Synthesis of Graphene Oxide-Melamine – Tio Oxalic acid Nanocomposite and its application in the elimination of Mercury (II) ions

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Abstract

In this study, a new method by applying of Graphene Oxide (GO) Nano sheets–Melamine –Tio Oxalic acid (MTO) composite was exhibited as adsorbent for the elimination of toxic mercury (II) ions from aqueous solutions. The combination has the authority to adsorb the organic and inorganic combines. Through the immobilization of Melamine-Tio Oxalic acid (MTO) onto Graphene Oxide Nanosheets, the desired composite was synthesized and introduced by field emission scanning electron microscopy (FE-SEM), UV-Vis and Fourier transform infrared (FT-IR) spectroscopic techniques. The different experimental parameters such as pH and concentration of the aqueous solution of Mercury (II) ion, amounts of the MTO and the Graphene Oxide (GO), temperature, contact time, have been optimized. It was presented that they carry out the efficiency of Mercury (II) ion importantly, increased after immobilization of MTO on the Graphene oxide Nano sheets. GO-MTO is a very suitable adsorbent for removing of heavy metal ions especially Mercury (II) ion. Mercury and Gold were interested in bonding with sulfur.

Keywords: Elimination of toxic Mercury ion; Graphene Oxide Nano sheets; Melamine-Tio Oxalic acid; sulfur.

Introduction

Various industrial sewerages concluding toxic heavy metal are polluting the aquatic circuits very much. The presence of these heavy metals in the aqueous environment is of significant worry due to their toxicity and health consequence of the human and animals. Therefore, removal of toxic metals is exhibited by many explorers. There are different methods for removing heavy metals from aqueous circuits such as chemical precipitation [1], reverse osmosis [2], ion exchange [3], coagulation [4], and an adsorption [5]. Mercury is one of the important pollutants listed by USEPA as it can easily pass the blood-brain barrier and affect the fetal brain [6]. High concentration of Mercury (II) ions causes disorder of lung function and kidney, chest pain and dyspnea [7]. Mercury intake is very toxic. Mercury poisoning could also be a consequence of disclosure to soluble forms of Mercury such as $HgCl_2$ or $Hg (CH_3)^+$. Mercury makes amalgams with other metals such as gold, zinc and sodium

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[8]. When heated, Mercury forms Mercury oxide by reacting with oxygen in air. Mercury is one of the most toxic pollutants that must be controlled. Amalgam is the main component in the electrolysis of salty water during production of caustic soda. Inorganic Mercury compositions such as $HgCl_2$ or Hg_2Cl_2 can be aggregated in the drinking water and are conceivable health hazards. If intake by a pregnant woman, it can cause incremental hindrance in children [9]. Therefore, Removal of Mercury (II) ion or Mercury metal from water due to the irregular credential of wastewater is supernatural significance. Adsorption is exhibited to be one of the most impressive and economical remedial methods for Mercury elimination of waters wastewaters. Notice the oxygen-containing functional groups on the Graphene Oxide (GO) surfaces and if the surface is high, the sorption capacity will be higher for removal of heavy metal ions from the vast volumes of aqueous solutions. But, the usage of graphene oxide Nano sheets as sorbent in the elimination of heavy metal ions from aqueous solution is very important and significant, that, in this scheme, has been applied to this target [10]. The Melamine-Tio Oxalic acid is one of the most extensively used adsorbents for trapping heavy metal pollutants. Melamine-Tio Oxalic acid has gained particular interest as a ligand for metal removal because of their high Mercury elimination efficiency and ligation properties. The nitrogen and sulfur atoms in the Melamine-Tio Oxalic acid act as ligation sites and also attract metal ions on account of their strong electron-donor properties [11], thus providing high elimination efficiency *via* the formation of Mercury(II)–nitrogen, Mercury (II) - sulfur and Mercury (II) -Oxygen dative bonds. In this study, we report Melamine-Tio Oxalic acid immobility Graphene Oxide Nano sheets as a Mercury (II) ion adsorbent.

Experimental

Reagent and material

All reactants (KOH, Melamine, Tio Oxalic acid, $KMnO_4$, $NaNO_3$, HNO_3, H_2SO_4, and NaOH) were purchased from analytical reagent grade chemicals produced by Merck, except Hg $(NO_3)_2$ which was prepared from Aldrich. The 10^{-3} M Mercury (II) ion standard stock solution was prepared by dissolving 0.0811 g of $HgCl_2$ in a 250 mL volumetric flask and diluting to the mark with distilled water. Lower concentrations were obtained by serial dilution of the safe solution with phosphate buffer; pH 9 general buffer solution (0.15 M) was obtained from phosphoric acid solutions and sodium hydroxide solutions and regulating pH to the desired value (0.1 M). The final pH was controlled with the addition of a sodium hydroxide.

