

# Silica–Gold Nanocomposite for Removal of Organophosphorous Pesticides

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**Abstract** Mesoporous silica nanoparticles–gold nanoparticles (MSNPs/AuNPs) nanocomposite was prepared using mono-dispersed mesoporous silica as a template for gold nanoparticles without any functional group on the silica surface. The growth of gold layer over the surface of mesoporous silica nanoparticles (MSNPs) was demonstrated via scanning electron microscopies (SEM), Fourier transform infrared (FTIR) spectra, high-resolution transmission electron microscopy (HRTEM), and ultraviolet-visible (UV) adsorption spectrum. The presence of gold on the mesoporous nanoparticles gave an absorption band at 520 nm, also X-ray diffraction (XRD) indicated the crystal structure of gold NPs which has a cubic shape. Raman spectra proofed the high ability of MSNPs/AuNPs nanocomposite for removing methacrifos from water which was also confirmed by using high-performance liquid chromatography (HPLC) at room temperature where the removal rate exceeded 98 %. MSNPs/AuNPs nanocomposite has high capacity as an adsorbent which could be considered as a new eco-friendly strategy for pesticide removal and appears to be the new promising material in water treatment application.

**Keywords** Nanocomposite · Mesoporous silica · Gold NPs · Adsorption · Methacrifos

## Introduction

Development of new metal nanoparticles has become a demanding task in different fields of research owing to their controlled and unique properties, which are very different from the behavior of the respective size material [1–4]. Gold nanoparticles (AuNPs) have attracted great attention because of their bio-sensing electronic, catalytic, photo-chemical pesticide removal, bio-medical, and surface-enhanced Raman scattering (SERS) properties [5]. Combining the properties of AuNPs with mesoporous silica nanoparticles (MSNPs) materials leads to the formation of advanced nanocomposite with superior adsorption capacity, since the MSNPs have high Brunner–Emmett–Teller (BET) specific surface area [6]. They are also considered as organophilic solids due to their ability to absorb significant quantities of organic molecules in gas phase, such as n-hexane, benzene, toluene, as well as various alcohols [7, 8]. MSNPs/AuNPs nanocomposite has rapid development in bio-medical fields such as the drug releasing, the cancer treating, biological sensor, imaging, and also in removal pesticide.

Pesticides are considered as an environmental pollution. Organophosphorous pesticide is one of the classes which are actually more widely used in the world [9], which affect the nervous system of insects and humans [10]. These chemical agents inhibit the activity of the enzyme cholinesterase (ChE), responsible for the nervous impulse in organisms [11]. Thus, it is important to prevent the increase of these compounds into the environment. Several methods are applied for removing organophosphorous pesticides from water including membrane technology (microfiltration, ultra filtration, nanofiltration and reverse osmosis), solid phase extraction, ozone and chemical oxidation, Fenton, photocatalysis, and adsorption on various substances such as activated carbon [12–16], but in some instances, the need of high energy, high

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costs of regeneration and the need to renew the adsorbent and decomposition of pesticides result in transformation products that are more toxic and are the disadvantages of these methods since they represent a greater risk to the environment than the parent molecule [17, 18]. Among the different techniques for the removal of organophosphorous pesticides, the adsorption process by using solid adsorbents has many advantages over the other methods due to its simple design, ease of using, low cost, and ability for recycling. Our focus is to develop adsorbent materials with high efficiency and economic feasibility to remove these pollutants to be able to improve the water quality.

In this study, we report a new method for the production of silica–gold nanoparticles for the removal of methacrifos (methyl (E)-3-dimethoxyphosphinothioxyloxy-2-methylprop-2-enoate) pesticides selected as a model organophosphorous pollutant. AuNPs have rapid detection of organophosphorous pesticides up to 0.5 ppm. MSNPs/AuNPs nanocomposite has high capacity as an adsorbent which resulted in rapid detection of methacrifos up to 0.5 ppm which presents a new biocompatible and eco-friendly strategy for pesticide removal and appears to be a new promising material in water treatment application and fast, non-toxic, and single-step method. MSNPs/AuNPs nanocomposite has high ability for the removal of organophosphorous pesticides up to 90 % which was indicated using high-performance liquid chromatography (HPLC) chromatogram.

