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A highly effective route for removal of Hg^{2+} from the waste water using 3-nitrobenzelidenemalononitrile as a modifier of $Fe_3O_4@SiO_2$ nanoparticles

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Abstract. SiO_2-coated magnetic nanoparticles ($Fe_3O_4@SiO_2$ NPs) were modified by 3-nitrobenzelidenmalononitrile and used as green linkages for removal of Hg^{2+} form the wastewater. In this research, it has been attempted to refer to the harmful effects of mercury ions for living things and how to remove such ions using very easy and practical technique. This study shows that by optimizing the test conditions, the efficiency of the removal of harmful ions such as mercury from the water contaminated with these ions can be increased. Conditions such as temperature, speed of agitation, pH of solution were tested for removal of mercury ions. The advantages of this method over other methods listed in the article are the rapid and easy nanocry synthesis. The generated and modified $Fe_3O_4@SiO_2$ nanoparticles were characterized by X-ray diffraction, fourier transform infrared and scanning electron microscopy spectroscopy. The results show that the synthesized magnetic nanoparticles have the excellent performance for the removal of mercury(II) ion from the waste water.
Keywords: mercury(II) ion removal; modified magnetic nanoparticles; 3-nitrobenzelidenemalononitrile

1. Introduction

In recent years, the diffusion of heavy metal ions is a serious problem for humans and their environment (Qasem *et al*. 2021). This dissemination is mostly due to population development and industrialization of communities and the growing need to use new products and produce more waste. Heavy metal ions such as mercury could be carcinogenic because they are non-biodegradable (Prabhu *et al*. 2018). Therefore, the entry of these ions into the living environment of organisms, even on a very small scale, can create irreparable dangers (Zou *et al*. 2016, Velusamy *et al*. 2021). The solubility of these ions in aqueous solutions causes to have a high potential to penetrate the living environment of organisms and pose risks such as poisoning and cancer (Mitra *et al*. 2022), (see Fig. 1). For example, the solubility of mercuric chloride at 25 °C in water is 69 g/Lit (Leeuwrn *et al*. 2000).

There are many techniques for the treatment of wastewater from the heavy metals such as chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation, and electrochemical treatment (Fu *et al*. 2011), but one of the most effective, interesting, and new ways could be nano-synthetic adsorbents with modified structures via organic compounds.

In recent years, utility advantages of $Fe_3O_4@SiO_2$ nanoparticles such as easy preparing and coating, low cost generation, ability of control on surface modification, absorption on nanoscale diameters and easy separation techniques (Machala *et al*. 2007, Amyn *et al*.2009) have caused to increasing use of them (Ahmad *et al*. 2018). Due to the presence of hydroxyl groups on the surfaces of hydrophobic nanoparticles, it is possible to graft some types of organic or inorganic molecules to modify the surfaces of nanoparticles, which can be used to absorb various types of ions (Manna *et al*. 2012). Direct or indirect linkage of some organic molecules to the surface of nanoparticles can create good and effective biocompatibility for the isolation of biologically active compounds (Pan *et al*. 1010, Ahmad *et al*. 2019). In addition to items that mentioned above, other parameters such as solution pH, nanoparticle size, temperature, duration of material contact on the nanoparticle surface, can affect in the absorption of ions or molecules by nanoparticles (Ahmad *et al*. 2019, Jasrotia *et al*. 2022).

Therefore, in respect to the importance of environmental problems dissolving, we decided to investigate the synthesis of modified $Fe_3O_4@SiO_2$ nanoparticles via 3-nitrobenzel-idenemalononitrile for the removal of Hg^{2+} (Zhang *et al*. 2014). The interesting aspect of this procedure is not only the absence of expensive instrumental techniques such as atomic fluorescence spectrometry, etc. (Hu *et al*. 2013, Leopold *et al*. 2008, Zhang *et al*. 2015), but also the use of nanomagnetic compounds coated with organic compounds containing the cyanide functional group to separate mercury (II) ions (Baby *et al*. 2019).

On the base of the literature survey, the adsorption protocol is one of the cheaper procedures among the remediation methods and a really efficient and advantageous method for removing heavy metal ions (Zou *et al*. 2016, Velusamy *et al*. 2021).

The binding ability of the –C≡N functional group to the metal ions gave us an opportunity to use 3-nitro-benzelidenemalononitrile for the synthesis of modified

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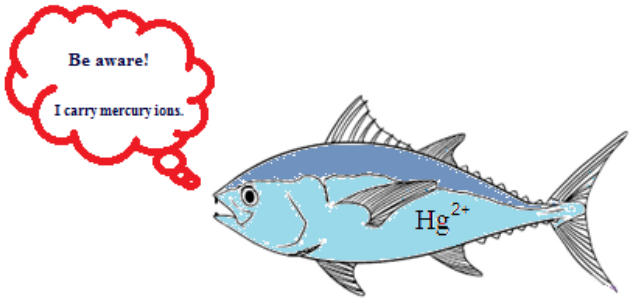

Fig. 1 The entry of heavy metal ions into the life cycle of animals and humans

Fe_3O_4@SiO_2 nanoparticles for the removal of mercury(II) ions from the wastewater (Girgis *et al*. 2015).