Equipments

IR spectra were measured with a Fourier transform infrared spectrophotometer (Nexus-670, Thermo Nicolet, USA). The UV–Vis (200–800 nm) and IR (200–4000cm^{-1}) spectra were recorded on a Perkin Elmer (Lambda 25, Shelton, CT, USA) and a Perkin Mattson 5000 FTIR spectrophotometers, respectively.

The absorbance measurements of the reagent and its Mercury (II) complex were also measured with a Perkin Elmer (Lambda 25, USA) spectrophotometer (200–800 nm) with 10mm (path width) quartz cell. A BrukerNMR (model VanceDPX400 MHz) was used for recording the proton NMR spectra of the reagent and its Mercury (II) ion complex in

deuterated DMSO solution using TMS as internal standard. A digital micro-pipette (Volac), an Orion pH-meter (model EA 940) and the scientific melting point SMP1 (UK) were employed for the preparation of the standard and test solutions, pH measurements and melting point, respectively. De-ionized water was obtained from Milli-Q Plus system (Millipore, Bedford, MA, USA) and was used for the preparation of all solutions. Carbon, hydrogen, nitrogen and sulfur content were determined by a Perkin Elmer 2400 C series elemental analyzer, USA. A Perkin Elmer ICP-MS spectrometer (model Elan DRC II, USA) was used under the optimum experimental conditions.

Synthesis of Graphene oxide

Graphene Oxide (GO) was synthesized from graphite powder using modified Hummer's method. So 2 g of graphite and 1.5 g of $NaNO_3$ were mixed together followed by the addition of 50 mL of concentrated H_2SO_4 under constant stirring. After 50 min, 7g of $KMnO_4$ was added little by little to the above solution while retaining the temperature less than 20 °C to arrest inflaming and outburst. The mixture was stirred at 35 °C for 12 h and the resulting solution was diluted by adding 1 L of water under vigorous stirring. To assure the perfection of the reaction with $KMnO_4$, the suspension was further remedied with 30% H_2O_2 solution (10 mL). The outcome mixture was washed with HCl and H_2O respectively, followed by filtration and drying; Graphene Oxide sheets were thus prepared (Figures 1 and 2) [12-15].
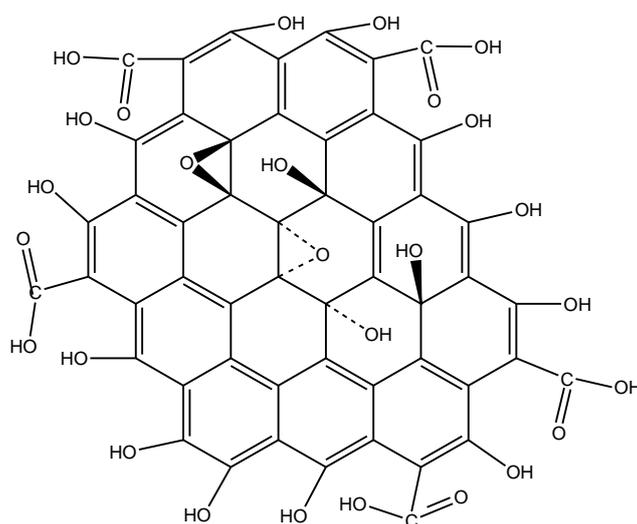

Figure 1. Structural formula of Grapheme Oxide

Figure 2. Images of synthesized GO powder and solution

Synthesis of covalently attached Melamine-Tio Oxalic acid Graphene Oxide hybrids (GO-MTO)

