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Synthesis and sustainable assessment of thiol-functionalization of magnetic graphene oxide and superparamagnetic Fe₃O₄@SiO₂ for Hg(II) removal from aqueous solution and petrochemical wastewater

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Abstract

Adsorbents used in adsorption processes play an important role in wastewater treatment technologies. It is therefore of interest how manufactured adsorbents can perform better or be more efficient. Is the adsorption capacity a sufficient indicator to select a good adsorbent? In this study, two nanoadsorbents of Hg(II) were successfully synthesized. They are magnetic graphene oxide (MGO-NH-SH) and magnetic nanoparticle ($\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$), both functionalized with a thiol group, acetylcysteine. The nanoadsorbents, in addition to their adsorption capacity, were investigated from the viewpoints of reuse and regeneration, economic costs, and environmental impact (carbon footprint). The prepared nanoadsorbents were characterized by FTIR, XRD, TGA, FE-SEM, VSM, AFM, Raman, and elemental analysis. Their adsorption of Hg(II) fits well with the Langmuir isotherm model and follows the pseudo-second-order kinetics. Under optimal conditions, the results of Hg(II) removal from real wastewater and polluted water by MGO-NH-SH exhibited a higher adsorption capacity, reuse, and regeneration, and as well lower cost and greenhouse gas emissions compared to $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$. The findings of the present study highlight that MGO-NH-SH as a promising adsorbent is more economically and environmentally friendly than $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ in the efficient removal of Hg(II) from real wastewater and polluted water.

Keywords: Adsorption process, thiol-functionalized MGO and Fe_3O_4 , reuse, economic costs, environmental impacts.

1. Introduction

During recent decades, with the increases in the world's population, water resources shortage, and discharge of wastewater polluted with heavy metals and other pollutants into water resources, pure water is no longer readily available [1–3]. In particular, deprived portions of society are periodically sickened by consuming contaminated water [1].

Heavy metals in wastewater and contaminated water don't naturally degrade. When heavy metals in wastewater are discharged into rivers and other water resources as a consequence of activities such as industries, mining, and agriculture without proper treatment, the result is often severe pollution [4]. Such pollution leads to negative environmental impacts on aquatic life, plants, and ecology and, finally, on human health and the economy [2,5–7]. Among the pollutants, Hg(II) is one of the most harmful metal ions to the environment, as it accumulates easily in living systems and has been confirmed to have toxic effects on the reproductive system, the central and peripheral nervous systems, the digestive and immune systems, and the liver and kidneys, and can cause sensory and psychological impairments [8,9]. Hg(II) can be released to aquatic ecosystems from a number of industrial activities, including oil refineries, wastewater from chloralkali plants, power generation plants, rubber processing, paper and pulp manufacturing, and the fertilizer industry [9,10].

After the Minamata event [11] and similar events around the world, such as the contamination crises in Iraq [12] and New Mexico [13], various methods have been developed to remove heavy metals from the aqueous environment. These include reverse osmosis, biological treatments, chemical precipitation, ion exchange, coagulation, electrochemical treatment, and adsorption [8,14].

Among these methods, adsorption has recently been widely recognized as an effective, economic, and simple method to remove various pollutants from wastewater [8,15,16][17]. The adsorption efficiency significantly depends on adsorbent properties. Hence, developing an effective, economic, and environmental friendly adsorbent is vital for extensive application of adsorption in water and wastewater treatment. In the past decade, many types of nanoadsorbents, such as Fe_3O_4 nanoparticles or magnetic graphene oxide, have been profoundly studied, not only from scientific interest, but also from many technological applications and industrial viewpoints. In many studies, low cost, low toxicity, and eco-friendliness are stated as nanoadsorbents' advantages over other adsorbents. Furthermore, these nanoadsorbents due to magnetic properties can be easily separated from water and wastewater solutions, and can be reused several times [7,18,19].

Accordingly, the present study has the following objectives: (a) the synthetization of the thiol-functional group, acetylcysteine, on the surface of the Fe_3O_4 nanoparticle, and magnetic graphene oxide for removal of mercury ions from an aqueous solution and real wastewater; (b) characterization of the nanoadsorbents through Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), Raman spectroscopy, thermogravimetric analysis (TGA), atomic-force microscopy (AFM), vibrating sample magnetometer (VSM), scanning electron microscope (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), and elemental analysis techniques; (c) investigations of the effects of pH, dose of adsorbent, temperature, and contact time on adsorption and subsequent removal of $\text{Hg}(\text{II})$; (d) studying thermodynamic properties, including enthalpy, entropy, and Gibbs free energy, of the nanoadsorbents by using experimental data; (e) examining the adsorption-desorption cycle of $\text{Hg}(\text{II})$ by nanoadsorbents; (f) to study of selectivity of prepared adsorbents, and finally, (g)

comparing two produced nanoadsorbents from capacity adsorption, environmental, and economic points of views.

2. Materials and methods

2.1. Materials

All of the chemical reagents used in the experiment were of analytical grade, and obtained from Sigma-Aldrich and Merck. The pH values were adjusted by adding HCl and NaOH (0.1 N) solution and monitored by a pH meter.

2.2. Synthesis process of thiol-functionalized magnetic graphene oxide

2.2.1. Preparation of graphite oxide

The graphite oxide was prepared from natural graphite powder, using the improved Hummers method [20]. Detailed explanations of the preparation of graphite oxide are given in Section 1 of the Supporting Information (SI).

2.2.2. Preparation of magnetic graphene oxide

The magnetic graphene oxide (MGO) was synthesized through the chemical co-precipitation method [21,22] (Fig. 1b). Details of the synthesis of magnetic graphene oxide can be found in Section 2 of the SI.

2.2.3. Preparation of thiol-functionalized magnetic graphene oxide

The thiol-functionalized magnetic graphene oxide was synthesized in two stages: a) the magnetic graphene oxide was functionalized with amine group (NH_2); and b) the product of the first stage was functionalized with thiol group (SH).

Regarding a) above, preparation of amine-functionalized magnetic graphene oxide (Fig. 1c): 0.2 g of magnetic graphene oxide was dispersed in 50 ml of dichloromethane (DCM). Next, 0.155 g of N, N'-dicyclohexylcarbodiimide (DCC) was added to the suspension, and after 20 min, 0.07 g of N-hydroxysuccinimide (NHS) was added and held for 4 h. Then, 0.5 ml of ethylenediamine (EDA) was added dropwise to the suspension and was maintained for 12 h. All reactions were performed under nitrogen flow at room temperature with vigorous stirring. Finally, the product was washed several times with ethanol and dried in a freeze dryer. The chemical reactions are given in SI (Fig. S.1).

Regarding b) above, preparation of thiol-functionalized magnetic graphene oxide (Fig. 1d): 0.08 g of acetyl cysteine was dispersed in 50 ml of methanol. Next, 0.155 g of DCC was added to the suspension, and after 20 min, 0.07 g of NHS was added and stirred at room temperature under nitrogen flow for 24 h. Then, 0.2 g of amine-functionalized magnetic graphene oxide was added gradually to the suspension and maintained for 12 h. Finally, the product was washed several times with ethanol and dried in a freeze dryer. The chemical reactions are given in SI (Fig. S.2).