## Materials

TEOS (Tetra ortho silicates ( $\geq 99.9$  % Sigma-Aldrich)), CTAB cetyltrimethylammonium bromide ( $\geq 98$  % Sigma-Aldrich), HAuCl<sub>4</sub> gold chloride ( $\geq 99.9$  % Sigma-Aldrich), and ascorbic acid used were from Sigma-Aldrich; NH<sub>4</sub>OH ammonia solution 32 % was from Sigma-Aldrich, ethanol absolute used was from Adwic, and standard pesticides such as methacrifos used were from Sigma-Aldrich.

## Experimental

### Preparation of MSNPs

The MSNPs were prepared by using CTAB surfactant as the structure-directing agent. Twenty-four milliliters of deionized water (DIW), 9.6 g of 0.5 M NaOH, and 1.0 g of CTAB were added in 100-ml beaker under vigorous stirring at room temperature. Two milliliters of TEOS as the silicon source was dropwise added and stirred continuously for 8 h. The product material was filtered off, washed for three times with DIW and ethanol, and then dried overnight at 60 °C. In order to remove CTAB, the final products were calcined at 550 °C for 5 h [19].

### Synthesis of Mesoporous Silica-AuNPs nanocomposite

0.5 g of the prepared mesoporous silica materials was mixed with 50 ml of deionized and stirred vigorously at room temperature for 1 h. Ten microliters of gold chloride was added until white MSNPs particles showed a golden color during stirring; 50 ml of (1 mmol) ascorbic acid was added for reducing gold on the surface of MSNPs particles where the color of the solution changed into wine red. After stirring for 2 h, the solution was filtrated and washed with deionized water for three times. The mixture was dried overnight at 200 °C for 3 h.

### Instrumentation

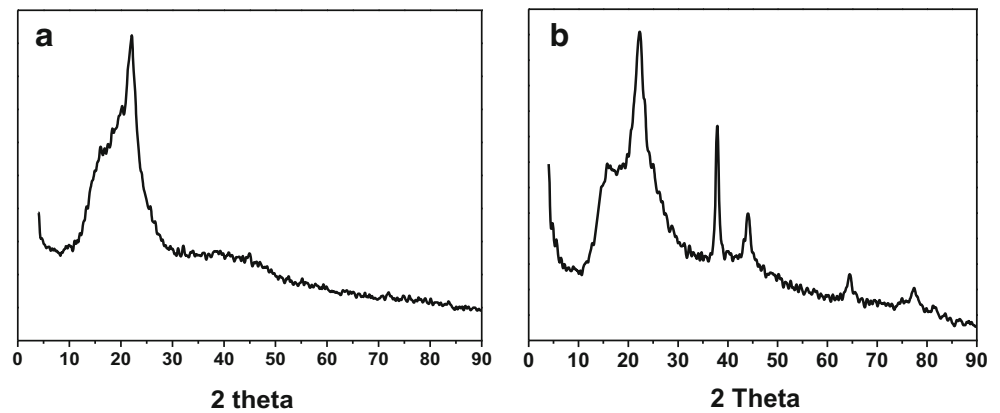
The crystal structure, and morphologies of silica NPs and MSNPs/AuNPs nanocomposite were characterized by high-resolution transmission electron microscopy (HRTEM) analysis using JEOL 2000 operated at high voltage 120 kV.

