Synthesis of graphene oxide-porphyrin nanocomposite and its application in removal of toxic metals

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Abstract

In this project a new method by using graphene oxide nanosheets–porphyrin composites was presented as sorbents for the removal of toxic mercury ions from aqueous solutions. The compound has the ability to adsorb the organic and inorganic compounds. Through the immobilization of THPP onto graphene oxide nanosheets, the desired composite was synthesized and identified by field emission scanning electron microscopy (FE-SEM), UV-Vis and Fourier transform infrared (FT-IR) spectroscopic techniques. The various experimental parameters such as pH and concentration of the aqueous solution of Hg (II), content of the THPP and the grapheme oxide have been optimized. It was shown that the uptake efficiency of Hg (II) significantly increased after immobilization of porphyrin on the graphene oxide nanosheets.

Keywords:

Removal of toxic heavy metals, Graphene oxide nanosheets, Porphyrin, toxic metal.

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1. Introduction

Removal of Heavy metal pollutants from wastewater has been one of the major investigations in the last few decades. Wastewaters from many industries such as metallurgical, mining, chemical manufacturing, and battery manufacturing industries contain many kinds of toxic heavy metal ions. Mercury is a highly toxic heavy metal that causes human health problems and environmental contamination, and is also more toxic even from lead and arsenic. This metal represents a major toxicity to microorganisms and environment even in low concentrations. Mercury triggers several serious disorders for humans including allergic reactions and brain and neurological damage. If ingested by a pregnant woman, it can cause developmental delays in children. Therefore, Removal of mercury metal from water due to the indiscriminate disposal of wastewater is extraordinarily important [1-5].

Adsorption is considered to be one of the most effective and economical treatment methods for mercury removal of effluents, rivers etc. Graphene has attracted multidisciplinary study because of its unique physicochemical properties. The preparation of graphene oxide nanosheets from graphite using Hummers method introduces many oxygen-containing functional groups such as carboxyl, hydroxyl and epoxy, on the surfaces of graphene oxide nanosheets. These functional groups are essential for the high sorption of heavy metal ions. Considering the oxygen-containing functional groups on the graphene oxide surfaces and high surface area (theoretical value of 2620 m^2 /g), the graphene oxide nanosheets should have high sorption capacity to remove of heavy metal ions from large volumes of aqueous solutions. However, the application of graphene oxide nanosheets as sorbents in the removal of heavy metal ions from aqueous solution is very Significant and important, that in this scheme has been used for this purpose [6, 7].

The Porphyrins are one of the most extensively used adsorbents for trapping Heavy metal pollutants. Porphyrins have gained particular interest as a ligand for metal removal because of their high metal removal efficiency and ligational properties. The nitrogen atoms in the tetrapyrrole ring act as ligational sites and also attract metal ions on account of their strong electron-donor properties, thus providing a high removal efficiency via the formation of metal–nitrogen coordination bonds [8-10]. In this paper, we report THPP immobilized graphene oxide nanosheets as a metal ion adsorbent [11].

2. Experimental

2.1 . Chemicals

All reagents were prepared from analytical reagent grade chemicals supplied from Merck (Darmstadt, Germany), except $HgCl_2$ which was obtained from Aldrich. The 10^{-3} M mercury 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 prepared by serial dilution of the stock solution with phosphate buffer, pH 7.5 Universal buffer solutions (0.1 M) were prepared from phosphoric acid solutions and sodium hydroxide solutions and adjusting pH to the desired value (0.08 M). The final pH was adjusted with the addition of a sodium hydroxide.

2.2 . Synthesis of GO-THPP

2.2.1. Synthesis of THPP

Tetrakis (4-hydroxyphenyl) porphyrin (THPP) was prepared using a modification of A. D. Adler-f. R. Longo method [12]. Briefly in a typical reaction, 80 mL of propionic acid was loaded in a 250 mL round-bottomed flask and refluxed for 0.5 h. Then 1.146 g 4-Hydroxybenzaldehyde dissolved in 10 mL of propionic acid are added. After about 15 minutes the amount of 6.0 g of fresh distilled pyrrole was slowly added into the solution. After 45 min the mixture was placed at room temperature to precipitate formed. The dark purple product was filtered and washed thoroughly with ethanol until the filtrate became clear.

2.2.2. Synthesis of graphene oxide nanosheets (GO)

Graphene oxide was prepared using a modification of Hummers and Offeman's method [13, 14]. Briefly in a typical reaction, 1 g graphite, 1 g $NaNO_3$, and 46 mL H_2SO_4 were stirred together in an ice bath. $KMnO_4$ (8 g) was slowly added while stirring, and the rate of addition was controlled to prevent the mixture temperature from exceeding 20 °C. The mixture was then transferred to a 35 °C water bath and stirred for about 1 h, forming a thick paste. Subsequently, 80 mL de-ionized water was added gradually and the temperature was raised to 90 °C. The mixture was further treated with 10 mL 30% H_2O_2 solution. The solution was then filtered and washed with de-ionized water until the pH was 6 and dried at 65 °C under vacuum.