2.3. Synthesis process of thiol-functionalized magnetic nanoparticle

2.3.1. Preparation of Fe₃O₄@SiO₂

The core-shell Fe₃O₄@SiO₂ nanoparticles were synthesized via a modified sol-gel process (Fig. 1A and B). First, 5 mmol FeCl₃.6H₂O (1.35 g) and 2.5 mmol FeCl₂.4H₂O (0.5 g) were dissolved in 50 ml deionized water and sonicated for 10 min. Next, under nitrogen flow at room temperature with vigorous stirring, 20 ml of NH₄OH solution was added dropwise into the reaction mixture over about 20 min. The reaction mixture was heated to 80 °C under N₂ and stirred for 5 h. Then, the temperature of the reaction was reduced to 40 °C, and after that, 40 ml

of ethanol (99.5%) was added to the mixture and stirred for 30 min. 10 ml of Tetraethyl orthosilicate (TEOS) was gradually added to the mixture, and the reaction maintained at 40 °C under N₂ for 22 h. Subsequently, the product was collected by external magnet, washed several times with deionized water and ethanol, and dried in a vacuum oven at 80 °C for 10 h to get Fe₃O₄@SiO₂ [23].

2.3.2. Preparation of Fe₃O₄@SiO-NH₂

For the preparation of amino-functionalized Fe₃O₄@SiO₂, 1 g Fe₃O₄@SiO₂ was dispersed in 50 ml of drying toluene and then ultrasonically dispersed for 15 min. 1 ml of (3-Aminopropyl) trimethoxysilane (APTMS) was then added to the suspension, and the suspension was refluxed at 60 °C with continuous stirring under nitrogen flow for 18 h. The nanoparticles were collected by external magnet and washed several times with toluene and finally dried at 80 °C under vacuum to obtain Fe₃O₄@SiO-NH₂ (Fig. 1B) [24–26].

2.3.3. Preparation of thiol-functionalized magnetic nanoparticle

For preparation of thiol-functionalized Fe₃O₄@SiO₂-NH₂, 0.08 g of acetyl cysteine was dispersed in 50 ml of methanol. Next, 0.155 g of DCC was added to the suspension. After 20 min, 0.07 g of NHS was added and stirred at room temperature under nitrogen flow for 24 h. Then, 0.2 g of Fe₃O₄@SiO₂-NH₂ was added gradually to the suspension and maintained for 12 h. Finally, the product was washed several times with ethanol and was dried at 80 °C under vacuum (Fig. 1C).

2.4. Characterization of nanoadsorbents

The FT-IR spectra were recorded in the range of 400–4000 cm⁻¹ with a Nicolet IR100 FT-IR with spectroscopic grade KBr. The powder X-ray diffraction patterns (XRD) were carried out at

room temperature by a Philips X-Pert 1710 diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$, voltage: 40 kV, current: 40 mA) and in the range 10° – 90° (2θ) at an angular speed of $0.02^\circ/\text{s}$. Raman spectra were recorded in the spectral range 100 to 4200 cm^{-1} on a Nicolet Almega Thermo Dispersive Raman Spectrometer using a 532 nm argon ion laser. Thermal gravimetric analysis (TGA) was carried out on a thermal analyzer with a heating rate of $20^\circ\text{C min}^{-1}$ over a temperature range of 25 – 900°C under flowing compressed N_2 using a METTLER TOLEDO System, TGA/SDTA 851. The morphology of adsorbents was investigated with field emission scanning electron microscopy (FESEM), using TESCAN MIRA FE-SEM on gold-coated samples, transmission electron microscopy (TEM, Philips CM-120, Netherland). The atomic force microscopy (AFM) images were employed using a Park Scientific CP-Research model (VEECO) to examine the thickness of GO sheets. Thermogravimetric analysis was carried out using thermal analyzer with a heating rate of $20^\circ\text{C min}^{-1}$ over a temperature range of 25 – 1100°C under flowing compressed nitrogen. The surface area and porosity characteristics of the prepared adsorbents were gained by N_2 adsorption–desorption experiments at 77 K using a Micromeritics ASAP 2020 nitrogen adsorption apparatus. Before the measurements, the samples were degassed at 100°C for 1 h. The specific surface area and the pore size distribution were calculated by the Brunauer–Emmett–Teller (BET) and Brunauer–Joyner–Hallenda (BJH) methods, respectively. The magnetic properties of adsorbents were obtained with a vibrating magnetometer/alternating gradient force magnetometer (VSM/AGFM, Meghnatis Daghigh Kavir Co., Iran).

Fig. 1. Schematic of the functionalization of the Fe_3O_4 nanoparticle and magnetic graphene oxide. The left hand side shows the Fe_3O_4 nanoparticle and the right hand side shows the magnetic graphene oxide.

2.5. Conditions of experiments

More details and conditions of the adsorption experiments, the adsorption isotherms, the adsorption kinetic experiments, and the adsorption thermodynamics are given in Sections 3, 4, 5, and 6 of SI, respectively.

2.6. Desorption Studies

To evaluate the reusability of the nanoadsorbents, adsorption of Hg(II) and regeneration of Hg-loaded nanoadsorbents were carried out in 10 adsorption-desorption cycles (Figs. 1D and 1e. The first optimized the type of acid (HNO₃, H₂SO₄, and HCl) for both nanoadsorbents, and then optimized the concentration of the selected acid (see SI, Figs. S.3 and S.4). After each cycle, the adsorbents were collected by a magnet and washed twice with deionized water for adsorption again. The desorption ratio was calculated by this equation [26]:

$$\text{Desorption Ratio} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \quad (1)$$

2.7. Selective adsorption experiment and real wastewater treatment

To study the selectivity of the prepared adsorbents for mercury (II) ion removal of a mixed system was used. Also, the real wastewater sample was taken from effluent sewage of wastewater treatment plan of petrochemical chloralkali unit of Mahshahr, Iran. Experiments were carried out based on optimized conditions of prepared adsorbents. Before and After adsorption, the concentration of metal ions in mixed system and real wastewater was determined by spectrophotometry (GBC, SensAA Dual, Australia).

2.8. Economic and carbon footprint evaluations

The cost of used materials for the production of nanoadsorbents for 1 kg Hg(II) removal was found based on their average cost as obtained from Sigma-Aldrich and Merck. Moreover, to calculate the cost of electricity used, the average worldwide cost of industrial electricity was utilized. The breakdown of the cost of each material used and electricity is presented in Table S.1.

Carbon footprint was employed to compare two produced adsorbents following ISO 14067 instructions [27]. Carbon footprint is a method by which the overall greenhouse gases emitted during production processes or other activities are assessed. Due to the fact that the produced adsorbents had different adsorption capacities, the functional unit was determined to be 1 kg Hg removal of pollutant water. It is worth noting that in economic and environmental evaluations, the total adsorption capacity for both nanoadsorbents was calculated based on an adsorption-desorption cycle of more than 90% (MGO-NH-SH, six times; Fe₃O₄@SiO-NH-SH, three times).

To correctly estimate the carbon footprint of the two above-mentioned products, all materials and energy carriers as well as their consequent emissions were taken into consideration. Foreground data were obtained from our laboratory experiments; the background information and data related to production of raw materials and infrastructures were from Ecoinvent 3.0 as presented in SimaPro software 8.2.3.0 (PRé Consultants BV, Amersfoort, The Netherlands) [27]. The predominant source of energy used in lab experiments was electricity, mainly employed for heating and cooling.

