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# Removal, preconcentration and spectrophotometric determination of picric acid in water samples using modified magnetic iron oxide nanoparticles as an efficient adsorbent

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## ABSTRACT

A simple, fast and sensitive spectrophotometric method is developed for removal, preconcentration and determination of trace amounts of picric acid in water samples. Magnetic iron oxide nanoparticles (MIONPs) were synthesized and characterized by transmission electron microscopy (TEM). The magnetic nanoparticles were coated with cetyltrimethylammonium bromide (CTAB) and were applied for fast separation, preconcentration and spectrophotometric determination of picrate anion (the ion of picric acid) in an aqueous solution. The separation, preconcentration procedure is fast and will be completed in 2 min. Methanol is used for desorption of adsorbed picrate anion. The effects of important parameters such as pH of aqueous medium, CTAB dosage, adsorbent amount, temperature, electrolyte concentration, desorbing solvent and interfering ions on the adsorption of picrate anion were investigated. The method showed good linearity for the determination of picric acid in the concentration range of 0.02–1.00  $\mu\text{g mL}^{-1}$  with a regression coefficient of 0.999. The limit of detection (LOD) is obtained to be 0.007  $\mu\text{g mL}^{-1}$ . The relative standard deviation (RSD) for 0.03  $\mu\text{g mL}^{-1}$  and 0.8  $\mu\text{g mL}^{-1}$  of picric acid were 3.98% and 1.97% respectively. Picric acid was separated, preconcentrated and determined successfully in spiked samples of Karoon River water.

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## 1. Introduction

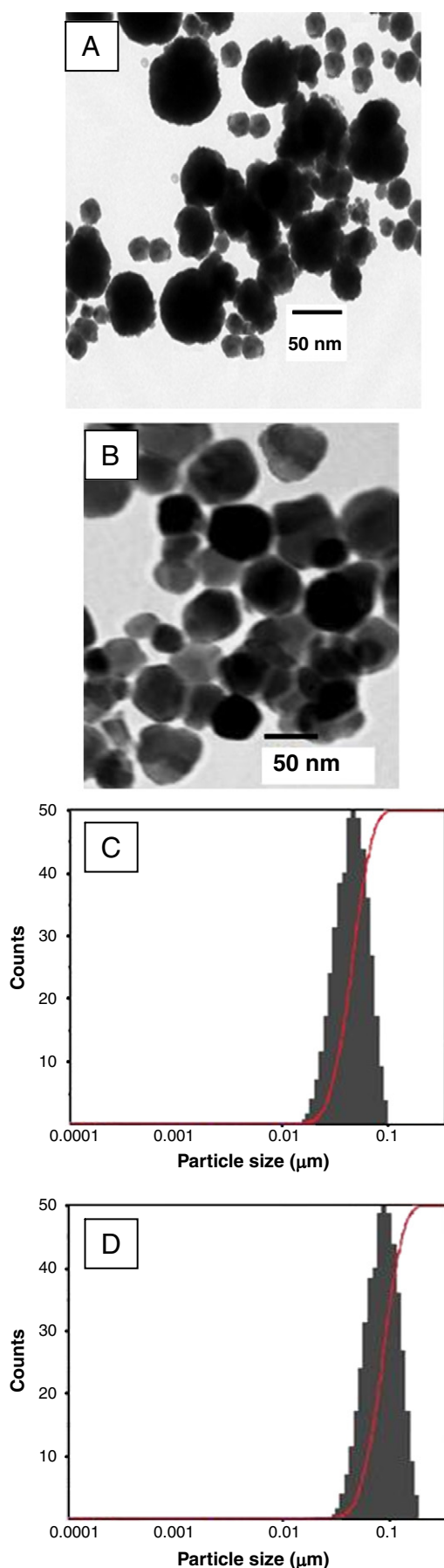
The treatment of industrial effluents is a challenging topic in environmental sciences, since control of water pollution has become of increasing importance in recent years [1]. Industrial effluents contaminated with hazardous chemicals can be found everywhere. There are about half a million chemical pollutant products and also hundreds of new toxic substances are introduced annually. Millions of humans are directly or indirectly exposed to one or more hazardous substance in the workplace and also around industrial plants. Many of these materials have properties that make them hazardous; they can create physical and/or health hazards. Depending upon magnitude, chemical exposure may cause or contribute to serious health effects.