2.2.3. Synthesis of GO–COCl

Briefly in a typical reaction, 0.5 g GO–COOH was suspended in 30 mL $SOCl_2$ and 5 mL of DMF. The mixture was refluxed for 24 h at 70°C under nitrogen atmosphere. The resultant solution was filtered and washed with anhydrous tetrahydrofuran (THF) and dried under vacuum.

2.2.4. Synthesis of covalently attached porphyrin graphene oxide hybrids (GO-THPP)

Briefly in a typical reaction, a mixture of 30 mg GO–COCl and 60 mg THPP were taken in a 100 mL round bottom flask and 3 mL of triethylamine and 15 mL of DMF were added and heated to 80 ° C for 72 h under a nitrogen atmosphere. After 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 8000 rpm for 30 min. The supernatant which contained dissolved THPP was discarded and the precipitate was washed thoroughly. After adding another 100 mL of diethyl ether, the mixture was sonicated for 5 min and then centrifuged at 8000 rpm for 30 min to collect the GO-THPP. Finally, the precipitate was washed with $CHCl_3$ five times following the above procedure.

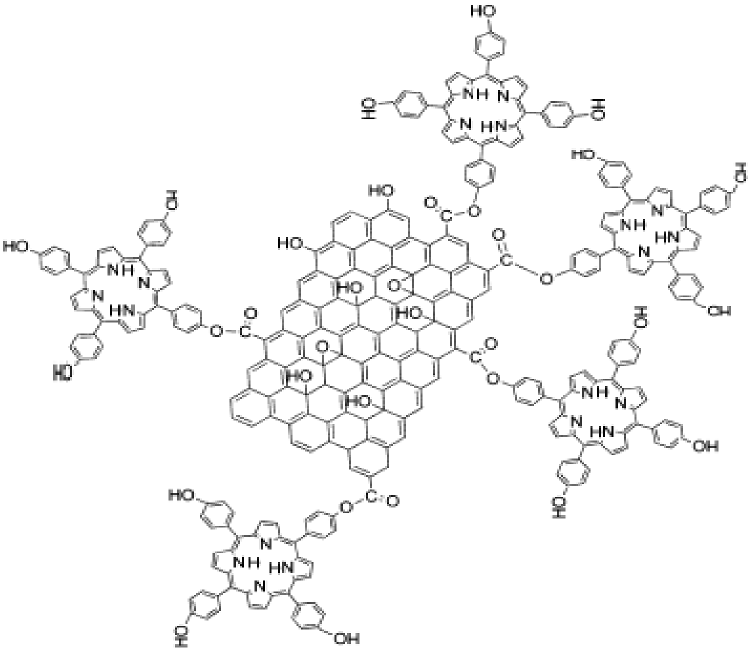

Fig. 1. The schematic illustration of GO-THPP

2.3. Structural and spectroscopic characterization of GO-THPP

The FTIR spectra were recorded using KBr plates in the range 500–4000 cm using a Nicolet 6700 FT-IR spectrometer. Fig. 2 shows the typical FTIR spectrum obtained for our graphite oxide material. The most characteristic features are the broad, intense band at 3430 cm^{-1} (O–H stretching vibrations) and the bands at 1725 cm^{-1} (C=O stretching vibrations from carbonyl and carboxylic groups), 1639 cm^{-1} (skeletal vibrations from unoxidized graphitic domains), 1380 cm^{-1} (C–OH stretching vibrations), and 1027 cm^{-1} (C–O stretching vibrations). The appearance of the peaks at around 2900 cm^{-1} is ascribed to the aromatic stretching vibrations of C–H bonds of GO. After covalent functionalization with porphyrins, a new peak appears at ~ 1582 cm^{-1} corresponding to the C=C vibrations of porphyrins and the peak of the C–O stretching vibration shifts to 1108 cm^{-1} ,and broadens. The peak present at ~1707 cm^{-1} is assigned to the bending vibration of the C=N of the porphyrin ring. The disappearance of the peak at 1380 cm^{-1} clearly indicates that in graphene oxide–porphyrin composites, the porphyrin molecules are covalently bonded to the graphene oxide via carboxylic acid linkage.