One of the main attractions of using Fe_3O_4 nanoparticles in the synthesis of chemical compounds is their separation by an external magnetic field. Therefore, for the first time, we used the same property to separate mercury ions in water. It should be noted, however, that the nanocomposite particles were coated using 3-nitrobenzelidenemalononitrile which had a high ability to bind to the mercury (II) ions (Lee *et al*. 2013, Nookala *et al*. 2015).

2. Experimental

2.1 Material and methods

All chemicals have been purchased from Merck, Sigma Aldrich and Fluka Companies and were used without further purification. The FT-IR spectra were recorded on a TENSOR II Model Bruker spectrometer. Also, the ^{1}H NMR spectrum for the 3-nitrobenzelidenemalononitrile was recorded on a BRUKER DRX-250 AVANCE instrument using $CDCl_3$ as a solvent and TMS as internal standard at 250 MHz. X-ray diffraction (XRD) patterns were recorded by using a XRD PW1730 Philips an X-ray diffractometer using a Cu K_α anode. Scanning electron microscopy (FE-SEM) images were obtained on ZEISS LEO 1430 VP instrument operated at 30 kV accelerating voltage. All the UV- Vis absorption spectra measurements were carried out in the 200-600 nm region using a UV600-Shimadzu UV-vis spectrophotometer with a 10 mm light-path black quartz spectrophotometer cell. The melting point of synthesized 3-nitrobenzelidenemalononitrile was recorded on a Barnstead Electrothermal 9200 apparatus. The stock solution of Hg^{2+} (1.0×10^{-3} M) was prepare by dissolving of $Hg(NO_3)_2$ in deionized water and a series of standard solutions of Hg^{2+} were prepared by stepwise diluting of stock solution.

2.2 Synthesis of 3-nitrobenzelidenemalononitrile

A magnetically stirred solution of 3-nitrobenzaldehyde (2 mmol) in ethanol (5 mL) was added a solution of malononitrile (2 mmol) in (5 mL) over 5 min at room temperature. After the addition of malononitrile, the reaction mixture was stirred for 6 hours at room temperature. The progress of the reaction was monitored by TLC in the solvent combination ethylacetate/*n*-hexane (2:8) as the mobile phase. After the completion of the reaction, the solvent was evaporated and the resulting precipitate was washed with (3×2 mL) of cold diethyl ether. The crude product has been recrystallized from ethanol (5 mL) to afford the pure 3-nitrobenzelidenemalononitrile.

2.3 Synthesis of modified Fe_3O_4@SiO_2 nanoparticles as absorbent of Hg^{2+} ion

A surface modification strategy was used for the successful synthesis of Fe_3O_4@SiO_2 which has shown in Scheme 1 (Zare *et al*. 2020, Qu *et al*. 1999). At the first step, 20 mmol of $FeCl_3.6H_2O$ and 10 mmol of $FeCl_2.4H_2O$ were added to 50 mL of distilled H_2O in a flask at room temperature, then the reaction mixture warms up to 80 °C. After that, the reaction mixture was brought to pH 10 by dropwise addition of NaOH (3 M). All reaction mixture stirred under N_2 atmosphere for 12 h. The black solid phase has been collected by a centrifuge and washed using deionized water. In the next step, 1 g of Fe_3O_4 was added to a mixture of ethanol (50 ml) and deionized water (5 ml), then, 25% ammonia solution (2 mL) was added to the reaction mixture. Then, 2 mL of tetraethyl orthosilicate (TEOS) was added dropwise to the mixture and was allowed to stir for 3 hours at 60 °C. The magnetic material is then collected again and washed with a mixture of water/ethanol (1:1) and then dried at 50 °C. In the last part, to prepare the adsorbent, 1 g of the obtained magnetic cores was added in a mixture of acetone (20 mL) as a solvent and 3-nitrobenzelidenemalononitrile (1 mmol), and then the reaction mixture was stirred for 24 hours at 50 °C. In the final step of absorbent generation, the solvent was removed and the residues were dried at room temperature for 24 hours. (Fig. 2)

3. Results and discussion

A simple well-known Knoevenagel condensation reaction has been used to synthesize of 3-nitro-benzylidenemalononitrile as an absorbent layer on the surface of nanoparticles (Zengin *et al*. 2020, Jadhav *et al*. 2019, Carvalho *et al*. 2018, Marandi *et al*. 2011).

The synthesized stable structure of 3-nitrobenzylidene-malononitrile was deduced from its spectroscopic data such as ^{1}H NMR and IR spectroscopy (see Fig. 3). The FT-IR spectrum of synthesized 3-nitrobenzylidenemalononitrile show a peak at 2213 cm^{-1} for –C≡N group and –NO_2 group shows vibration signals at 1374 and 1449 cm^{-1} and also, ^{1}H NMR spectrum shows that all protons of olefinic and aromatic moieties resonate between 7.71 and 8.45 ppm.

Different analytical techniques have been used for the characterization of Fe_3O_4@SiO_2@3-nitrobenzylidene-malononitrile NPs such as XRD, SEM, and IR.