X-ray diffraction (XRD) analysis of test samples was performed with a Philips (The Netherlands) diffractometer (Model PW 2103,  $\lambda = 1.5418$  Å, 35 kV, and 20 mA) with a source of Cu K $\alpha$  radiation (Ni filtered). The diffraction patterns were recorded in the range of the diffraction angle  $2\theta$  from 10° to 90° with a step of 0.06°. Fourier transform infrared (FTIR) spectra of MSNPs/Fe<sub>3</sub>O<sub>4</sub> were measured using a Nicolet™ iS™10 FTIR spectrometer in the wave number range 400–4000 cm<sup>-1</sup>. The samples have been mixed with KBr under a vacuum and at pressure of 1.88 t/cm<sup>2</sup>. Nitrogen adsorption was recorded for mesoporous silica using a model NOVA 3200 automated gas sorption system (Quantachrome, USA). Ultraviolet-visible (UV-VIS) spectroscopy double beam PC scanning spectrophotometer UV Evolution 300 from Labomed a computer data system is the UV Win 5 software v 5.0.5 used for measuring the wavelength and absorbance. Spectrophotometer range 200–900 nm using 1-cm matched Stoppard quartz cells was used for following the pesticide removal. HPLC samples were analyzed using Agilent 1100 HPLC system fitted with a diode array detector and an autosampler. Raman spectra were recorded with a Bruker Senterra Raman microscope (Bruker Optics Inc., Germany) with 785-nm excitation, 1200 rulings per millimeter holographic grating, and a charge-coupled device (CCD) detector. The acquisition time was 3 s with the power of 50 mW.

**Table 1** Comparison between the BET surface area for mesoporous silica and MSNPs/AuNPs nanocomposite

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{P}}$ (cm <sup>3</sup> /g)	$R$ (Å)
Mesoporous silica	818	0.7	33
Au/MSNPs	402	0.9	29

**Fig. 1** (a) XRD of mesoporous silica and (b) XRD of (MSNPs/AuNPs) nanocomposite



## Results and Discussion

### Characterizations of MSNPs/AuNPs Nanocomposite

The structural properties and morphology of MSNPs/AuNPs nanocomposite were characterized using different tools:

- $N_2$  adsorption of MSNPs/AuNPs nanocomposite

The synthesis of MSNPs/AuNPs nanocomposite is based on deposition of Au onto MSNPs. Loading of Au molecules onto the surface of mesoporous silica results in decreasing the BET surface area to become  $412 \text{ m}^2/\text{g}$  as showed in Table 1.

- X-ray diffraction

The powder XRD patterns (Fig. 1) were used to study the structural properties of the synthesized MSNPs/AuNPs nanocomposite, as shown in Fig. 1a; one intense diffraction peak at  $2\theta = 22$  is found, which corresponds to 100 indicating the formation of ordered mesostructure. The XRD pattern of gold nanoparticles showed in Fig. 1b which demonstrated characteristic reflections of face-centered cubic (fcc) gold planes.

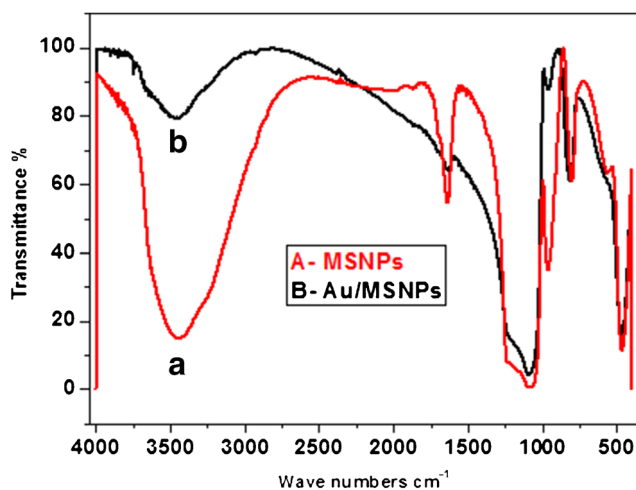
The diffraction features appearing  $2\theta = 38.20^\circ$ ,  $44.41^\circ$ ,  $64.54^\circ$ , and  $77.48^\circ$  corresponds to the (111), (200), (220), and (311), respectively. Therefore, the XRD result indicates gold nanoparticles with a cubic shape.

