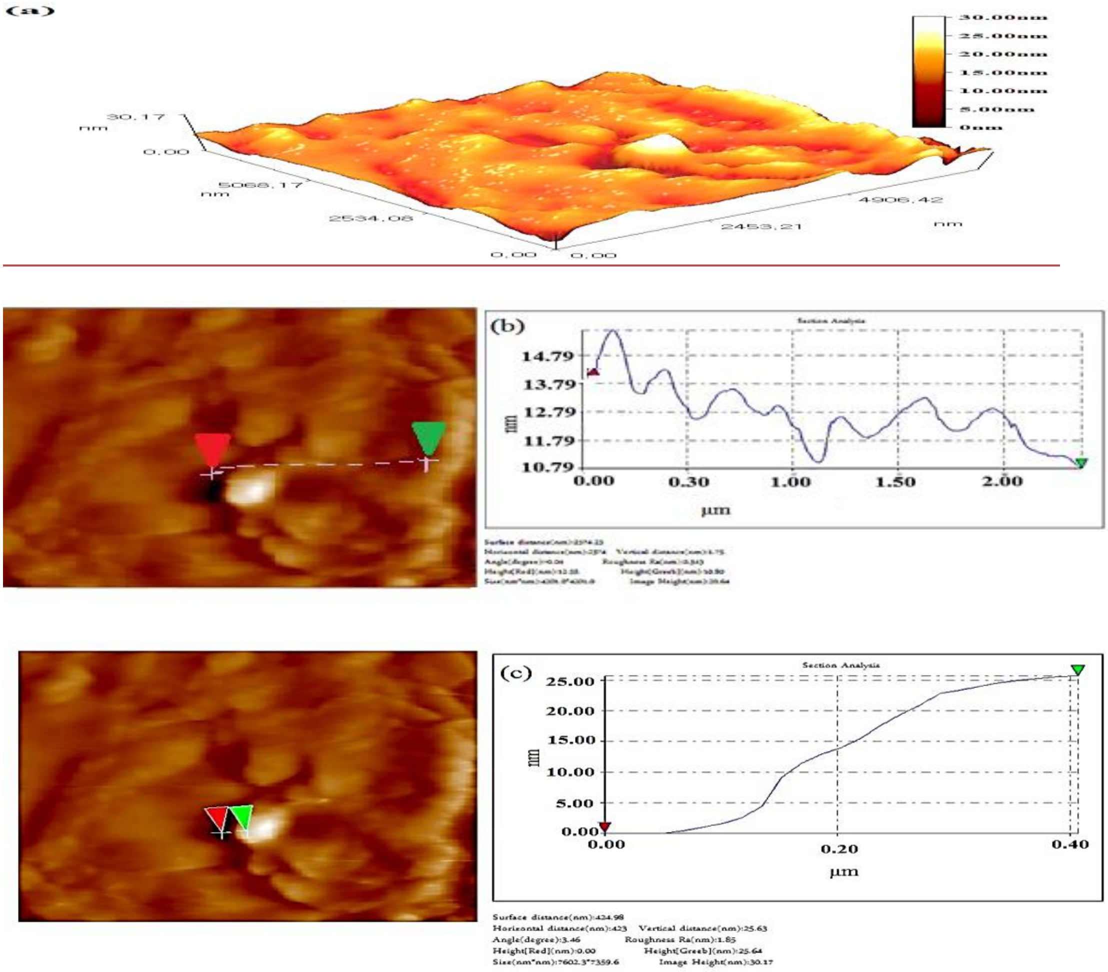


Fig.(9). AFM results of MRGO- TSB: (a) 3D-image, (b) the section area of length of sheet and (c) the section area of thickness of sheet.