3. Results and discussion

3.1. Characterization of MGO-NH-SH

Fig. 2 shows FTIR spectra of the (A) thiol-functionalized magnetic/graphene oxide and (B) thiol-functionalized magnetic nanoparticle. Fig. 2A shows (a) FTIR spectra of the graphite, (b) graphite oxide, (c) magnetic graphene oxide, (d) amine-functionalized MGO, and (e) thiol-functionalized MGO-NH₂. Compared to the spectrum graphite in Fig. 2A(a), the appearance of some strong absorption peaks in the FTIR of graphite oxide (b) can confirm the successful oxidation of graphite powder with KMnO₄ in the presence of concentrated sulfuric acid; the original extended conjugated π -orbital system of the graphite was destroyed, and oxygen functional groups were embedded into the carbon skeleton [28]. The absorption bands at 3412 cm⁻¹ can be attributed to the stretching vibration and deformation vibration of hydroxyl (–OH) groups. The presence of strong peaks at 1725 cm⁻¹, 1624 cm⁻¹, and 1373 cm⁻¹ can be assigned to C=O stretching vibration of the COOH groups located at the edges of the graphite oxide sheets, C=C configurable vibrations from the aromatic zones, and C–OH stretching vibrations, respectively. The presence of epoxy and alkoxy functional groups is also indicated at around 1259 cm⁻¹ and 1053 cm⁻¹, respectively [29]. The spectrum (c) of magnetic graphene oxide reveals at 559 cm⁻¹ a strong peak, which is related to Fe–O stretching vibration of Fe₃O₄. Compared to (c) spectrum of MGO, the (d) spectrum of MGO-NH₂ shows two characteristic absorbance bands at 1633 and 1560 cm⁻¹, which relate to the C=O stretching vibration of NHCO (amide I) and the N–H bending of NH₂, respectively [30,31]. The absorption bands at 3271 and 3079 cm⁻¹ can be attributed to amide A, with more than 95% due to the N–H stretching vibration and amide B overtone of amide II, respectively [32]. This is confirmed by the successful engulfing of the EDA to the carboxyl groups of MGO. Finally, the absorption band relates to the SH group in the spectrum of MGO-NH-SH, which was not clearly viewed owing to the relatively low content of thiol and the poor sensitivity of the IR to the thiol [33]. However, the shift of the

absorbance bands at 1633 and 1560 cm^{-1} in MGO-NH₂ may be due to successful grafting of the acetylcysteine to the surface of MGO-NH₂ (Fig. 2A (e)).

The FTIR spectrum of thiol-functionalized magnetic nanoparticle is presented in Fig. 2B. The absorption bands at around 575 and 3420 cm^{-1} in four materials (a, b, c, and d) were attributed to the Fe–O bond vibration of Fe₃O₄ and O–H stretching mode, respectively. With the addition of TEOS, in the spectra of (b) Fe₃O₄@SiO₂, (c) Fe₃O₄@SiO–NH₂, and (d) Fe₃O₄@SiO–NH–SH, broad strong bands emerged at around 1094, 955, 798, and 467 cm^{-1} , which can be due to Si–O–Si antisymmetric stretching vibrations. The absorption bands at 1094, 955, 798, and 467 cm^{-1} on spectra (b), (c), and (d) may be attributed to the stretching and deformation vibrations of SiO₂, reflecting the coating of silica on the magnetite surface [34,35]. As Figs. 2B (c and d) show, the absorption peaks in the region of 2800–3045 cm^{-1} corresponded to the stretching vibration of methylene groups of Fe₃O₄@SiO–NH₂ and Fe₃O₄@SiO–NH–SH. The results confirm the amino-functionalization of the silica shell [24,35]. In the spectrum of (d) Fe₃O₄@SiO–NH–SH, a new weak peak at 2505 cm^{-1} was observed, and can be ascribed to the SH bond vibration [36].

Fig. 2. FTIR spectra of (A) the thiol-functionalized of magnetic graphene oxide: (a) graphite, (b) GO, (c) MGO, (d) MGO-NH₂, (e) MGO-NH-SH, and (f) MGO-NH-SH after ten times adsorption-desorption; and of (B) magnetic nanoparticle: (a) Fe₃O₄, (b) Fe₃O₄@SiO₂, (c) Fe₃O₄@SiO–NH₂, (d) Fe₃O₄@SiO–NH–SH, and (e) Fe₃O₄@SiO–NH–SH after ten times adsorption-desorption.

The XRD patterns of graphene oxide, MGO, MGO-NH₂, and MGO-NH-SH are visible in Fig. 3A. The diffraction peak at $2\theta = 10.9^\circ$ of GO relates to the typical diffraction peak of GO nanosheets, ascribed to the (0 0 2) plane [37,38]. For MGO, MGO-NH₂, and MGO-NH-SH, the peaks at 2θ values of 18.3° , 30.3° , 35.8° , 43.3° , 53.9° , 57.3° , and 62.9° were assigned to the (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) reflections, respectively. These peaks are in accordance with the standard XRD data for the cubic phase Fe₃O₄ (JCPDS no. 89-4319) with a face-centered cubic (fcc) structure, and illustrate that the main structure of MGO did not change when it was functionalized by ethylenediamine and acetylcysteine [38,39]. While it should be noted that the GO peak vanished in the XRD pattern of MGO, this phenomenon was also observed in the earlier literature. These earlier researchers expressed that the disappearance of the GO peak in the XRD pattern of MGO might be due to the strong peaks of Fe₃O₄, which overwhelm the weak carbon peaks. Additionally, more monolayer graphene resulted from the reduction of the graphene sheets' accumulation in the presence of magnetite, giving the appearance of weaker peaks from carbon ($2\theta = 27^\circ$) [40,41]. In addition, the peaks at $2\theta = 18.3^\circ$ were attributed to goethite, and the weak peak at 27° showed the characteristics of carbon on adsorbents. The peaks at $2\theta = 30.3^\circ$, 35.8° , 43.3° , and 57.3° were assigned to maghemite or magnetite, and the peaks at $2\theta = 53.9^\circ$ and 62.9° were assigned to hematite [40,41].

The XRD patterns of Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@SiO-NH-SH is showed in Fig. 3B. All diffraction peaks of the XRD patterns of the prepared nanoparticles are consistent with the Joint Committee on Powder Diffraction Standards XRD data (JCPDS no. 89-4319), which are confirmed to the cubic spinel phase of Fe₃O₄. [19]. After coating with a silica layer (TEOS), the broad peak of non-crystalline state SiO₂ in the region of 20° – 30° was observed, perhaps because of the amorphous silica structure. However, after being functionalized with the amine and thiol

groups, the XRD pattern of $\text{Fe}_3\text{O}_4@\text{SiO}-\text{NH}-\text{SH}$ is very similar to that of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, indicating the functionalization did not have an effect on the structure of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ [42–44].

Fig. 3. XRD patterns of (A) the thiol-functionalized of magnetic graphene oxide and (B) magnetic nanoparticles (B)

In order to study the porous structure and surface area of prepared adsorbents, the BET analysis was used. The results of N₂ sorption-desorption isotherms, pore size distribution the total pore volumes of synthesized adsorbents (Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}-\text{NH}-\text{SH}$ and GO, MGO, MGO-NH-SH) are showed and summarized in Fig. S.5 and Table 1. The BET results (Table 1) displays that the specific surface area of GO, MGO, and MGO-NH-SH is 263.75, 137.03, and 88.07 m²/g, respectively. As it is expected, the BET surface area is decreased after grafting with the functional groups [45,46].