The XRD pattern suggests the formation of crystalline AuNPs with fcc structure. Broadening of XRD peaks clearly indicates that the samples are nanocrystalline in nature.

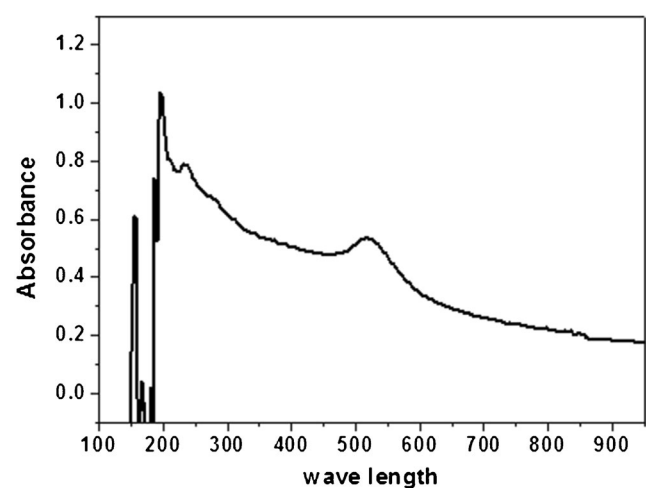
- Fourier transform infrared (FTIR) spectra

FTIR spectrum of MSNPs and MSNPs/AuNPs nanocomposite shown in Fig. 2 indicates that the Au molecules were deposited onto silica NPs, from Fig. 2(A). The broad peak at  $1081.85 \text{ cm}^{-1}$  can be assigned to Si–O–Si bond, and the peak at  $976.05 \text{ cm}^{-1}$  can be attributed to Si–OH bond. Also, broad peak at  $3269.12 \text{ cm}^{-1}$  can be assigned to NH bond. In the spectrum of the MSNPs/AuNPs nanocomposite, the intensity of Si–O–Si and Si–OH peaks has been reduced significantly. This indicates the presence of AuNPs in silica particle as shown in Fig. 2(B).