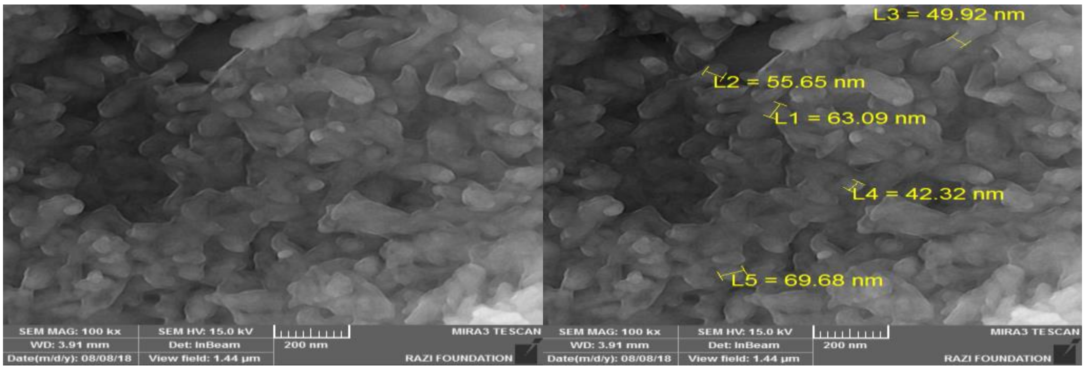


Fig. (10) SEM image of MRGO-TSB

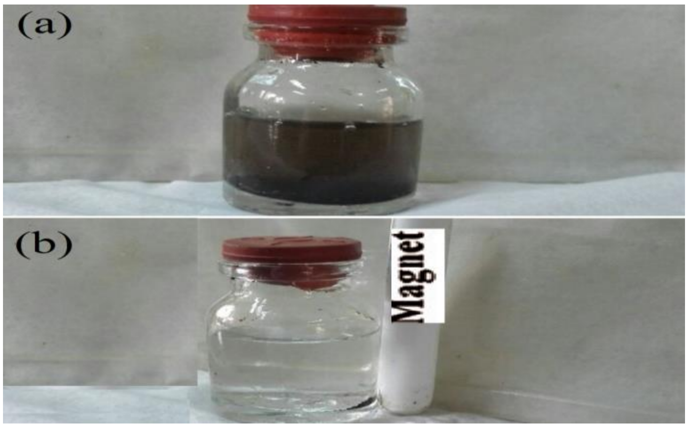


Fig (11)**.** Photographs of the dispersion and separation process of(MRGO-TSB) by magnatic effect: (a) at 5 minute an external magnetic field and (b) after 1 hour an external magnetic field.

In order to examine the efficiency of the functionalized graphene(RGO-TSB,MRGO-TSB) 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.

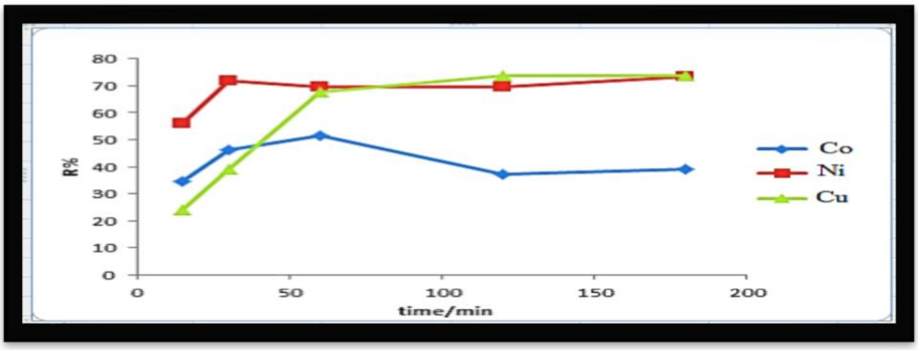
The metal ions Cu^{+2}, Ni^{+2} and Co^{+2} were used as examples of heavy metals. The removal process strongly depended on the ion exchange and chelating properties of adsorbents, which are linked further with the network composition and most important factor determination of adsorption capacity[21].

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

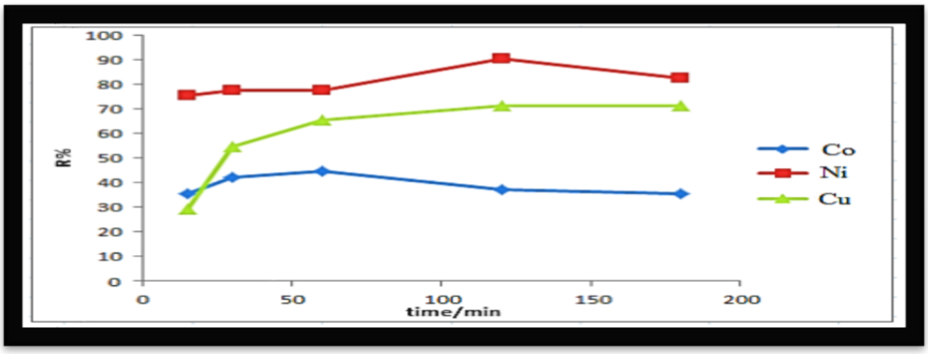
$$R\% = \frac{C_i - C_e}{C_i} \times 100$$

Where C_i and C_e are the initial and equilibrium concentrations of ions[22].