The measured BET surface areas are 45.77, 127.47, and 9.81 m²/g for Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}-\text{NH}-\text{SH}$ nanoparticles, respectively (listed in Table1). By compering, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ exhibit a relatively higher BET surface area then that of Fe_3O_4 , that it can be due to the coating of SiO₂ component. However, like MGO-NH-SH, the functionalization of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ decreased the BET surface area from 127.47 to 9.81 m²/g.

Table 1. BET Surface Area (S_{BET}), total poer volume and average pore size of prepared adsorbents.

Adsorbent sample	S_{BET} (m^2/g)	Pore Diameter (nm)		Pore Volume (cm^3/g)
		BJH Adsorption	BJH Desorption	
GO	263.75	3.42	4.11	0.31
MGO	137.03	2.32	3.40	0.09
MGO-NH-SH	88.07	3.90	4.29	0.16
Fe_3O_4	45.77	3.60	4.85	0.16
$\text{Fe}_3\text{O}_4@\text{SiO}_2$	127.47	1.96	4.43	0.09
$\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$	9.81	2.78	4.66	0.02

The technique known as thermal gravimetric analysis (TGA) is a useful tool to determine the composition of materials and their thermal stability. Fig. 4A illustrates TGA curves of graphite, GO and MGO, MGO-NH₂, and MGO-NH-SH heated in a nitrogen atmosphere. Commonly, a slight weight loss below 120 °C can be attributed to the evaporation of physically adsorbed water molecules. The TGA curve of raw graphite displays little weight loss, and is about 5% below 900 °C, suggesting that graphite is most stable and has few functional groups. In comparison with raw graphite, GO indicates much lower thermal stability, which can be caused by a reduced van der Waals interaction. Weight loss in the temperature range of 120–250 °C is associated with the decomposition of labile oxygen-containing functional groups dependent on GO, such as carboxyl, carbonyl, epoxide, and hydroxyl, resulting in the loss of CO, CO₂, and H₂O vapors [47–49]. After Fe₃O₄ nanoparticles were bonded onto GO, the TGA curve of MGO showed a gradually descending sloping line of about 30%, which confirmed that Fe₃O₄ nanoparticles were bonded onto the surface of GO [48,50]. Compared with MGO, the greater loss of weight of MGO-NH₂ and MGO-NH-SH is due to the thermal instability of most of the organic functional groups (amine and thiol) with MGO-NH₂ and MGO-NH-SH. In MGO-NH₂, roughly 10% weight loss was attained after 230 °C; this can be ascribed to dislocations of carbon materials, covalent bonding between amine group (EDA), and oxygenated groups on the surface of MGO-NH₂. The

curves of MGO-NH-SH and MGO-NH₂ have similar behavior until 600 °C, but over 600 °C in the MGO-NH-SH curve, greater weight loss can be due to the presence of amine and thiol functional groups on the surface of MGO [18,51,52].

Fig. 4B depicts the TGA curves of Fe₃O₄, Fe₃O₄@SiO-NH₂, and Fe₃O₄@SiO-NH-SH. The weight loss of the Fe₃O₄ is about 7% over the entire temperature range, which may be caused by the loss of adsorbed physical and chemical water [53]. The TGA curves of Fe₃O₄@SiO-NH₂ and Fe₃O₄@SiO-NH-SH showed similar fluctuation at three points below 150 °C (H₂O evaporation), around 150 °C–500 °C (organic motif combustion), and over 500 °C (carbonized shell on the Fe₃O₄), which can be ascribed to the desorption and loss of moisture from the surface of the silica layer, decomposition of organic matter grafted to the silica surface, and the escape of hydroxyl ions from the particles, respectively [24,54,55]. In addition, the weight loss rate of Fe₃O₄@SiO-NH-SH was somewhat more than that of Fe₃O₄ and Fe₃O₄@SiO-NH₂ through the entire temperature range, confirming the existence of acetylcysteine.

Fig. 4. TGA curves of (A) thiol-functionalized magnetic graphene oxide and (B) magnetic nanoparticle.

Table 2 lists the results of elemental analysis. Elemental analysis shows that the nitrogen content of MGO-NH₂ increased from 1.14 to 3.03%, compared with MGO. Moreover, with

functionalized MGO-NH₂ with acetylcysteine, the sulphur content of MGO-NH-SH increased to 1.54%. The results of elemental analysis support a successful functionalization of amine and thiol groups on the MGO surface. In addition, the percentage of amine and thiol groups in MGO-NH₂ and MGO-NH-SH is approximately in agreement with TGA curves (the weight loss in the thermogram).

As the elemental analysis of Fe₃O₄ nanoparticles functionalized with amine and thiol groups in Table 2 indicate, the nitrogen and sulphur content of Fe₃O₄@SiO-NH₂ and Fe₃O₄@SiO-NH-SH increased to 2.67 and 1.70%, respectively, in comparison with that of the Fe₃O₄ nanoparticle. As well, the results of elemental analysis are almost consistent with the TGA curves of amine- and thiol-functionalized Fe₃O₄ nanoparticles (Fig. 4B), confirming the successful functionalization of the Fe₃O₄ nanoparticle.

Table 2. Elemental analysis of each step of thiol- and amine-functionalized MGO and Fe₃O₄

Weight (%)	MGO-NH-SH			Fe ₃ O ₄ @SiO-NH-SH		
	MGO	MGO-NH ₂	MGO-NH-SH	Fe ₃ O ₄	Fe ₃ O ₄ @SiO-NH ₂	Fe ₃ O ₄ @SiO-NH-SH
Carbon	11.42	14.06	14.93	0.51	6.82	8.19
Hydrogen	0.78	1.16	3.01	1.68	3.84	4.11
Nitrogen	1.49	3.03	3.98	0.16	2.42	2.67
Sulphur	-	-	1.54	-	-	1.70

The magnetic properties of Fe₃O₄, MGO, and MGO-NH-SH were performed with a vibrating sample magnetometer (VSM) at room temperature (Fig. 5A). The saturation magnetization intensity of Fe₃O₄ nanoparticles, MGO, and MGO-NH-SH was measured at 63.37, 47.11, and 36.20 emu/g, respectively. As a result, VSM showed that the saturation magnetization of MGO-NH-SH is lower than that of MGO, and MGO magnetization is lower than that of Fe₃O₄ nanoparticles; their decreases in magnetism properties confirmed the introduction of amine and thiol functional groups on MGO, and the existence of GO in Fe₃O₄ nanoparticles [56,57]. The magnetism spectra also display negligible coercivity and remanence, indicating that almost no

magnetization remained to remove the external magnetic field, which confirms the superparamagnetic properties of the synthesized adsorbents [19,50].

The samples for atomic force microscopy (AFM) images were prepared by dropping a GO suspension on exfoliated mica, followed by drying in an ambient atmosphere. According to the cross-sectional view of the AFM image (Fig. 6a), the height of the GO nanosheets was between approximately 0.8 and 1 nm, suggesting a monolayer graphene sheet, because the thickness ranges for monolayer GO nanosheet are reported to range from about 0.8 to 1.0 nm [6,58]. It is well known that based on van der Waals force, the thickness of the ideal pristine graphene sheet is 0.34 nm. Hence, graphene oxide nanosheets are expected to be “thicker” owing to the existence of epoxy, hydroxyl, or carboxylic groups covalently bonded with carbon atoms and the displacement of a planar sp^2 -hybridized to a distorted sp^3 -hybridized geometry [48,57,59].