Briefly, in a typical reaction, a mixture of 40 mg GO and 80 mg Melamine-Tio Oxalic acid (MTO) were taken in a 100 mL round bottom flask and 3 mL of $(C_2H_5)_3N$ case a catalyst and 15 mL of DMF were added and heated to 85 ° C for 70 h under a nitrogen atmosphere. After completion the reaction, the solution was cooled to room temperature, and then poured into 250 mL diethyl ether to precipitate the product. The precipitate was collected by centrifuging at 6000 rpm for 30 min. The floated nanoparticles which contained dissolved MTO was discarded and the precipitate was washed thoroughly (28-29). After adding another 100 mL of diethyl ether, the mixture was sonicated for 10 min and then centrifuged at 6000 rpm for 30 min to collect the GO-MTO. Finally, the precipitate was washed with chloroform six times following the above procedure (Figure 3).
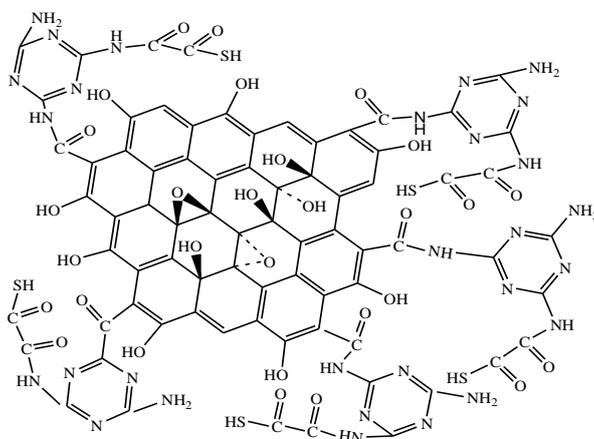

Figure 3. Structural formula of Grapheme Oxide- Melamine-Tio Oxalic acid (GO-MTO)

Structural and spectroscopic characterization of GO-MTO

The FTIR spectra were recorded using KBr plates in the range 500–4000 cm^{-1} using a Nicolet 6700 FT-IR spectrometer. Figure 4 shows the typical FTIR spectrum obtained for our graphite oxide material. The most characteristic features are the broad, intense band at 3550cm^{-1} (N–H stretching vibrations amine and amide), band at 3435 cm^{-1} (O–H stretching vibrations) and the bands at 1725 cm^{-1} (C=O stretching vibrations from Carbonyl and Carboxylic groups), 1650cm^{-1} (C=O stretching vibrations from amide) 1639 cm^{-1} (skeletal vibrations from free oxidized Graphitic domains), 1385 cm^{-1} (C–OH stretching vibrations), and 1027 cm^{-1} (C–O is stretching vibrations). The appearance of the peaks at around 1700 cm^{-1} is imputed to the aromatic stretching vibrations of C=C bonds of GO. The O-H imputed to the Carboxyl groups was disappeared in 2715cm^{-1} due to form amide. After covalent functionalization with Melamine-Tio Oxalic acids, a new peak appears at 2200 cm^{-1}

corresponding to the C-C vibrations of Melamine-Tio Oxalic acids and the peak of the C–O stretch vibration shifts at 1108 cm^{-1}, and broadens. The peak present at 1717 cm^{-1} is assigned to the bending vibration of the C=N of the Melamine-Tio Oxalic acid. The disappearance of the peak at 1380 cm^{-1} clearly indicates that in Graphene Oxide–MTO composites, the Melamine-Tio Oxalic acid molecules are covalently bonded to the graphite oxide via carboxylic acid linkage. The SEM image (Figure 5) shows that few layered Graphene Oxides are formed, although the SEM image does not assess the layer numbers of the Graphene Oxide Nano sheets precisely. Pure graphite presents ordered flakes of a 4–5μm range. The scanning electron micrograph for the GO–MTO hybrid materials (Figure 5 B), evidences that show a homogeneous system with a micrometer order of magnitude was provided. On functional design, GO presented a three-dimensional network of randomly sacked sheet like structures with a creased sinew and systematic vent with a wide size administration.
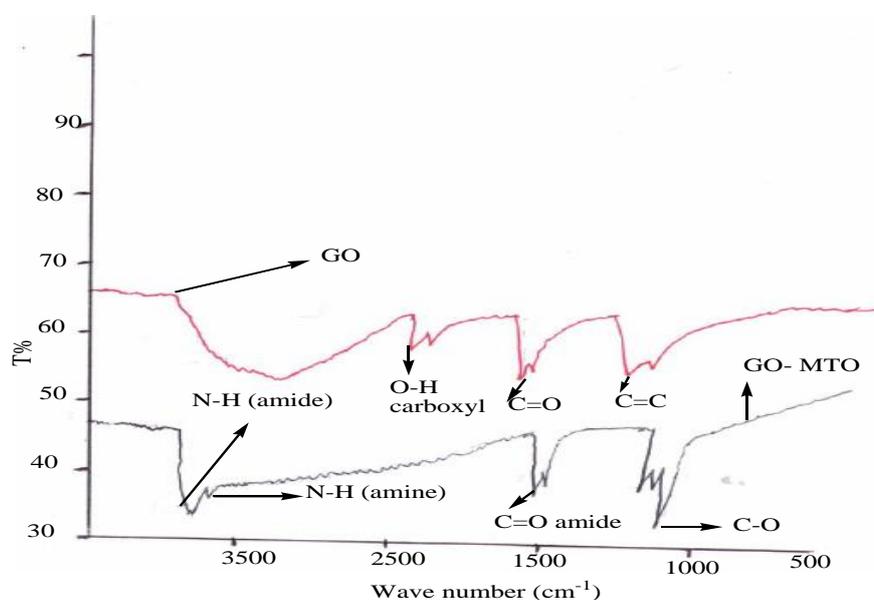