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).



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



Fig(13): Effect of the contact time on metal ions removal by MRGO-TSB

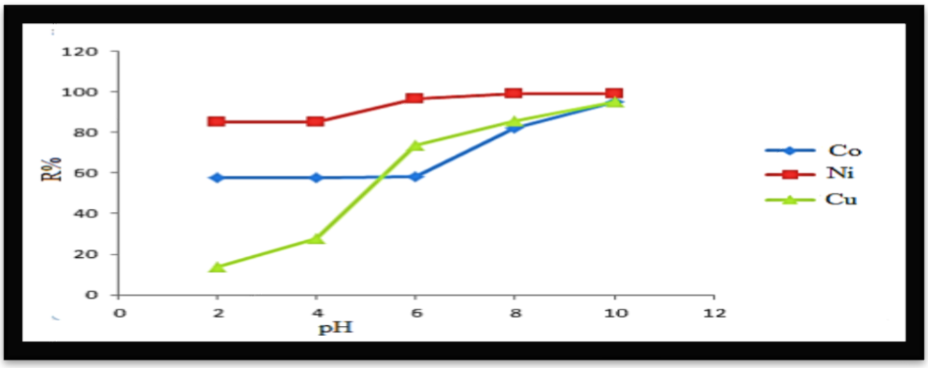


Figure (14): Effect of the pH on metal ions removal by RGO-TSB

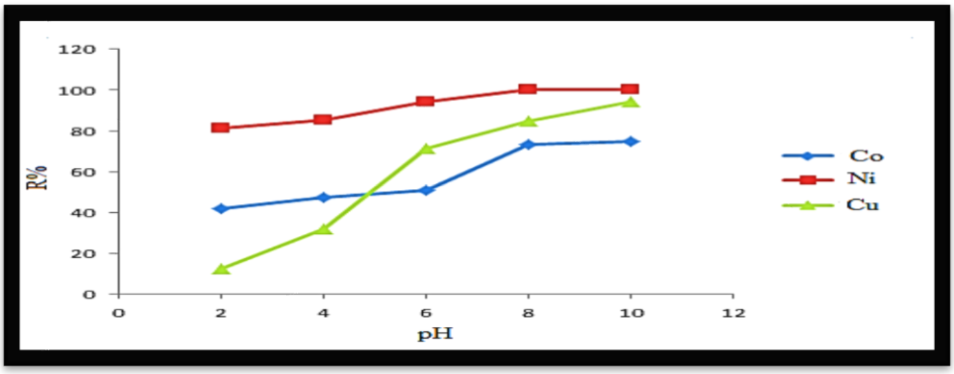


Figure (15): Effect of the pH on metal ions removal by MRGO-TSB

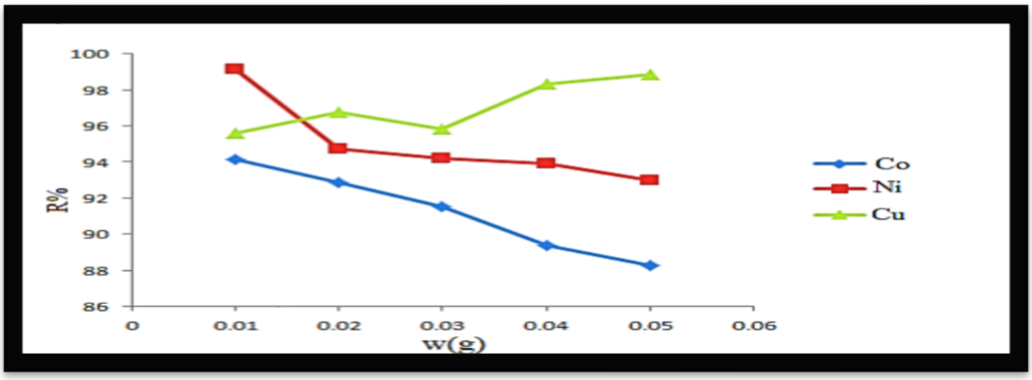