Fig. 5B shows the magnetization curve of Fe_3O_4 and $Fe_3O_4@SiO-NH-SH$, measured by VSM at room temperature. The saturation magnetization values of Fe_3O_4 and $Fe_3O_4@SiO-NH-SH$ were obtained at 60.02 and 21.83 emu/g, respectively, and showed the remanence and coercivity to be nearly zero. This observed decrease in magnetic property reflects the surface modification of Fe_3O_4 by TEOS, APTMS, and acetylcysteine. Besides, the magnetic remanence and coercivity at nearly zero Fe_3O_4 and functionalized Fe_3O_4 nanoparticles suggests that the adsorbents reveal a superparamagnetic behavior [60,61].

Fig. 5. VSM curves of (A) thiol-functionalized magnetic graphene oxide and (B) magnetic nanoparticles

Raman spectroscopy efficaciously characterizes the structure and properties of graphene-based materials [48]. The Raman spectra of GO usually present two prominent peaks at around 1590 and 1340 cm^{-1} , which are attributed to the D band (the vibration of sp^3 carbon atoms with defects and disorder) and the G band (the vibration of sp^2 -bonded carbon atoms in a graphitic domain), respectively. The intensity ratio of D and G bands (ID/IG) is the standard for evaluating the extent of disorder defects in the lattice. In the case of GO, the ID/IG ratio is nearly 1 [62,63]. As the Raman spectrum of MGO-NH-SH in Fig 6(b) shows, the ID/IG ratio is about 1.33, higher than that of $\text{GO} \approx 1$, meaning that graphene oxide was modified by functional groups [52,64] .

Fig. 6. (a) Typical AFM image and corresponding cross-section analysis, and (b) Raman spectra of GO

The FE-SEM of (a) GO, (b) MGO, and (c) MGO-NH-SH is indicated in Fig. 7. It was obvious that the GO nanosheets displayed layered, thin, and some crumpled structures. After combination with the magnetic, the SEM image of the composite revealed the regular sphere morphology of the content of Fe_3O_4 loaded at the surface of GO, with an average size of 23 nm. Afterward, with functionalization of oxygen-containing functional groups GO with thiol and amine groups in MGO, the SEM image indicates that functional groups are charged on the GO surface, owing to the increased thickness of GO layers. In addition to, the morphology of as-synthesized GO and MGO-NH-SH nanosheets were characterized by using TEM. Fig. 8 (a and b) provides the corresponding TEM images of GO and MGO-NH-SH. The TEM image of the GO nanosheets is clearly visible that the GO nanosheets have a lamellar structure and are greatly transparent. GO TEM image suggests further demonstration of AFM (Fig. 6a) and SEM (Fig. 7(a)) results were made on GO, as well as, signifying the very thin layer and can be provide numerous oxygen-

functional sites for more functionalization [65]. Also, The TEM images Fig. 8 (b) suggested that Fe_3O_4 nanoparticles was successfully distributed on the surface of GO.

Fig. 7 shows FE-SEM images of Fe_3O_4 (e and f) and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ (g). Fig. 7 (e and f) shows that Fe_3O_4 nanoparticles have a spherical structure with an average size of less of 50 nm. The SEM image of the as-prepared $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ (Fig. 7(g)) displays that the size of composite nanoparticles increases with the modification of Fe_3O_4 with TEOS, APTMS, and acetylcysteine. This result substantiates that the modification of Fe_3O_4 was successfully performed. As well as, The TEM images of $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ are shown in Fig. 8 (c and d), displaying the core-shell structure of $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ and the formation of single-phase Fe_3O_4 nanoparticles.

Fig. 7. FE-SEM images of (a) graphene oxide, (b) MGO, (c) MGO-NH-SH, (d) MGO-NH-SH after adsorption –desorption, (e and f) magnetic nanoparticle, (g) $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$, and (h) $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ after adsorption -desorption.

Fig. 8. TEM images of (a) graphene oxide, (b) MGO-NH-SH, and (c and d) Fe₃O₄@SiO-NH-SH.

3.2. Optimization of adsorption of Hg(II)

3.2.1. Effect of contact time

One of the most important economical parameters in the wastewater treatment process is contact time [18]. Hence, the study of the effect of contact time on the removal efficiency of Hg(II) by studied nanoadsorbents is crucial. The effect of contact time on the removal of Hg(II) was checked in the time range of 15–150 min for different Hg(II) concentrations, and the results are

available in Fig. 9A. The results of contact time for both studied nanoadsorbents showed that removal efficiency quickly increases with an increase in contact time before equilibrium is attained, at which point the removal efficiency reaches a constant value. This initial increase in adsorption can be the result of a huge number of available vacant sites on the adsorbent surfaces [18,66]. After a while, the residual sites can be difficult to employ by reason of repulsive forces operating between the already adsorbed Hg(II) ions on the adsorbents and those existing in the solution. As Fig. 9A shows, the adsorption of Hg(II) by studied nanoadsorbents reached equilibrium at about 60 min, but the adsorption rate of Hg(II) for Fe₃O₄@SiO-NH-SH was slightly faster than that of MGO-NH-SH.

3.2.2. Effect of solution pH

pH is one of the most vital parameters in the adsorption process of heavy metals. pH affects the adsorption process by type of ion (H⁺ or OH⁻) solution and also by the type of adsorbent and the properties of active sites on the adsorbent surface [2,6,51]. As shown in Fig. 9B, the highest adsorptions were achieved at pH = 7 and 6, respectively, for MGO-NH-SH and Fe₃O₄@SiO-NH-SH. Based on the results, it is clear that pH has a significant effect on the process of adsorption, and the low and high (> 7) values of pH lead to a reduction of capacity adsorption. In effect, the reaction of the SH functional group and mercury ions increases the H⁺ in the solution. Therefore, increasing OH⁻ leads to the consumption of H⁺ in the solution, allowing the reactions to continue properly. Increasing the H⁺ in the solution generates competition between H⁺ and Hg(II) ions for binding to active sites, leading to a decrease of the removal percentage [2,51].

Fig. 9. Effect of (A) contact time and (B) pH on the removal of Hg(II) by MGO-NH-SH and Fe₃O₄@SiO-NH-SH.

3.2.3. Effect of dose of adsorbents

The effect of studied adsorbents' doses on the removal efficiency of Hg(II) was evaluated, and the results are shown in Fig. 10 (A and B). As apparent in Fig. 10, the adsorption efficiency of Hg(II) for each studied adsorbent increased with increases of the adsorbents' dose masses. Therefore, increasing the removal percentage of Hg(II) results from an increase in the number of available active sites on the adsorbents. Moreover, the maximum removal efficiency (%) of both adsorbents was obtained in 20 mg of adsorbent dose. However, initial concentrations, 25 mg/l and 20 mg/l, of Hg(II) for investigating removal efficiency were tested by MGO-SH and Fe₃O₄-SiO-SH, respectively. It was found that the number of available active sites in MGO-NH-SH is more than in Fe₃O₄@SiO-NH-SH.