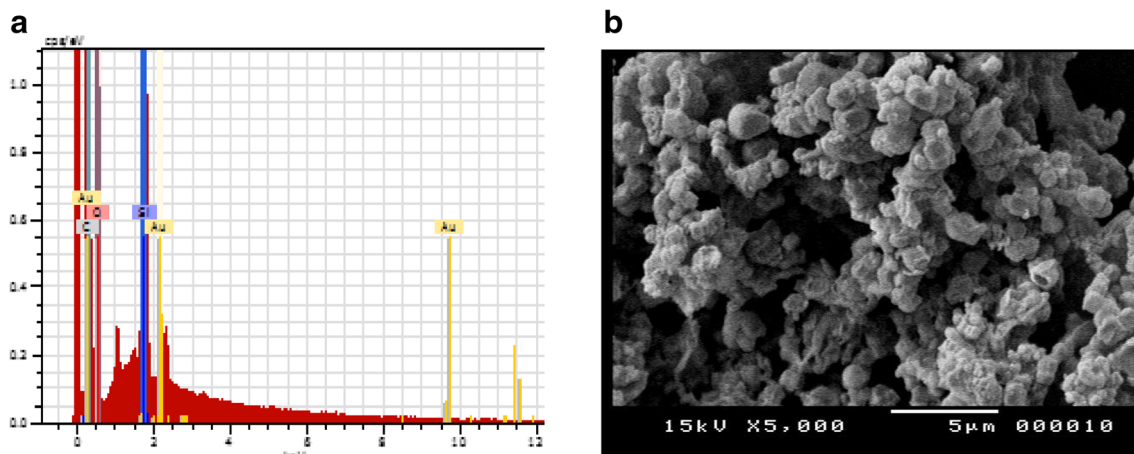
- UV-VIS spectroscopy



**Fig. 2** FTIR spectra of (a) MSNPs and (b) MSNPs/AuNPs nanocomposite



**Fig. 3** UV-vis spectrum of MSNPs/AuNPs nanocomposite



**Fig. 4** (a) EDX of MSNPs/AuNPs nanocomposite and (b) SEM of MSNPs/AuNPs nanocomposite

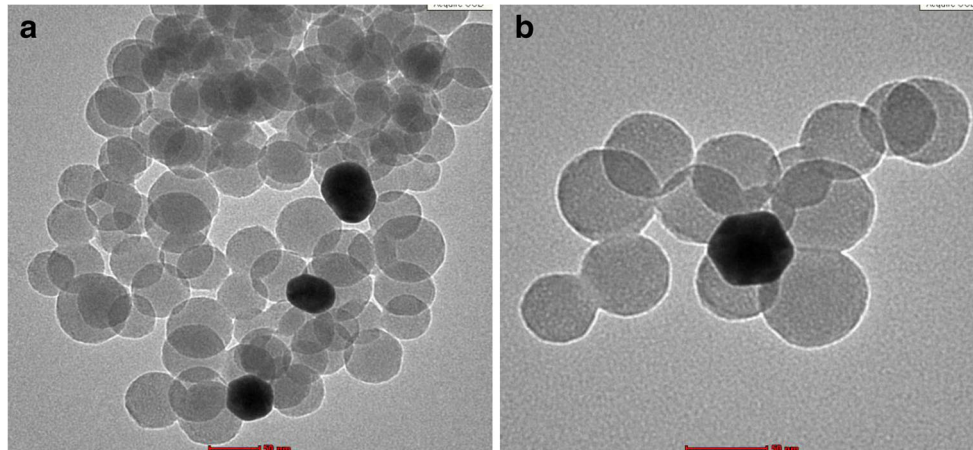
AuNPs were found to be attached to mesoporous silica. It could be observed that the originally white particles of silica turned into wine red color. Optical absorption was recorded using UV-VIS spectroscopy. Optical absorption of MSNPs/AuNPs nanocomposite was found at 520 nm as shown in Fig. 3.

- Scanning electron microscope (SEM) and energy diffusive X-ray (EDX) of MSNPs/AuNPs nanocomposites

EDX spectrum recorded a strong signal for the silica and gold atoms as shown in Fig. 4a. The elemental analysis measurements show that the MSNPs/AuNPs nanocomposite composed of metallic Au and Si and some other contaminants is also present. SEM images of MSNPs/AuNPs refer to the aggregation of the gold nanoparticles, and small grains are present at the surface of the silica as shown in Fig. 4b.

- High-resolution transmission electron microscopy (HRTEM)

**Fig. 5** (a, b) HRTEM of MSNPs/AuNPs nanocomposite

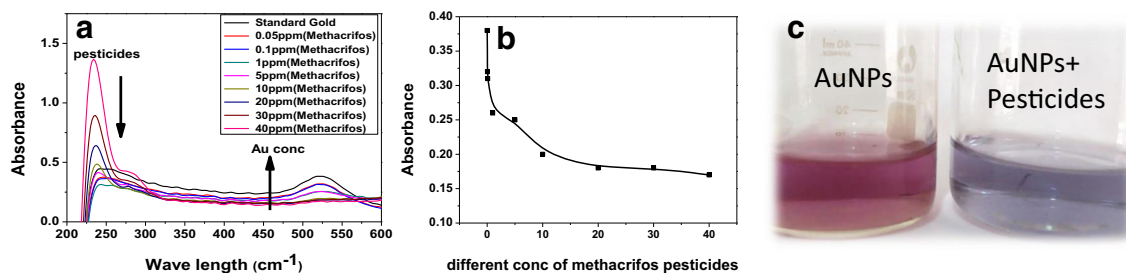


HRTEM images of AuNPs/MSNPs nanocomposite (Fig. 5) showed a cubic shape of gold nanoparticles, and it is clearly seen that gold nanoparticles have been attached to the surface of silica.