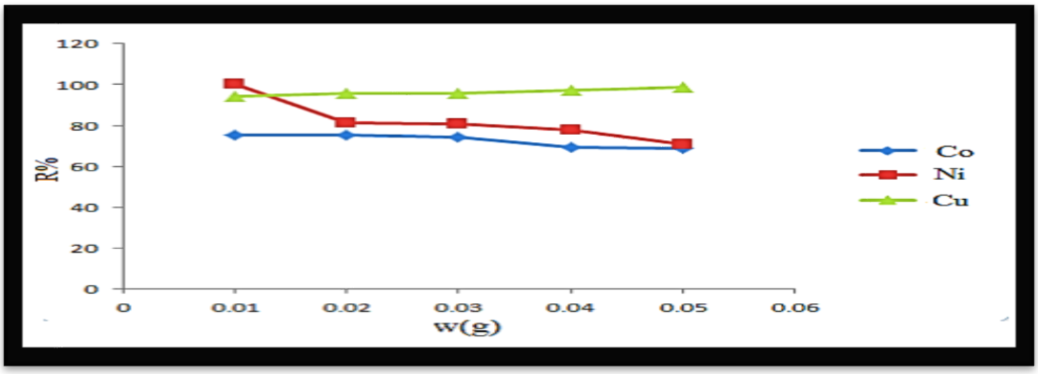
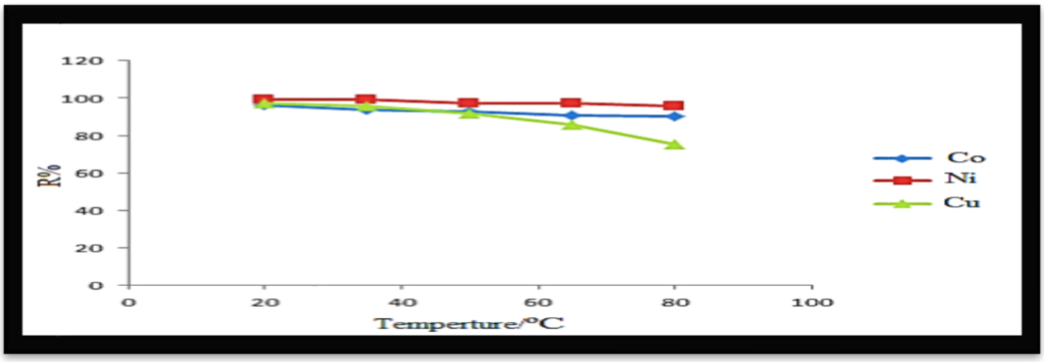


Fig (16): Effect of the absorbent wight on metal ions removal by RGO-TSB



Fig(17): Effect of the absorbent wight on metal ions removal by MRGO-TSB



Fig(18): Effect of the Temperture on metal ions removal by RGO-TSB

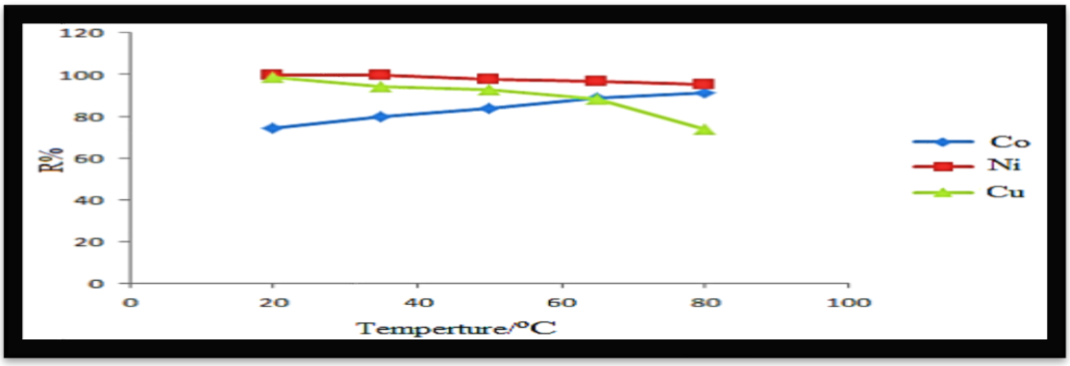


Fig (19): Effect of the Temperture on metal ions removal by MRGO-TSB

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