The FT-IR spectrum of naked Fe_3O_4 shows strong peak at 617 cm^{-1} and it is attributed to the Fe-O band and also, the existence of broad peaks at 3000-3400 cm^{-1} is according to the structure of Fe_3O_4 and indicates the symmetric and asymmetric vibration modes of OH bonds which are linked

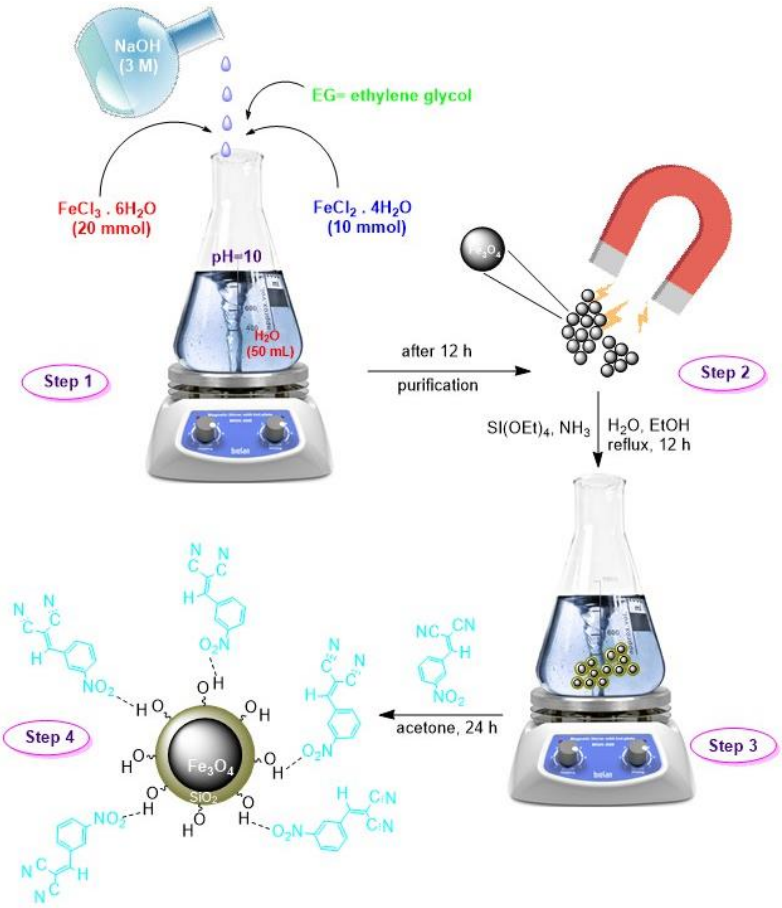

Fig. 2 Synthesis of modified Fe_3O_4@SiO_2 nanoparticles as Hg^{2+} absorbent

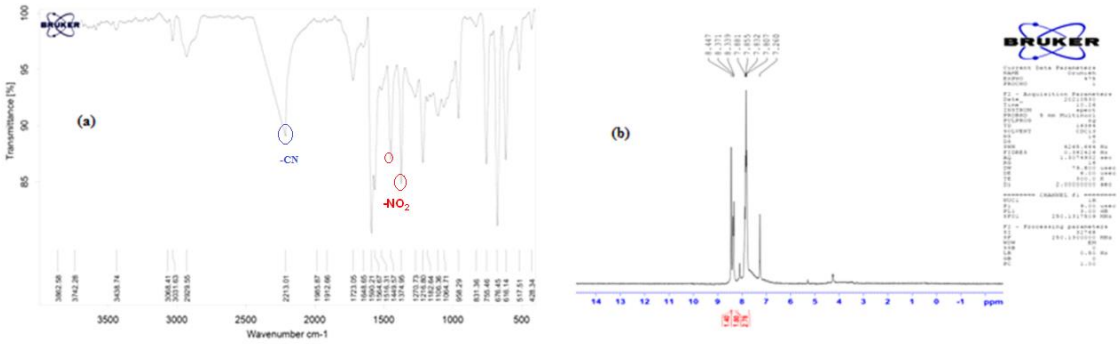

Fig. 3 (a) FT-IR and (b) ^1H NMR spectra of synthesized 3-nitrobenzylidenemalononitrile