Fig. 10. Effect of adsorbent doses, (A) MGO-NH-SH and (B) Fe₃O₄@SiO-NH-SH, on removal efficiency (%) of Hg(II)

3.3. Adsorption isotherms

In calculating adsorption isotherms, it is important to develop an equation that accurately demonstrates the results and could be used for designing a desired adsorption system [67]. The linear fitting curves of the Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Redlich–Peterson (R–P) adsorption isotherms of the Hg(II) ion are displayed in Fig. 11 for MGO-NH-SH and Fe₃O₄@SiO-NH-SH and Fig.S.6 for Fe₃O₄, Fe₃O₄@SiO-NH₂, GO and MGO-NH₂. For the studied nanoadsorbents, Table 3 and Table S.2 presents the Langmuir and Freundlich, D–R, and R–P constants and the regression coefficients (R^2). As shown in Fig. 11 and S.6, all synthesized nanoadsorbents illustrate a sharp initial slope in both Langmuir and Freundlich adsorption isotherms showing the high efficiency of the adsorbent in low Hg(II) concentrations. As the concentration of Hg(II) ions in solution increases, the efficiency decreases due to the impregnation of active sites on the adsorbent surface. According to the regression coefficients R^2 presented in Table 3 and S.2, for MGO-NH-SH, Fe₃O₄@SiO-NH-SH, Fe₃O₄@SiO-NH₂, and MGO-NH₂ nanoadsorbents, the Langmuir isotherm is more suitable than the Freundlich isotherm, suggesting that the Langmuir isotherm fits the experimental better data than the

Freundlich isotherm. Also, for GO and Fe₃O₄, The isotherms are fitting better by Freundlich model than the Langmuir isotherm.

In addition, the obtained R^2 values of the Langmuir and R–P isotherms indicated that the adsorption mechanisms of Hg(II) onto MGO-NH-SH, Fe₃O₄@SiO-NH-SH, Fe₃O₄@SiO-NH₂, and MGO-NH₂ nanoadsorbents and GO and Fe₃O₄ nanoadsorbents are homogeneous and heterogeneous in nature, respectively. The R–P isotherm model combines the postulation of both the Langmuir and Freundlich models; hence, the results of R–P isotherm model indicated that the adsorption mechanism has better conformity to the Langmuir model in MGO-NH-SH, Fe₃O₄@SiO-NH-SH, Fe₃O₄@SiO-NH₂, and MGO-NH₂ nanoadsorbents and Freundlich model in GO and Fe₃O₄. Therefore, the result can be that the adsorption of Hg(II) ions by MGO-NH-SH, Fe₃O₄@SiO-NH-SH, Fe₃O₄@SiO-NH₂, and MGO-NH₂ demonstrate monolayer uniform adsorption without interaction among the adsorbed ions. Additionally, the essential feature of the Langmuir isotherm can be represented by a dimensionless constant separation factor (RL), which can show whether the adsorption is favorable or not, as calculated by the following equation:

$$RL = \frac{1}{1+bC_o} \quad (2)$$

where b and C_o are the constants of the Langmuir isotherm in l/mg and the initial concentration of Hg(II) ions in the liquid phase in mg/l, respectively. As mentioned above, the RL value indicates the adsorption nature to be unfavorable if $RL > 1$, linear if $RL = 1$, favorable if $0 < RL < 1$, and irreversible if $RL = 0$. For adsorption of Hg(II) on MGO-NH-SH and Fe₃O₄@SiO-NH-SH, the calculated RL values are in the range of 0.004–0.03 and 0.005–0.02, respectively, thereby confirming that the adsorptions are effective.

The obtained maximum adsorption capacity q_m of Hg(II) ions in MGO-NH-SH, Fe₃O₄@SiO-NH-SH, GO, Fe₃O₄, Fe₃O₄@SiO-NH₂, and MGO-NH₂ is 208.78, 176.80, 74.07, 72.46, 129.87, and 138.88 mg/g with the Langmuir equation, respectively (Table 3 and S.2). Table S.3 compares the maximum adsorption capacity q_m of Hg(II) ions for the studied adsorbents to other adsorbents. It shows that the studied adsorbents have higher and better adsorption capacity than most other materials.

3.4. Sorption energy

The experimental data of Hg(II) removal showed that the Langmuir and R-P isotherms fitted well for MGO-NH-SH, Fe₃O₄@SiO-NH-SH, Fe₃O₄@SiO-NH₂, and MGO-NH₂ nanoadsorbents, but it was not possible to determine the sorption type, either physical or chemical. Therefore, the D-R isotherm model was carried out to calculate the sorption energy and type. With respect to the regression equation (Table 3 and S.2, Fig. 11 and S.6), the free sorption energies (E) of the D-R isotherm model were between 0.24 and 3.80 kJ/mol for all synthesized nanoadsorbents. The mean free energy of sorption gives information about the sorption mechanism. When one mole of ions is transferred, the value of E between 1 and 8 kJ/mol shows physisorption sorption, while its value between 8 and 16 kJ/mol indicates that the adsorption process is chemisorption. If E > 16 kJ/mol, the sorption is dominated by intra-particle diffusion sorption. Therefore, the obtained results of values of the free sorption energy for all synthesized nanoadsorbents confirm that the sorption mechanisms are physical for both adsorbents.

Table 3. Adsorption isotherm parameters for Hg(II) adsorption on MGO-NH-SH and Fe₃O₄@SiO-NH-SH

Isotherm type	MGO-SH	Fe ₃ O ₄ @SiO-NH-SH
Langmuir		
q_m (mg/g)	208.78	176.80
b (l/mg)	3.71	4.25
R^2	0.985	0.996
Freundlich		
K_f	137.60	116.78
n	5.84	5.48
R^2	0.90	0.93
Redlich–Peterson (R–P)		
K_{RP}	1.67	3.44
α	1.12	1.04
R^2	0.996	0.998
Dubinin–Radushkevich (D–R)		
q_m (mg/g)	167.35	197.82
β	0.035	0.048
E	3.80	3.24
R^2	0.9902	0.9955

Fig. 11. The equilibrium isotherm trends for Hg(II) adsorption on MGO-NH-SH and Fe₃O₄@SiO-NH-SH.

3.5. Adsorption kinetics

In wastewater treatment, adsorption kinetic of an adsorption process is vital and necessary, as it enables critical information on the reaction pathways and solute uptake rate. The results of kinetic models of MGO-NH-SH and Fe₃O₄@SiO-NH-SH are listed in Table 4 and GO, Fe₃O₄, Fe₃O₄@SiO-NH₂, and MGO-NH₂ are listed in Table S.4. the plots of the pseudo-first-order and pseudo-second-order are shown in SI (Figs. S.7 and S.8). The values of R^2 by the pseudo-second-order adsorption model are higher (> 0.99 for all synthesized adsorbents) and the calculated adsorption capacities by the pseudo-second-order adsorption model are also closer to those

determined by experiments than are those of the pseudo-first-order adsorption model. These clearly indicate the pseudo-second-order adsorption model is a better fit model for both adsorbents. As Table 4 shows, the pseudo-second-order constants (k_2) fall from 0.004 to 0.0005 g/mg/min for MGO-NH-SH and 0.003 to 0.0008 g/mg/min for Fe₃O₄-SiO₂-NH-SH. This demonstrates that the available active sites on both adsorbents are saturated quickly by Hg(II) ions, additionally indicating the possibility of a monolayer uniform adsorption of Hg(II) by the adsorbents [68,69].