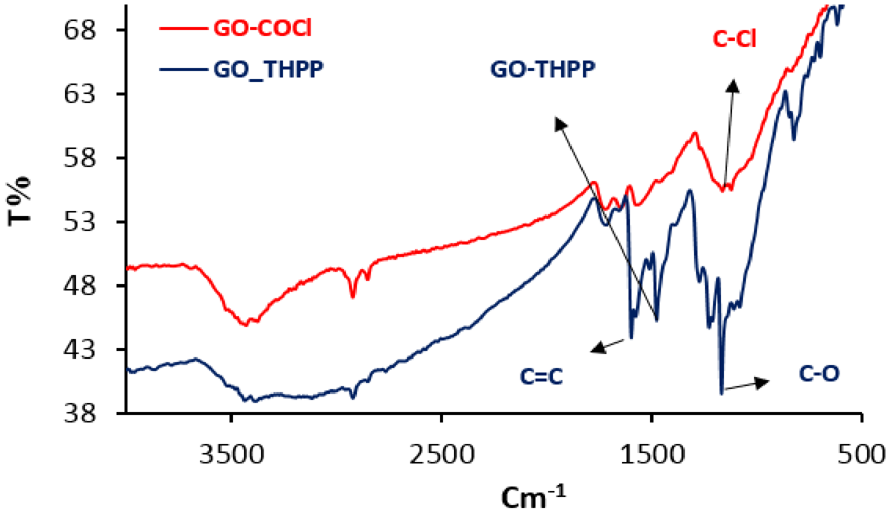

Fig. 2. FT-IR spectrum of graphene oxide and porphyrin–GO composites.

The SEM image (Figure 3) shows that few layered graphene oxides are formed, although the SEM image does not estimate the layer numbers of the graphene oxide nanosheets exactly. Pure graphite exhibits ordered flakes of a 4–5µm range. The scanning electron micrograph for the GO–porphyrin hybrid materials (Fig. 3 B) demonstrates that a homogeneous system with a micrometer order of magnitude was obtained. On functionalization, GO exhibits a three-dimensional network of randomly oriented sheet-like structures with a wrinkled texture and hierarchical pores with a wide size distribution.

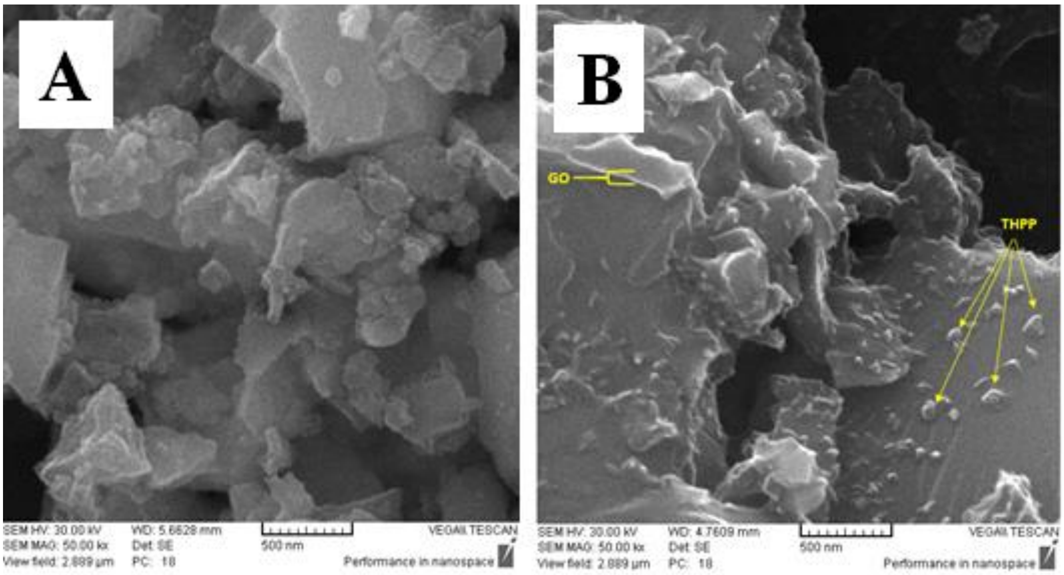

Fig. 3. SEM images of A) graphene oxide nanosheets and B) graphene oxide-porphyrin composites.

The optical absorption measurements were carried out by UV-Visible spectrometry. Fig. 4 shows optical absorption spectra of graphene oxide–porphyrin composites which agrees with the literature value.