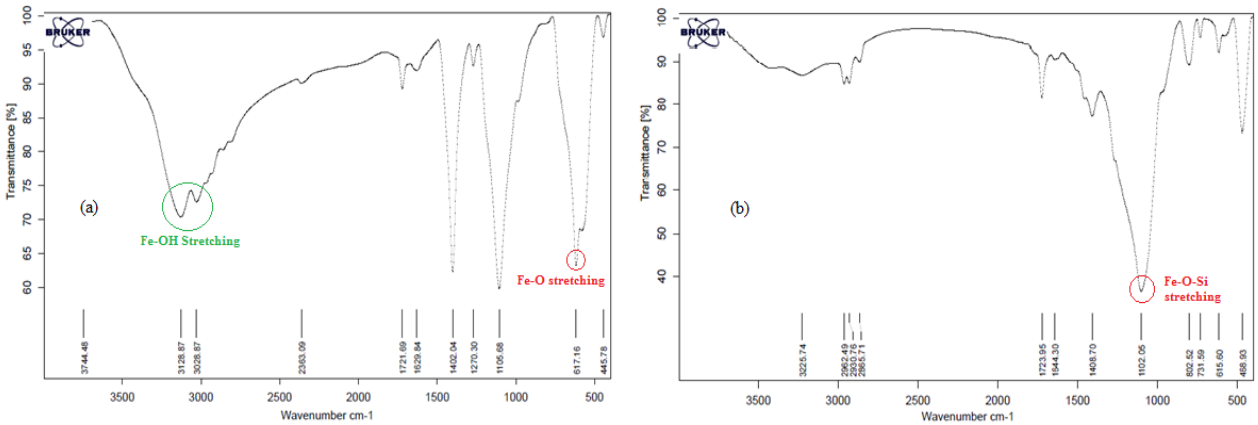

Fig. 4 FT-IR spectra of (a) naked Fe_3O_4 NPs, (b) silica coated Fe_3O_4 NPs

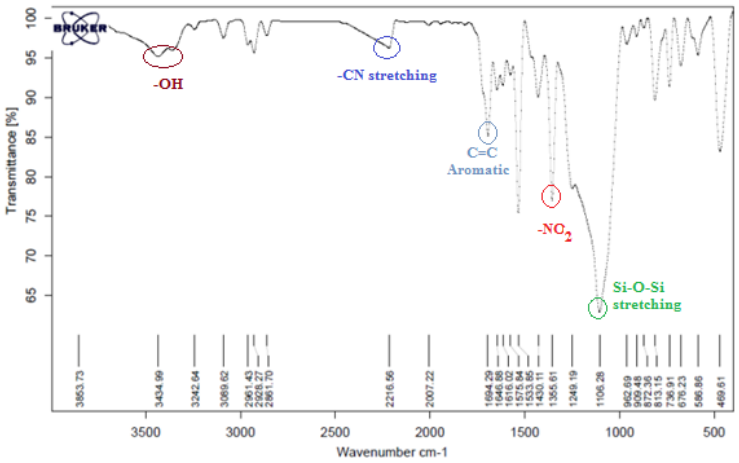

Fig. 5 FT-IR of modified silica coated Fe_3O_4 NPs

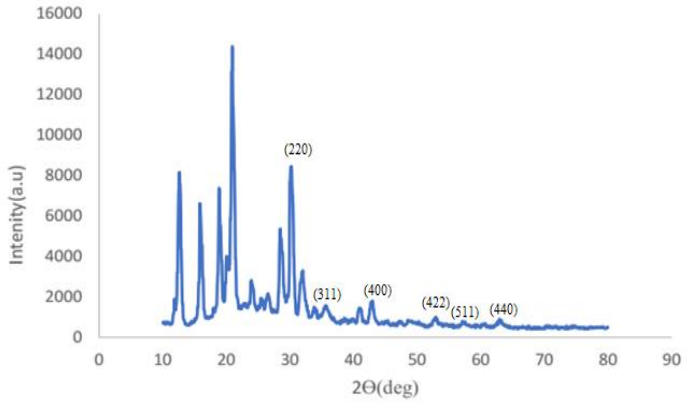

Fig. 6 The XRD pattern of nano-absorbent

to the surface of Fe_3O_4 NPs. After that the surface of Fe_3O_4 NPs is coated by SiO_2, its FT-IR spectrum exhibits a strong peak at 1102 cm^{-1} and which is attributed to Fe-O-Si stretching vibration mode (Gemeay *et al*. 2020) (see Fig. 4).

After the modification of the surface of Fe_3O_4 NPs via 3-nitrobenzylidenemalononitrile, its FT-IR spectrum shows characteristic peaks at 2216 cm^{-1} for –C≡N, 1355, 1533 cm^{-1} for symmetric and asymmetric vibration of $–NO_2$ groups and also peak at 1106.28 attributed to stretching vibration of Si-O-Si, respectively (Fig. 5).

The FT-IR results show that both the silica as coating ofFe_3O_4 NPs and the synthesized organic compound, 3-nitrobenzylidenemalononitrile are present as adsorbents on the surface of nanoparticles.

Moreover, information obtained from X-ray diffraction (XRD) analysis of synthesized nanoparticles is in good agreement with the standard Fe_3O_4 patterns which were reported in literature (Zare *et al*. 2020, 2019).
The diffraction peaks at 2θ = 28.54, 30.14, 32.14, 35.10, 41.45, 50.65, 63.25 are observed in the XRD diagram and are related to Fe3O4 and a broadened area has been seen at 2θ = 15-25° in this XRD pattern and it can belong to amorphous SiO2 layer (Fig. 6). The peaks (220), (311), (400), (422), (511) and (440) are characteristic peaks of as standard Fe3O4 sample (Wang et al. 2018). However, in according to XRD pattern, it can be said that most of the peaks indicate that the nanoparticles are amorphous nanoparticles (Mobinikhaledi et al. 2018, Yao et al. 2014, Farooq et al. 2020).

The morphology of the synthesized magnetic nano-particles was investigated using field emission scanning electron microscopy (FE-SEM) and the results show that the synthesized absorbent MNPs with a size under 100 nm have been done (Fig. 7). However, it should be mentioned that due to the aggregation of the particles with paramagnetic nature, it is also possible for nanoparticles to clump. This phenomenon is seen in part (c) of Fig 7. for synthesized Fe3O4 NPs.