Table 4. Kinetic adsorption parameters obtained using pseudo-first-order and pseudo-second-order models

Adsorbent	Metal concs. (mg/l)	$q_e \text{ exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
			k_1 (g/mg/min)	qe_1 (mg/g)	R^2	k_2 (g/mg/min)	qe_2 (mg/g)	R^2
MGO-NH-SH	10	51.82	0.023	15.79	0.794	0.0043	52.91	0.999
	20	101.61	0.028	29.31	0.805	0.0025	104.16	0.999
	25	124.88	0.0439	52.00	0.614	0.0018	128.20	0.999
	30	148.54	0.0384	52.42	0.772	0.0015	153.84	0.999
	35	170.38	0.038	51.60	0.715	0.0012	175.43	0.9993
	45	199.31	0.035	86.33	0.899	0.0010	204.08	0.9998
	50	206.27	0.036	80.94	0.832	0.0008	217.39	0.9988
	60	213.81	0.027	50.74	0.807	0.0005	217.39	0.9999
Fe ₃ O ₄ -SiO ₂ -NH-SH	10	55.16	0.016	18.45	0.585	0.003	55.24	0.9959
	20	101.81	0.035	39.90	0.868	0.002	104.16	0.9997
	30	144.20	0.059	43.56	0.841	0.005	144.92	1
	40	183.83	0.027	73.34	0.905	0.001	188.67	0.9995
	50	195.33	0.025	91.74	0.824	0.0008	200	0.9974

3.6. Adsorption thermodynamics

In the adsorption process, temperature plays an important and essential role. The thermodynamic parameters (ΔG° , ΔS° , and ΔH°) are used to obtain information about the energy changes related to the adsorption process, and, generally, to explain whether the adsorption process on adsorbents is endothermic or exothermic and spontaneous [2,70]. The thermodynamic

parameters calculated for the adsorption process on studied nanoadsorbents at different temperatures are listed in Table 5. The plots of $\ln K_d$ versus $1/T$ for Hg(II) adsorption on studied nanoadsorbents are shown in Fig. S.9 in SI. As shown in Table 5, the values of ΔG° are negative for both nanoadsorbents at different temperatures, suggesting the spontaneous nature of the process. Albeit, with MGO-NH-SH, the ΔG° values decrease with the increase of temperature, indicating more efficient adsorption at higher temperature, but with $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$, the ΔG° values increase with the increase in temperature, indicating more efficient adsorption at lower temperature. In addition, to understand whether the adsorption of Hg(II) on studied nanoadsorbents is chemisorption or physisorption, the value of ΔG° occurs in the range of -20–0 *KJ/mol* for physisorption, -20–80 *KJ/mol* for physisorption and chemisorption together, and -80–400 *KJ/mol* for chemisorption [51]. On this basis, the calculated ΔG° values for both studied nanoadsorbents suggest that interactions between Hg(II) and nanoadsorbents can be reflected as physisorption mechanisms.

The obtained positive ΔH° demonstrates the endothermic nature of the adsorption mechanism, which was also confirmed by the increase in the sorption of Hg(II) onto MGO-NH-SH with increasing temperature. The value ΔS° of Hg(II) adsorption onto MGO-NH-SH is also positive, suggesting that the adsorption process is spontaneous with high affinity and suggests increased randomness at the solid-solution interface during the adsorption process. This also supports that there are some structural changes in both the adsorbate and adsorbent [38]. As Table 4 shows, the obtained ΔH° and ΔS° of Hg(II) adsorption onto $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ are negative, which suggests the sorption of Hg(II) on adsorbent is an exothermic process in nature and that there is a tendency to decreased disorder at the solid-solution interface during the adsorption process. Besides, the negative value of ΔS° indicates that no ion replacement reactions occurred, for the

reason that the increasing entropy of the system could have happened due to escape of the ion from the adsorbent surface to the solution [51,71].

Table 5. Thermodynamic parameters of Hg(II) adsorption on MGO-NH-SH and Fe₃O₄@SiO₂-NH-SH at different temperatures (in K)

Nanoadsorbents	ΔH° (KJ/mol)	ΔS° (KJ/mol/K)	ΔG° (KJ/mol)				R^2
			288 K	298 K	308 K	318 K	
MGO-NH-SH	22.84	0.09	- 5.85	- 6.85	- 7.85	- 8.84	0.87
Fe ₃ O ₄ @SiO-NH-SH	-25.84	-0.06T	- 7.05	- 6.44	- 5.77	- 5.13	0.95

3.7. Desorption studies

The stability and regeneration of the adsorbents are crucial in improving the economics of the wastewater treatment process. During the desorption process, three factor types, concentrations, and volumes of acid became optimized, and the obtained results are described in Supplementary Information (Figs. S.4 and S.5). As shown in Figs. 2, 7, and 12, the prepared adsorbents are stable in the several adsorption and desorption cycles. The results of FTIR and SEM in Figs. 2 (A(f) and B(e)) and 7 (d and h) show that chemical structure and morphology of both nanoadsorbents are a low considerable changes after desorption by acidic solution. The nanoadsorbents can be easily separated by a commercial magnet before and after adsorption-desorption as shown in the inset of Fig. 12; these results indicate that the prepared adsorbents could be an ideal heavy metal adsorbent, saving either more time or economic costs. The desorption capacity for MGO-NH-SH (HCl, 0.8 M) and Fe₃O₄@SiO-NH-SH (HNO₃, 2 M) were over 90% after six and three successive adsorption-desorption cycles, respectively (Fig. 12). Additionally, the Hg(II) adsorption capacity was calculated at over 93% for both nanoadsorbents after the adsorption-desorption cycles. The lower efficiency of Fe₃O₄@SiO-NH-SH in adsorption-desorption cycles can be caused by the destruction of thiol groups with HNO₃, which

is a strong oxidizing acid [33]. Therefore, the results suggest that the MGO-NH-SH composite is more stable and has better regeneration potential than the $\text{Fe}_3\text{O}_4@\text{SiO}-\text{NH-SH}$ composite.

Fig. 12. The adsorption-desorption cycles of Hg(II) on MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO}-\text{NH-SH}$, and magnetic properties of nanoadsorbents (A) before and (B) after adsorption-desorption

3.8. Mixed system study and petrochemical wastewater treatment

The selectivity of adsorbents is a crucial issue when sorbent is used for a real wastewater treatment. Hence, the selectivity of adsorbents was investigated using a mixed system of different metals (including; Hg(II) , Cd(II) , Cu(II) , Zn(II) , pb(II) , Ni(II) , Co(II) , Ca(II) , Mg(II) , K(I) , and Na(I)), that sorption conditions were the same as previous steps. In Fig. 13, It can be revealed that removal efficiency (%) of Hg(II) for both studied nanoadsorbents was significant

higher than that of other metals. This result proves that the significant removal of Hg(II) may be attributed to the chemical interactions between Hg(II) and thiol functional group on synthesized nanoadsorbents. On the other hand, by comparing the synthesized nanoadsorbents in this study, it can be mentioned that MGO-NH-SH shows higher selectivity than $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ (according to Fig. 13).

In order to application evaluation of the prepared nanoadsorbents for Hg(II) removal from real wastewater, some batch experiments were conducted on petrochemical wastewater. The concentration and removal efficiency (%) of metal ions in petrochemical wastewater before and after adsorption by using MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ adsorbents are presented in Table 6. As the results show, petrochemical wastewater contains a high concentration of different metal ions, especially of calcium, magnesium, and potassium, which can interfere with adsorption of Hg(II) on the nanoadsorbents. As the Fig. 13 shows, the MGO-NH-SH is a good sorbent with high ability for adsorption of Hg(II) (removal efficiency; 90.6%) from petrochemical wastewater in comparison with $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ (removal efficiency; 51%). In totally, in the light of these results, it could be concluded that the MGO-NH-SH sorbent was found to be suitable efficient for the removal of mercury (II) ions from real wastewater.

Fig. 13. Removal of Hg ions from petrochemical wastewater with different adsorbents. Adsorbent dose 20 mg, pH = 7, and room temperature.