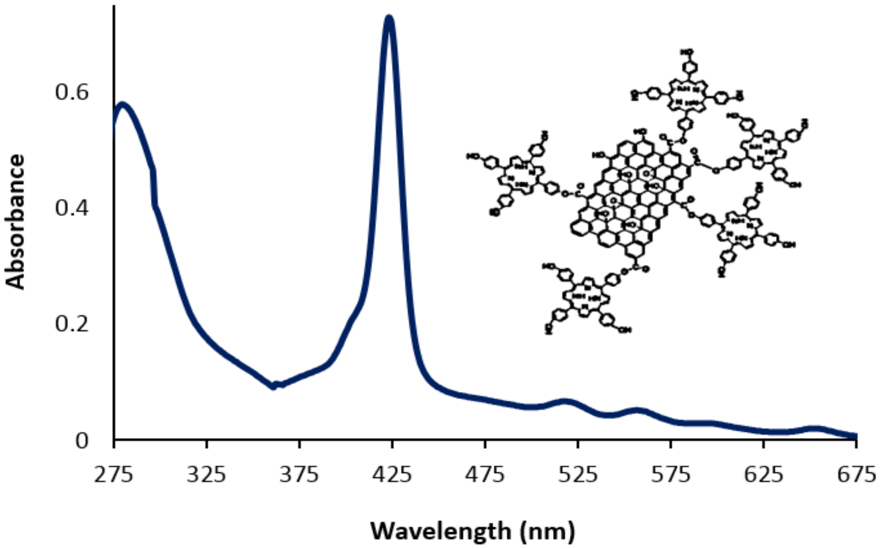

Fig. 4. UV/Vis spectrum of graphene oxide–porphyrin composites in DMF.

3. Adsorption–desorption experiments

To optimize the adsorption efficiency, adsorption experiments were performed at various pH levels of the aqueous solution of Hg (II). All experiments were run in triplicate. Experiments were carried out using 1 g/L of adsorbent each time (0.025 g of adsorbents' mass were added to 25 mL of deionized water in a conical flask). the pH-effect experiments was initially adjusted with aqueous solutions of acid and base (0.01 M H_3PO_4 and NaOH). Buffer solution is used to control the pH. Considering mercury precipitation in higher concentration, the equilibrium adsorption experiments were conducted at pH 7.5 in batch modes. The process of removal metal was performed. The metal solution were shaken on an orbital shaker at 150 rpm for a specified period of time. Samples were collected from the supernatant and filtered. The equilibrium concentrations of mercury ions that remained in solution were measured using ICP.

The removal percentage of Hg (II) (%) from aqueous solutions was calculated as follows:

$$Removal(\%) = 100x\frac{(C_0 - C_e)}{C_0} \tag{1}$$

Where C_0 and C_e (mg/L) is the concentration of Hg (II) before and after adsorption.

The effect of contact time on the mercury ion uptake was studied at constant pH. The results showed that adsorption increased rapidly during the first 20 min. After 20 min, the adsorption reached to the equilibrium state. As evident from Fig 5, 20 min contact time was required to attain adsorption equilibrium for the mercury solution. During this time, more than 93% of the Hg (II) was adsorbed. At equilibrium, coordinate interaction between GO-THPP and Hg (II) ions occurred, and adsorption became almost constant up to the end of the experiment. It can be concluded that the binding of Hg (II) with GO-THPP is high during the initial stages and that, the reactive functional groups of GO-THPP were exhausted after a certain period of time.

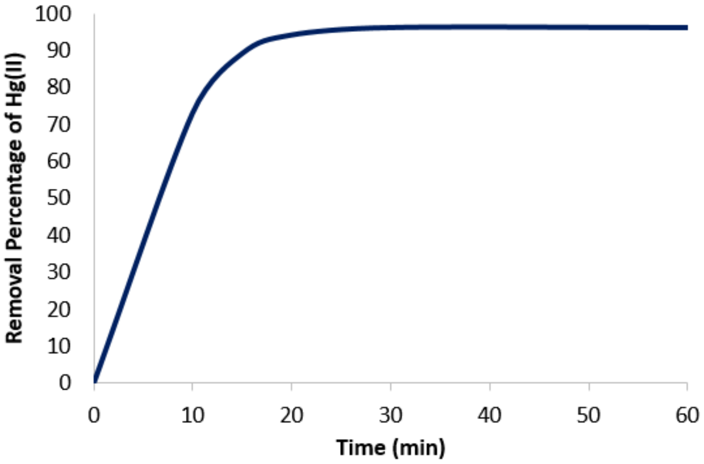

Fig. 5. Removal percentage of Hg (II) by 0.05 g of GO-THPP composite in 50 ml of 50 ppm Hg (II) aqueous solution at pH= 7.5 in the period of 60 min

4. Conclusion

In this work a new composites was synthesized based on the tetrakis (4-hydroxyphenyl) porphyrin (THPP) stabilized with graphene oxide as sorbents for the removal of amounts toxic mercury ions from aqueous solutions. Based on the results, it is clear that the mercury-removal values achieved with graphene oxide–porphyrin composites were higher than graphene oxide. The main advantages of this removal procedure include simplicity, cost effectiveness, rapidity, and higher removal efficiency of toxic mercury ions. The graphene oxide–porphyrin composites can be regenerated readily with a solution of EDTA and it has a long lifetime. The composites was concluded to be reproducible with a good Hg (II) selectivity over other potentially interfering ions. This composites was examined in different water samples, which was shown high adsorption capacity for the removal of amounts Hg (II).

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