The Energy Dispersive X-ray (EDX) experiment of the nanoparticle shows that Fe, Si and O elements are present in the structure of the nanoparticle. However, it should be mentioned that there is a small amount of S atom as impurity next to these elements with corresponding weight percents 13.40%, 33.36%, 52.24% and 1.00%, respectively (Fig. 8).

After the synthesis and characterization of the nano-particle, the absorbent moiety was placed on the nano-particle shell. The final nanocomposite was then used to adsorb mercury (II) ions. The illustrative figure below shows how the synthesized nanomaterial works as Hg^{2+}

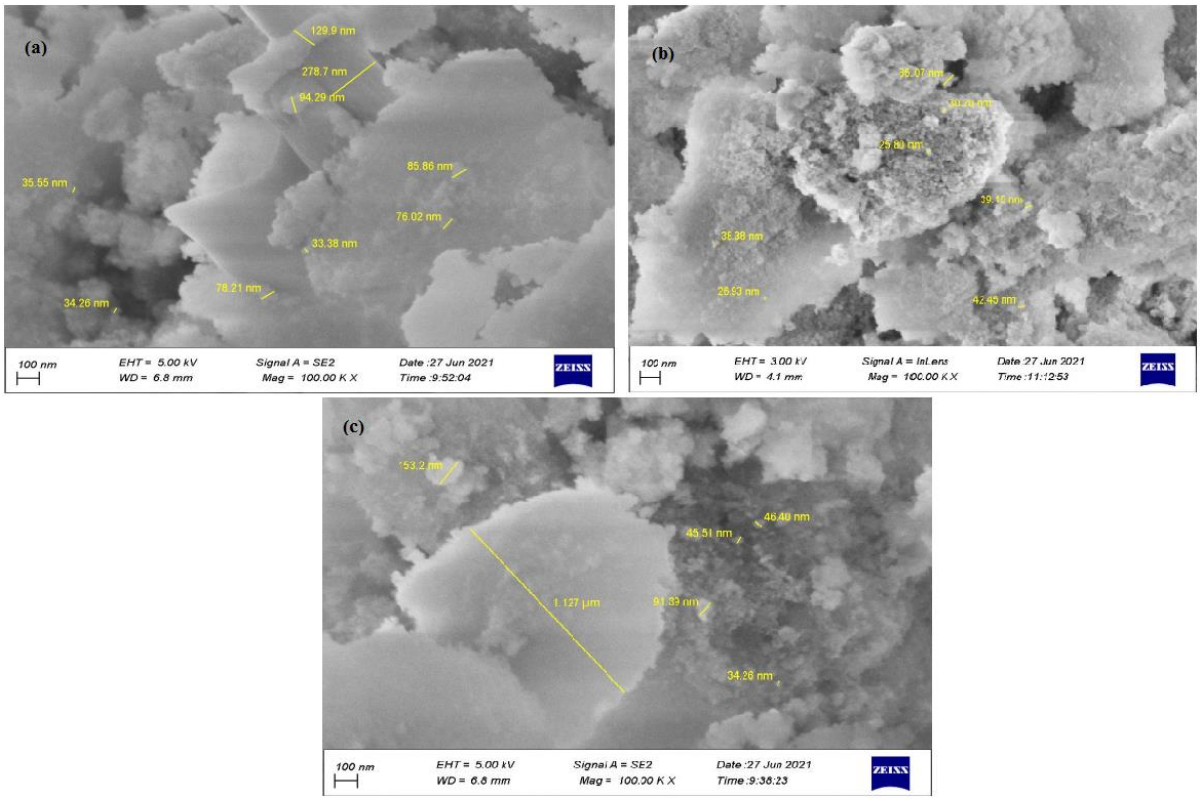

Fig. 7 The FE-SEM images of magnetic nanoparticles

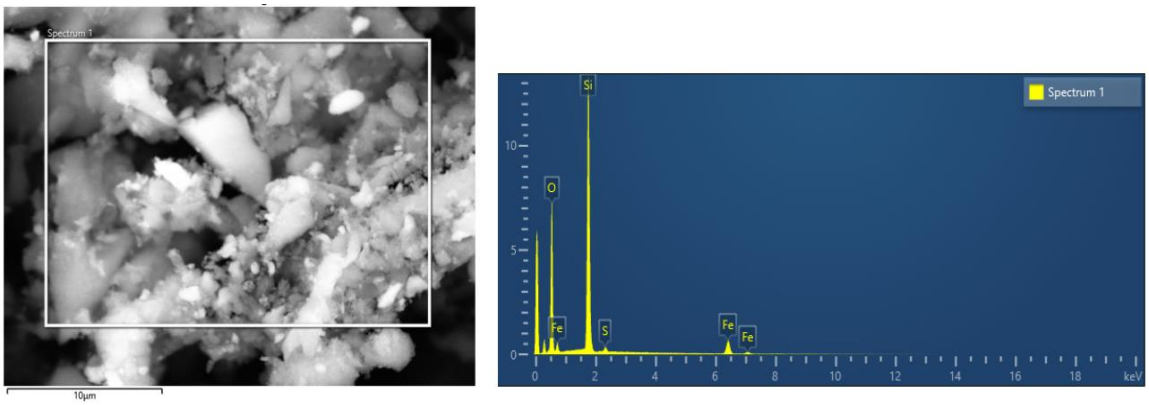

Fig. 8 SEM and EDX spectrum of Fe_3O_4@SiO_2 NPs

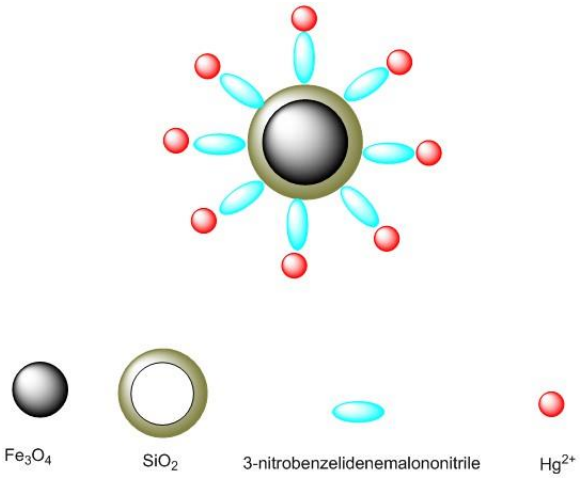

Fig. 9 A proposed route for Hg^{2+} ions adsorption by the synthesized nanocomposites

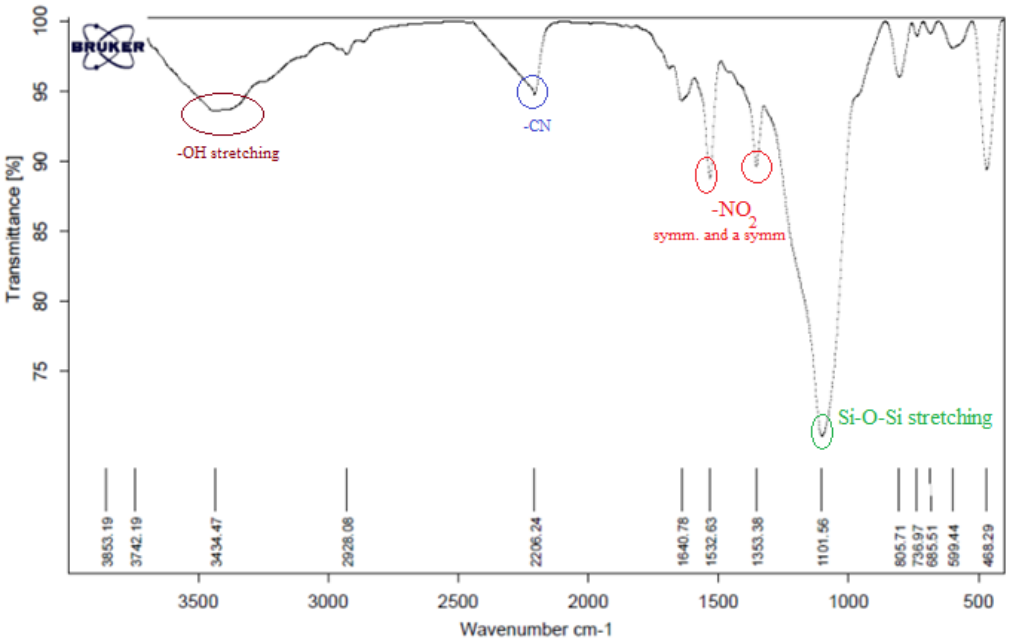

Fig. 10 The FT-IR spectrum of synthesized nanocomposites after the absorption of Hg^{2+} ions