Table 6: concentration and removal efficiency (%) of metal ions in petrochemical wastewater before and after adsorption with Synthesized nanoadsorbents.

Characteristics	A (mg/l)	B (mg/l)	C (%)	D (mg/l)	E (%)
Ca	154.46	149.06	3.50	151.57	1.87
Cd	5.23	5.22	0.29	5.22	0.29
Co	0.00	0.00	0.00	0.00	0.00
Cu	0.21	0.13	39.91	0.11	50.70
Hg	0.13	0.06	51.00	0.02	83.45
Mg	200.66	189.92	5.35	200.44	0.11
Ni	1.04	0.83	20.25	0.86	17.95
pb	0.27	0.23	14.34	0.17	39.34
Zn	5.12	3.86	24.75	1.74	65.96
K	90.96	89.98	1.08	77.12	15.22

A: Characteristics of petrochemical wastewater, **B:** Concentration of metal in petrochemical wastewater after adsorption with Fe₃O₄@SiO-NH-SH, **C:** Removal efficiency (%) of metal in petrochemical wastewater after adsorption with Fe₃O₄@SiO-NH-SH, **D:** Concentration of metal in petrochemical wastewater after adsorption with MGO-NH-SH, **E:** Removal efficiency (%) of metal in petrochemical

3.9. Economic and environmental evaluations

In addition to absorption capacity, economic and environmental factors are effective and vital parameters in selecting a good adsorbent. For this purpose, in the present study, economic and environmental parameters were investigated for the studied nanoadsorbents. The results of this

evaluation reflect the economic and environmental costs of the current production, which has been demonstrated in the laboratory, i.e, the technology and manufacturing readiness levels are rather low. It has been shown that scaling up production can reduce environmental impacts (and potentially economic costs) by up to 94% in the case of carbon nanotubes [72]. As mentioned, economic evaluation is one of the most important issues for comparing the industrial application of adsorbent materials; nevertheless, it is hardly ever reported in the literature. The availability, required processing, cost of materials and reuse of the adsorbent material are vital parameters for economic evaluation [73,74]. As shown in Table S.1, the total cost for the production of MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ for 1 kg Hg(II) removal is calculated to be about 32000 and 40000 USD, respectively. The results support that MGO-NH-SH has a lower cost of production than $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ for 1 kg Hg(II) removal.

Carbon footprint is the overall amount of greenhouse gas emissions, calculated in units of carbon dioxide, and is one of the most important sustainability indices for measuring the environmental impacts of different products. The results of the calculated carbon footprint of MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ in both the production and use stages are presented in Table 7. The total GHG emission, calculated by adding the production and use stages, is 6473.11 and 10431.26 kg $\text{CO}_{2\text{eq}}$ per 1 kg Hg(II) removal from polluted water for MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$, respectively. On the other hand, as the results in Table 7 show, electricity, used more for cooling and heating, and ethanol, used for washing, in the production of adsorbents played significant roles in the amount of greenhouse gas emissions. Hence, the recovery of ethanol and use of green electricity or sustainable energy can decrease by about 90% the greenhouse gas emissions in the production stage of both nanoadsorbents. As well, the use of replacement material such as bioethanol or if possible water instead of chemical ethanol can have an effect on greenhouse gas

emissions. As the results in Table S.1 show, even though electricity consumption only slightly affects the cost of production and the use of both studied nanoadsorbents, it significantly affects the environmental impact. The results of economic and environmental evaluations have proven that MGO-NH-SH is more efficient in removing Hg from polluted water than is $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$.

Table 7. Results of carbon footprint evaluations of MGO-NH-SH and Fe₃O₄@SiO-NH-SH for 1 kg Hg removal

Production stage	Unit	GWP MGO-NH-SH (kg CO _{2eq} per 1 kg Hg removal)		GWP Fe ₃ O ₄ @SiO-NH-SH (kg CO _{2eq} per 1 kg Hg removal)	
		kg	%	kg	%
Graphite	kg	0.02	0.0003	-	-
Sodium nitrate	kg	0.65	0.010	-	-
Potassium permanganate	kg	1.70	0.027	-	-
Sulfuric acid	L	1.50	0.024	-	-
Hydrochloric acid	L	0.73	0.012	-	-
Hydrogen peroxide	L	3.78	0.060	-	-
DCC	kg	0.51	0.008	0.63	0.01
NHS	kg	0.31	0.005	0.38	0.004
Acetylcysteine	kg	0.19	0.003	0.45	0.004
Iron(II) chloride	kg	0.10	0.002	0.09	0.001
Iron (III) chloride	kg	1.19	0.019	0.87	0.01
TEOS	L	-	-	18.54	0.18
APTMS	L	-	-	6.72	0.07
Toluene	L	-	-	340.54	3.39
Ethanol	L	1367.06	21.849	1830.84	18.22
Ethylenediamine	L	9.28	0.148	-	-
Methanol	L	67.82	1.084	164.38	1.64
Ammonia	L	70.90	1.133	18.07	0.18
Dichloromethane	L	693.28	11.080	-	-
Water	L	3.98	0.064	0.48	0.005
Electricity	kWh	4033.86	64.471	7665.84	76.29
Total GHG emission	kg CO _{2eq}	6256.86	0.0003	10047.83	

Use stage	Unit	GWP MGO-NH-SH (kg CO _{2eq} per 1 kg Hg removal)		GWP Fe ₃ O ₄ @SiO ₂ -NH-SH (kg CO _{2eq} per 1 kg Hg removal)	
		kg	%	kg	%
Hydrochloric acid	L	1.06	0.48	-	-
Nitric acid	L	-	-	120.23	31.36
Water	L	0.33	0.15	0.35	0.09
Electricity	kWh	220.86	99.38	262.84	68.55
Total GHG emission	kg CO _{2eq}	222.25		383.43	
Total GHG emission (production + use stage)	kg CO _{2eq}	6473.11		10431.26	

4. Conclusions

Adsorption processes play a crucial role in water and wastewater treatment technologies. Thiol-functionalized MGO and Fe₃O₄ were successfully synthesized for the removal of mercury ions from aqueous solution. The prepared nanoadsorbents were successfully characterized and

confirmed by FTIR, XRD, TGA, FE-SEM, VSM, AFM, Raman, and elemental analysis. The adsorption of Hg(II) by thiol-functionalized MGO and Fe₃O₄ fits well with the Langmuir isotherm model and follows the pseudo-second-order kinetics. The maximum adsorption capacities of MGO-NH-SH and Fe₃O₄@SiO-NH-SH for Hg(II) removal were attained at 208.8 and 176.8 mg/g, respectively. The nanoadsorbents, in addition to their adsorption capacity, were examined from the points of view of reuse and regeneration, economic costs, and environmental impact (carbon footprint). The results showed that under optimal conditions, Hg(II) removal from real wastewater and polluted water by MGO-NH-SH displayed higher adsorption capacity, reuse, and regeneration, and as well lower cost and greenhouse gas emissions compared to Fe₃O₄@SiO-NH-SH. In total, The findings of the present study highlight that MGO-NH-SH as a promising adsorbent is more economically and environmentally friendly than Fe₃O₄@SiO-NH-SH in the efficient removal of Hg(II) from real wastewater and polluted water. However, it can be understood that there is no clear “winner” in the sense that both nanoadsorbent productions for Hg(II) removal can be best carried out from the points of view of reuse and regeneration, economic costs, and the environmental impact.

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