#### Removal Organophosphorous Pesticides Using MSNPs/AuNPs Nanocomposite

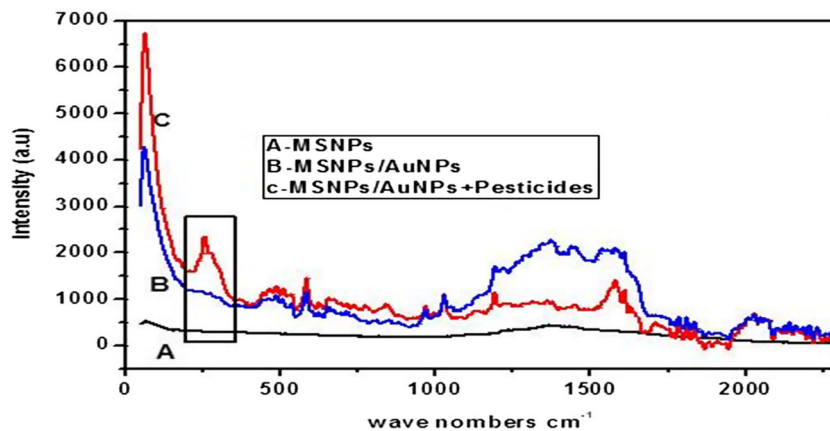
Continues monitoring of the pesticides represents an environmental challenge due to the stability and long resistance time in the environment, therefore, developing simple, ease of using, and low cost with high ability for recycling adsorption process by using solid adsorbents.

Our first attempt is to study the ability of gold nanoparticles to detect and remove methacrifos. AuNPs were mixed with various concentrations of pesticide (40–0.05 ppm). A change in the color of the mixture of AuNPs and methacrifos was observed. Changing the color was highly dependent on methacrifos concentration. The high concentration (40 ppm) of methacrifos changed its color dramatically from red to blue as seen in Fig. 6c,