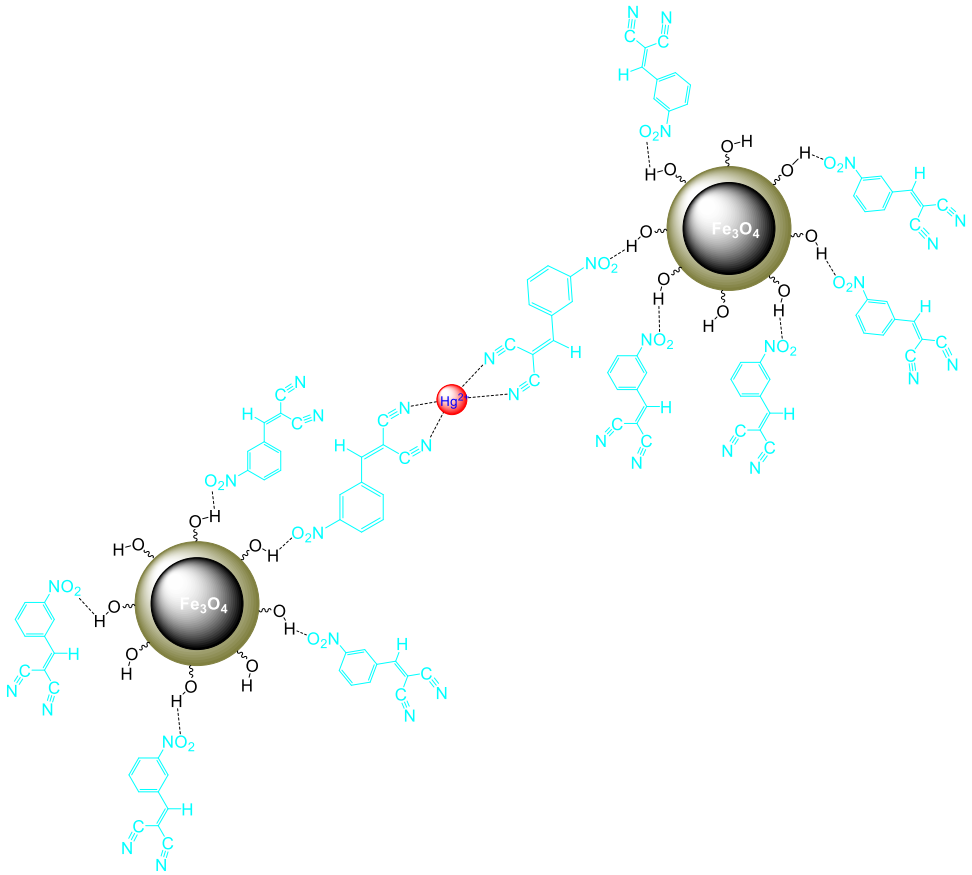

Fig. 11 an acceptable route for absorption of Hg^{2+} ions by synthesized nano-absorbent

ions absorbent (Fig. 9). After the proving of the synthesis of the nano-absorbent, its absorption activity was investigated using a 0.1 M solution of $Hg(NO_3)_2$. The FT-IR spectrum of nano-particles after the adsorption of Hg^{2+} ions from a 0.1 M solution of $Hg(NO_3)_2$ shows a characteristic peak at 2206 cm^{-1} (Fig. 10) which is attributed to –C≡N and the difference between before and after absorption indicates the possibility of cyanide groups being involved with mercury ions. This decreases in wave number ($\Delta\upsilon_{-C\equiv N}$= 10 cm^{-1}) in malononitrile moiety after absorption of mercury ions can

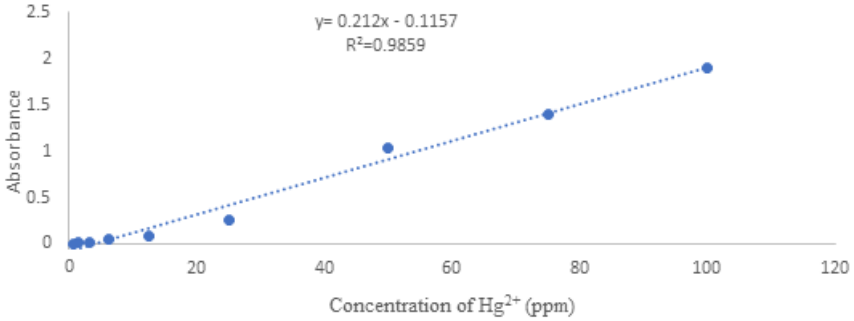

Fig. 12 The calibration curve of the mercury ions in terms of concentration at 25 °C

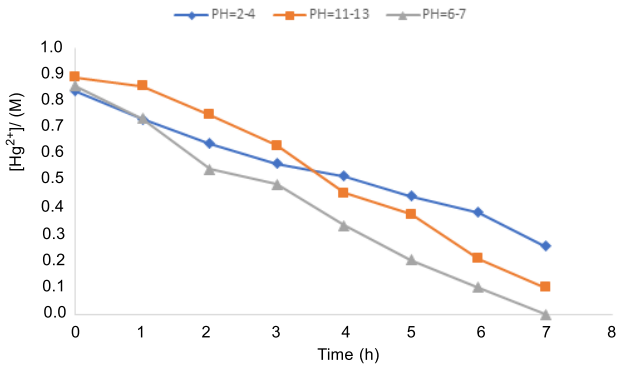

Fig. 13 Effect of pH on absorption of Hg^{2+} by nano-absorbent at 25 °C

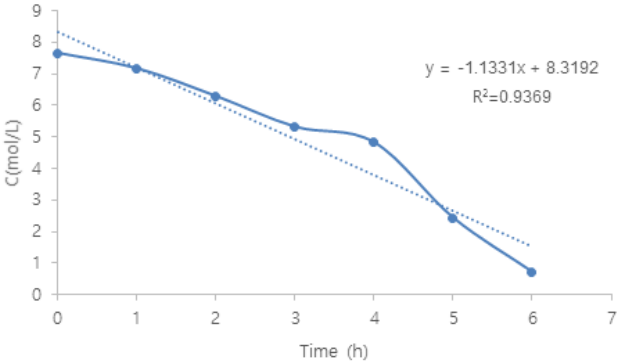

Fig. 14 The effect of absorption time to absorb Hg^{2+} ions by nano-absorbent

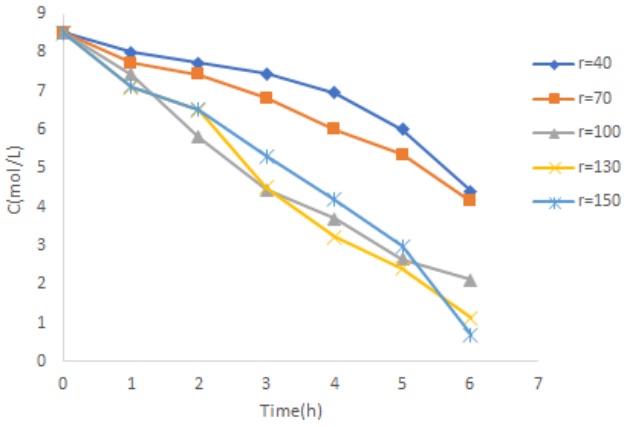

Fig. 15 The effect of speed of agitation on absorption of Hg^{2+} ions by nano-absorbent