Phenols and their derivatives are irritating and corrosive to the skin. Repeated or prolonged exposure to phenolic compounds or their vapors may cause headache, nausea, dizziness, difficulty swallowing, diarrhea, vomiting, shock, convulsions, or death. Phenol can affect the central nervous system, liver, and kidneys. Nitroaromatic compounds (NACs) are used as basic chemicals for paints, agrochemicals, plastics and pharmaceuticals. For example, Picric acid (2,4,6-trinitrophenol,

PA) is an anionic phenol derivative used mainly in the explosives industry and also used as antiseptic, in electric batteries, leather industry, inks, manufacture of colored glass, textile mordants, and in the synthesis of chloropicrin, or nitrotrichloromethane,  $\text{CCl}_3\text{NO}_2$  a powerful insecticide [2,3]. It was found that PA can be toxic to both humans and the environment and is in the list of Environmental Protection Agency [4]. PA will react with metals (such as copper, iron, lead, mercury and zinc) to form metal picrates that are extremely shock sensitive and can be detonated by the slightest movement or vibration. Water contamination by priority pollutants such as phenolic compounds is of major concern due to their high toxicity and persistence in the environment [5,6]. Therefore, attention has been paid to its direct determination in the areas of water pollution analysis. Phenolic compounds are common by-products of the coal, tar, plastics, leather, paint, pharmaceutical and steel industries and are therefore frequently found in water reservoirs, rivers and lakes [6].

Picric acid was determined by different methods, such as follows: liquid chromatography–mass spectrometry [7], spectrophotometry [8–13], classical chemical methods [14], fluorometry [15–18], polarography [19], gas chromatography [20], ion-selective electrodes [21–27]. These methods require expensive instrumentation, need extensive pretreatment of the sample solution. For example, in liquid chromatography–mass spectrometry and gas chromatography it is necessary to extract picric acid by a volatile organic solvent and then concentrate it in order to be used. According to the

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above-mentioned reasons, determination of picric acid requires a fast, simple, low-cost, selective and reliable method, which can be used routinely.

Magnetic iron oxide nanoparticles (MIONPs) were used in analytical science as a new effective adsorbent in solid-phase extraction (SPE) method for separation, removal and determination of chemical species [28–30]. New SPE techniques based on the use of magnetic or magnetizable adsorbents called magnetic solid-phase extraction (MSPE) have been used for separation and preconcentration of an analyte from large volumes of solution by using a permanent external magnet [31,32]. Generally, most of the dissolved environmental pollutants are nonmagnetic, and thus do not respond to magnetic field. Magnetic nanoparticles possess large surface areas and have unique magnetic properties. Selective removal of toxic target compounds from complex environmental matrices can be obtained when certain special functional ligands with affinities for target molecules are bound onto these magnetic nanoparticles [33].

In the present work, cetyltrimethylammonium bromide (CTAB) cationic surfactant was used to coat on the surface of magnetic iron oxide nanoparticles and the mixture was used for separation (removal), preconcentration and determination of picric acid. CTAB can form a stable ion pair with picrate anion [34].

## 2. Experimental

### 2.1. Instrumentation

The spectrophotometric measurements were carried out with a Cintra 101 spectrophotometer (GBC SCIENTIFIC EQUIPMENT, Australia) equipped with 1.0 cm matched cells. A transmission electron microscope (TEM, 906E, LEO, Germany), pH-meter (632 Metrohm, Herisau, Switzerland) and a super magnet (1.2 Tesla,  $10 \times 5 \times 2$  cm) were used. FRITTSCH Laser particle sizer ANALYSETTE 22 nanotech plus (Germany) was used for measuring the size distribution of both  $\text{Fe}_3\text{O}_4$  and CTAB coated  $\text{Fe}_3\text{O}_4$  (CTAB@ $\text{Fe}_3\text{O}_4$ ).

### 2.2. Reagents

All chemicals used, were of analytical reagent grade. Picric acid, phosphoric acid (85% w/w), hydrochloric acid (37% w/w), methanol (99.9% w/w), ammonia solution (25% w/w),  $\text{FeCl}_3$  (96% w/w),  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (99.9% w/w), and cetyltrimethylammonium bromide (>99% w/w) were purchased from Merck (Darmstadt, Germany). Ammonia buffer solution (pH 9) was prepared by mixing appropriate volumes of hydrochloric acid ( $1.0 \text{ mol L}^{-1}$ ) ammonia solution ( $1.0 \text{ mol L}^{-1}$ ) solutions.