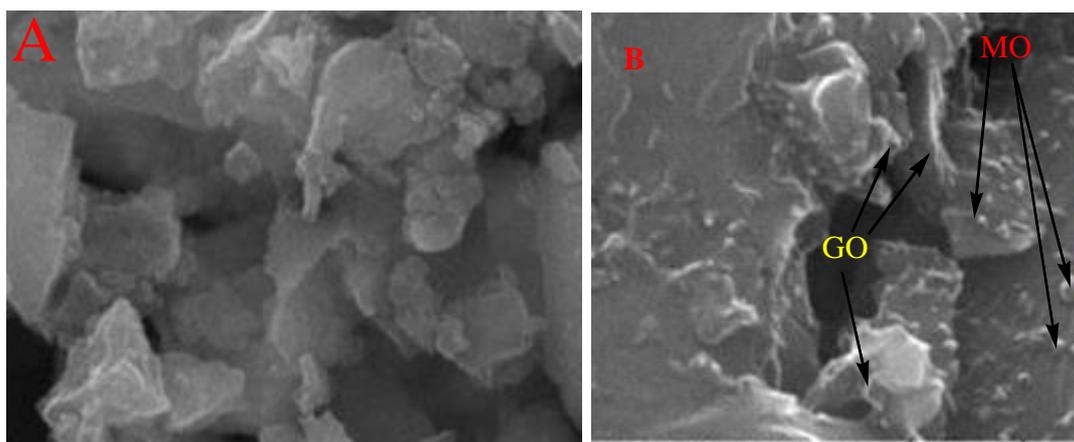**Figure 4.** FT-IR spectrum of Graphene Oxide and GO-MTO composites

Figure 5. SEM images of graphene oxide Nano sheets (A) and Graphene oxide-MTO composite (B)

Adsorption–desorption tests

To optimize the adsorption efficiency, adsorption tested was administrated at different pH levels of the aqueous solution of Mercury (II) ion. All tests were continuing in triplicate. Tests were performed using 2g/L of adsorbent each time (0.05 g of adsorbents' mass was added to 25 mL of deionized water in a flask). The pH-effect tests were initially controlled with aqueous solutions of acid and base (0.01 M H_3PO_4 and NaOH). Buffer solution was used to control the pH. Considering mercury precipitation in higher concentration, the equilibrium adsorption tested was adjusted at pH 6 in batch modes. The process of removing Mercury was performed. The Mercury (II) ion solution was shaken on an orbital shaker at 180 RPM for a specified period of time. Samples were mustered from the afloat and filtered. The equilibrium concentrations of the Mercuric ion that resided in solution determined the application of ICP. The elimination percentage of Mercury (II) (%) from aqueous solutions was computed as follows:

$$Elimination\% = \frac{(C_o - C_e) \times 100}{C_o}$$

(1)

Where C_o and C_e (mg/L) is the concentration of Mercury (II) ion

before and after adsorption. The effect of contact time on the Mercury (II) ion uptake was investigated at constant pH. The results exhibited that adsorption increased fast during the first 15 min. After 15 min, the adsorption received to the equilibrium state. As obvious from Figure 6, 15 min contact time was needed to reach adsorption equilibrium for the mercury solution. During this time, more than 99% of the Mercury (II) ion was adsorbed. At equilibrium, Dative interaction between GO-MTO and Mercury (II) ion happened, and adsorption suited almost constant up to the end of the test (Figure 7). The result is that the linkage of Mercury (II) ion with the GO-MTO is high during the primal stages and that; the interactive functional groups of GO-MTO was aversed after an especial period of time. Or for a description of Mercury (II) ions, aqueous 0.2M HNO_3 was used. The GO-MTO –mercury-ion, a complex in which adsorption was carried out at pH 6, was immersed in the 0.2M HNO_3 solution with a magnetic stirrer at 25 ºC for 1 h. After filtration, the final Mercury (II) ion concentration in the solution was estimated by ICP [16]. The desorption ratio (D %) was calculated; the equation is as follows:

$$D\% = \frac{\text{Mili moles of Mercury (II) ions desorbed to HNO3 solution}}{\text{Mili moles of Mercury (II)Ions adsorbed to GO} - \text{MTO (Adsorbent)}} \times 100$$