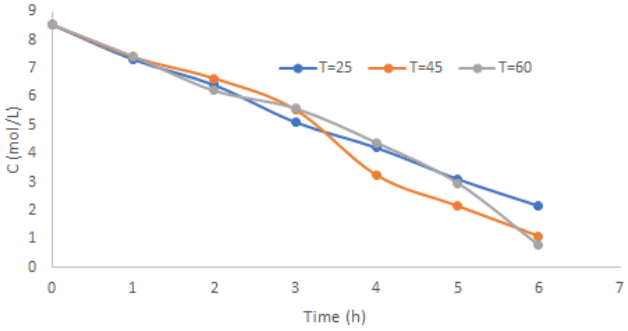

Fig. 16 The effect of Temperature on absorption of Hg^{2+} by nano-absorbent

be attributed to the back-donation of an electron pair from the metal to one π* orbital of the nitrile group (Storhoff *et al*. 1977, Bresciani *et al*. 2021). This interaction between Hg^{2+} and cyanide groups shows that synthesized absorbent has a high potential to removing of mercury(II) ion.

Fig. 11 shows one of the acceptable routes for absorption of Hg^{2+} ions in the presence of a nano-absorbent. Although, another plausible mechanism can exist for the removal of Hg^{2+} ions (see Fig. 11).

In the following, to obtain the optimal procedure conditions for the best absorption, some parameters such as absorption time, pH, temperature, and agitation speed were evaluated and the results were presented.

In the first step, to calibrate and draw the plot of the absorbance changes in terms of concentration of Hg^{2+} in λ_{max} (525 nm), for this purpose, standard solutions (0.3-100 ppm) of $Hg(NO_3)_2$ were prepared and experimented under neutral conditions at room temperature. Fig. 12 shows the calibration graph of the mercury ions.

After the calibration of the system, the effect of pH on the absorption of Hg^{2+} by absorbent was studied at 25 °C.

The experiments were performed at different pHs (2-4), (6-7) and (11-13), and as shown in Fig. 13, the highest amount of absorption of Hg^{2+} ions occurred in environments with pH 6-7.

Another parameter that highly influences the absorption of Hg^{2+} ions in this procedure is the absorption time. Fig. 14 shows that after 6 hours the highest amount of Hg^{2+} ions are absorbed by the nano-absorbent. It seems to be true that the more contact time of the nano-adsorbent with the Hg^{2+} ions, the more ions are absorbed by the nano-adsorbent.

Table 1 The absorption performance of nano-absorbent in various conditions

Absorbent	Absorbed ion	Conditions						Remarks
		pH	capacity (mol/L)	stirred speed (rpm)	capacity (mol/L)	Temperature (°C)	capacity (mol/L)	
Modified Fe_3O_4 NPs	Hg^{2+}	2-4	5.806	40	4.1			The best conditions for Hg^{2+} removal by modified silica coated Fe_3O_4 NPs are under neutral pH, stirred speed 150 rpm and 60 °C conditions.
		6-7	7.889	70	4.36	25	6.37	
				100	6.36	45	7.43	
				130	7.39	**60**	7.752	
		11-13	5.562	**150**	7.814			

To optimize this procedure, the speed of agitation for absorption of Hg^{2+} ions was investigated. It was found that the range of stirrer speed can affect the absorption of Hg^{2+} ions by nano-absorbent. Additional experiments were carried out at 40, 70, 100, 130, and 150 rpm. The experiments show that among the mentioned stirred speeds, the speed of 150 rpm has the best performance for absorption of Hg^{2+} ions (Fig. 15).

Temperature parameter for this procedure in another series of experiments was studied and the results showed that nano-absorbent at 60 °C has the excellent performance among the 25, 45 and 60 °C (Fig. 16).

Table 1. shows the results of Hg^{2+} ion absorption experiments in different conditions such as pH, temperature and stirring speed.

4. Conclusions

In summary, we describe an interesting route for the removal of Hg^{2+} ion as one of the extra harmful and toxic ions with high pathogenic potential from the wastewaters. Synthesized Fe_3O_4 bearing nano-absorbents have a rapid performance to remove of Hg^{2+} ion which its function is excellent in comparison to the other spectroscopic methods. The experimental results show that the best performance for modified Fe_3O_4 MNPs was occurred in neutral pH, stirred speed 150 rpm and 60 °C. It should be mentioned that the use of 3-nitrobenzylidenemalononitrile supported on Fe_3O_4 MNPs is the first facile, non-toxic and non-expensive method for the removal of Hg^{2+} ions from the wastewater.

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