### 2.3. Preparation of magnetic iron oxide nanoparticles

MIONPs were prepared according to method represented by Jang et al. [35]. The size distribution of the MIONPs (average size of particles is about 50–70 nm) is shown in Fig. 1A.

### 2.4. Preparation of modified magnetic iron oxide nanoparticles

In order to coat the iron oxide nanoparticles, 1 mL of CTAB solution (0.5% w/v) was added to 0.6 g of damped nanoparticles and the mixture was diluted to 50 mL with distilled water. The solution mixture was stirred for 2 min with a glass rod. After complete mixing, the beaker was placed on the magnet and C-MIONPs were collected at the beaker bottom. In order to eliminate excess amount of the surfactant from nanoparticles, the supernatant solution was decanted and the ferrofluid was washed with distilled water several times. The transmission electron microscope (TEM) image of C-MIONPs is shown in

Fig. 1. Transmission electron microscope (TEM) image of MIONPs and C-MIONPs (A and B) and graphs of particle size distribution for both MIONPs (C) and C-MIONPs (D).

Fig. 1B. The graph of size distribution of C-MIONPs (average size of particles is about 80–100 nm) is shown in Fig. 1C.

### 2.5. Extraction and determination procedure

A batch procedure was carried out for the extraction process. A beaker containing 100 mL solution of PA ( $0.02\text{--}1.10\ \mu\text{g mL}^{-1}$ ) and 3 mL of  $0.5\ \text{mol L}^{-1}$  ammonia buffer solution (pH 9), was stirred (300 rpm) with 0.6 g of damped C-MIONPs (the damped C-MIONPs contains 90% water, so 0.55 g of the damped adsorbent is equivalent to 0.06 g of the dry C-MIONPs) for 2 min. Nanoparticles were collected using a strong magnet (1.2 Tesla) and after settlement of C-MIONPs, the initial yellow colored solution became colorless (meaning the removal of yellow picrate anion from the solution). After decanting the solution above the nanoparticles, the magnetic solid phase was washed with about 10 mL distilled water and then the adsorbed PA on the C-MIONPs were washed and desorbed with 5 mL of methanol by stirring for 1 min. Then the beaker was placed on the magnet and C-MIONPs were collected. The PA yellow color appeared again in methanol solvent as the desorbing solvent. The desorbed solution was transferred into a 1.0 cm cell and its absorbance was measured spectrophotometrically at 348 nm ( $\lambda_{\text{max}}$  of PA) against a blank solution prepared under the same conditions without adding the analyte.

## 3. Results and discussion

The adsorption and preconcentration of PA by CTAB modified MIONPs (C-MIONPs) showed fast separation of picrate anion from the bulk of water solutions (it must be mentioned that PA is converted to picrate anion in ammonia buffer, pH 9). The adsorption of the picrate by C-MIONPs may be due to ion pair formation between positive charge of the cationic surfactant adsorbed on the iron oxide nanoparticles and negative charge of picrate anion at pH 9. The adsorption was completed within 2 min. Such a fast adsorption rate could be due to the absence of internal diffusion resistance (Fig. 2).

### 3.1. Effect of solution pH

Critical role of the pH of the solution in the SPE procedure is well known and must be controlled to improve the adsorption efficiency. The effect of pH on the adsorption of PA ( $0.50\ \mu\text{g mL}^{-1}$ ) is shown in Fig. 3. The pH of the analyte solution was adjusted by using hydrochloric acid (HCl) and sodium hydroxide (NaOH) in the pH range of 4 to 10. As can be seen from Fig. 2, quantitative removal (solid phase extraction) was obtained at pH 9. At low pH values, the magnetic iron oxide nanoparticles dissolve in the acidic solution,