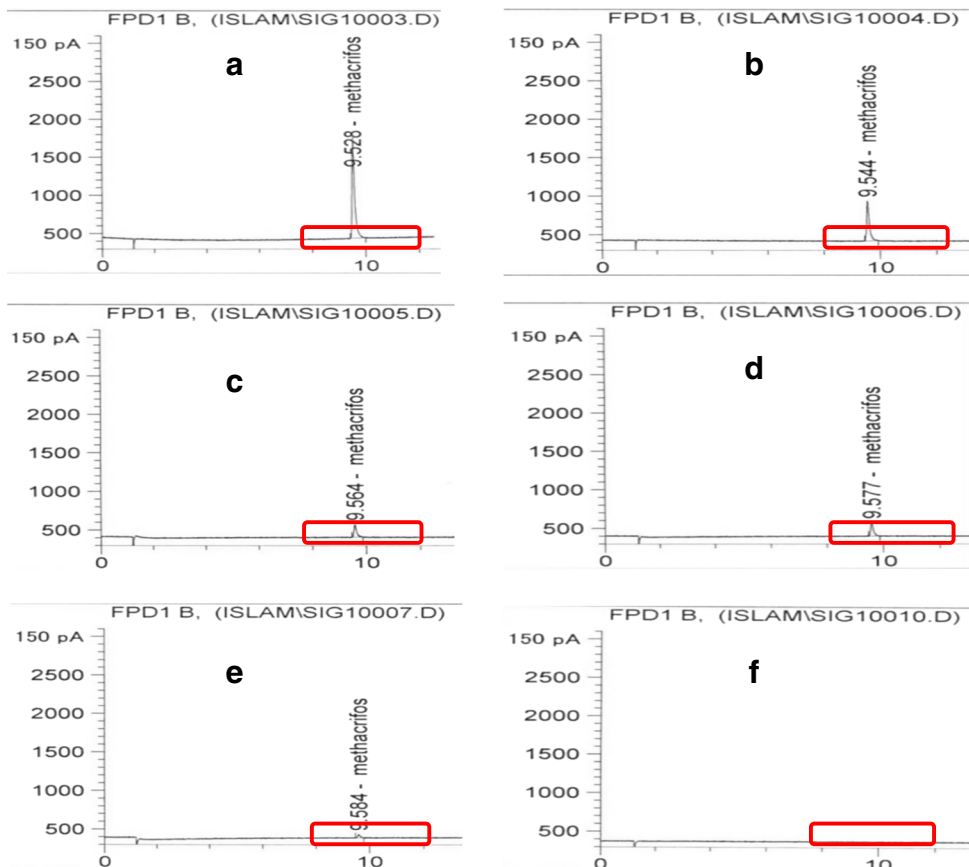


**Fig. 6** (a) UV-vis spectrum of detection methacrifos, (b) Influence of amount sorbent of detection of methacrifos, and (c) optical images for the detection of methacrifos by using AuNPs

**Fig. 7** Raman spectra of (a) MSNPs and (b) MSNPs/AuNPs, and (c) MSNPs/AuNPs treated with methacrifos pesticides



**Fig. 8** chromatogram for solution (a) standard methacrifos (b-e) remaining amount of methacrifos using (20, 30, 40, 50 and 60 mg) of (MSNPs/AuNPs) nanocomposite respectively



which could be attributed to the surface plasmon phenomena [19, 20]. Surface plasmon has the ability to confine (trap) light at a metal/dielectric interface, which either localizes or propagates depending upon the dimensionality of the nanostructured material [21]. The extent of color change of low concentration (0.05 ppm) was much less compared to high concentration. As the pesticide concentration increased, the absorbance at 522 nm decreased as shown in Fig. 6a, b. For larger particles, the light cannot polarize the nanoparticles homogeneously, and as a result, the optical absorption spectra are directly related to the size of the nanoparticles which is known as the extrinsic size effect [22]. The adsorption of methacrifos by using MSNPs/AuNPs nanocomposite as a solid adsorbent was confirmed by the Raman spectra. As shown in Fig. 7, parent MSNPs and AuNPs exhibit Raman peaks at 1360 and 1578  $\text{cm}^{-1}$ , respectively; MSNPs/AuNPs nanocomposite was treated with 10 ppm methacrifos solution, and a new peak at 248  $\text{cm}^{-1}$  is noticed that may be assigned to AuNPs-S interaction, possibly in the form of an AuNPs-S complex [23, 24].

HPLC technique was used to confirm the removal of methacrifos by using MSNPs/AuNPs nanocomposite. HPLC technique showed that methacrifos has one sharp peak at retention time 9.5 min; the results shown in Fig. 8 illustrate that by increasing the amount of nanocomposite (20–60 mg) that are added to methacrifos, there is a marked decrease in the peak area and the integration area percentage, and the decrease in the peak area and height confirms the complete removal of the methacrifos solution due to its binding to gold nanoparticles as presented in Fig. 8f.

The sorbet concentration of methacrifos into sorbents was calculated by the difference in the detector response absorbance before ( $A_i$ ) and after ( $A_t$ ) removal.

$$\text{Removal of Pesticides\%} = \frac{A_i - A_t}{A_i} * 100 \quad (1)$$

Equation (1) indicated that the removal efficiency of the developed solid adsorbent against methacrifos pesticide exceeds 98 %.

## Conclusion

Our study presents new method for the preparation of MSNPs/AuNPs nanocomposite which has high capacity as an adsorbent which could explore a new bio-compatible and eco-friendly strategy for pesticide removal and appears to be a new promising material in water treatment application. Raman spectra and HPLC at room temperature (RT) proofed the ability of MSNPs/AuNPs nanocomposite for removing methacrifos where the removal rate exceeded 98 %.

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