In this work, percentage of desorption for Mercury (II) ions from the GO-MTO–mercury-ion complexes is 99.3 %.
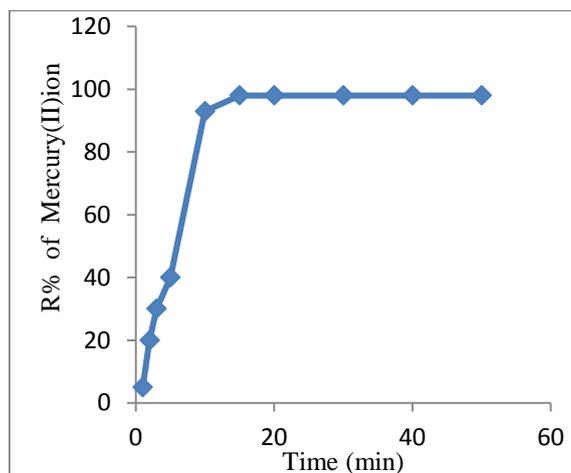

Figure 6. Removal percentage of Mercury (II) ion by 0.05 g of GO-MTO composite in 50 mL of 50 ppm Mercury (II) ion aqueous solution at pH= 6 during the period of 50 min
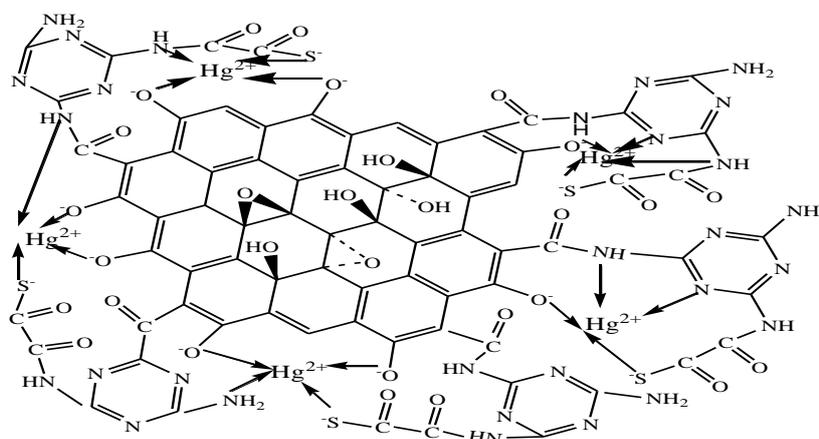

Figure 7. Structural formula of GO-MTO-Hg (II) complexes

Analysis of mercury in dental-unit (DU) waste water

DU wastewater samples were collected from the dental chair, Farhangian Hospital, Urmia city, at the end of the working day. An accurate volume of the sample was digested by UV-digested in the presence of suitable volumes of both concentrated HNO_3 and H_2O_2 (30%) for 1 h. The obtained solution was neutralized with NaOH (6 M) and 10 mL of this solution was treated under the conditions of the recommended procedure and found the amount of mercury (II) ion is 3.5 ± 0.63 ppm and recovery of mercury from the adsorbent is $99.24 \pm 0.51\%$.

Conclusion

In this study, a new composite was synthesized based on the Melamine-Tio Oxalic acid stabilized with Graphene

Oxide as Sorbent for the elimination of amounts toxic mercury (II) ion from aqueous solutions thus, the synthesized GO exhibits very interesting and unique properties that can be used in several of the applications. Based on the results, it is clear that the mercury-removal values achieved with graphite oxide–MTO composite was higher than Graphene Oxide. The main benefits of this elimination method contain simple, inexpensive, fast, higher elimination efficiency and higher precision of toxic mercury (II) ion. The Graphene Oxide–MTO composite can be reproduced readily with a solution of EDTA and it has a long lifetime or adsorption of Mercuric ion in acidic media. The composite outcome was to be reproducible with a good Mercury (II) ion selectivity over other strongly intervention ions. This composite was tested with various water samples, which exhibited a high adsorption capacity for the removal of amounts Mercury (II) ions. This adsorbent is very suitable for removing heavy metal ions, especially Mercury (II) ion from aqueous solutions.

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