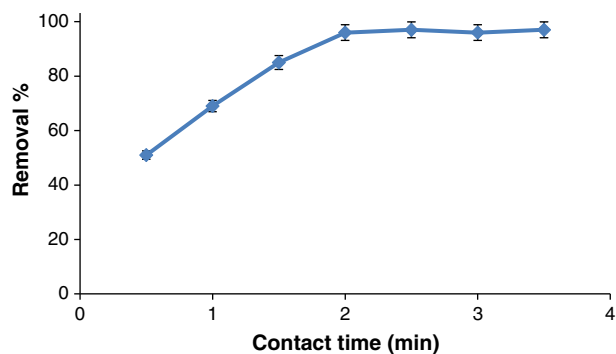


Fig. 2. Removal kinetics of PA by C-MIONPs. Conditions: 100 mL solution containing fixed amount ( $50\ \mu\text{g}$ ) of PA; 0.60 g of damped C-MIONPs; methanol as desorbent, 4 mL; temperature, 25 °C.

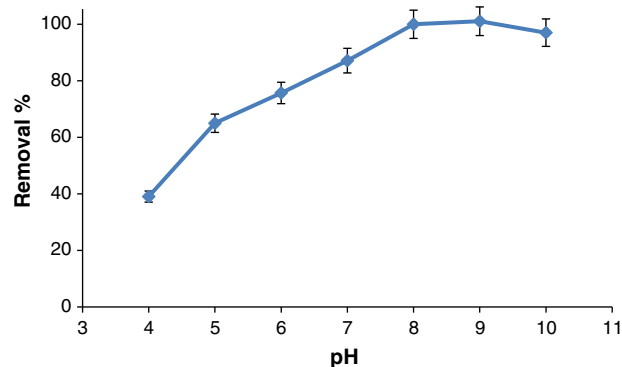


Fig. 3. Effect of pH on the PA separation. Conditions: 100 mL solution containing fixed amount ( $50\ \mu\text{g}$ ) of PA; 0.60 g of damped C-MIONPs; methanol as desorbent, 4 mL; temperature, 25 °C.

the solution becomes dark brown and no adsorption takes place. At high pH values, (pH >7) PA molecules are dissociated to picrate anions that can form ion pair with  $\text{CTA}^+$  cation coated on MIONPs [34]. In further works, the pH of the solutions was adjusted by using ammonia buffer (pH 9) solution. The optimum volume of the buffer solution added to 100 mL of the PA solution was 3 mL; higher volumes have no considerable effect on adsorption and separation of PA.

### 3.2. Effect of the CTAB amount

The effect of CTAB amount on the adsorption of PA was investigated by coating different amounts of this compound on the surface of nanoparticles. In the case of non-coated MIONPs, only 40% removal and recovery of PA was obtained. Maximum removal of PA was obtained when 2 mL of 0.5% (w/v) solution of CTAB was used (equivalent to 0.01 g of CTAB) for coating 0.60 g of damped MIONPs as shown in Fig. 4. Higher amounts of CTAB did not provide more efficiency.

### 3.3. Effect of the amount of C-MIONPs as adsorbent

The amount of C-MIONPs adsorbent required for quantitative removal of PA was optimized. The effect of different quantities of pretreated C-MIONPs ranging from 0.25 to 0.60 g was investigated. Maximum adsorption was obtained when 0.60 g of MIONPs was in contact with PA solution for 2 min. The results are shown in Fig. 5.

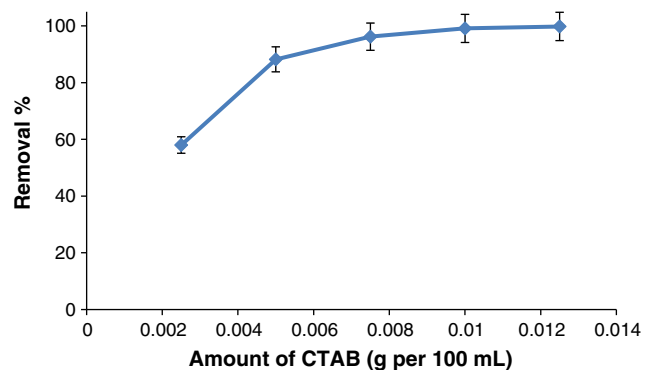


Fig. 4. Effect of CTAB amount (0.5% w/v) on the separation of PA. Conditions: 100 mL solution containing fixed amount ( $50\ \mu\text{g}$ ) of PA; 0.60 g of damped MIONPs; pH 9; volume of buffer solution, 3.0 mL; methanol desorbent solvent, 4 mL; temperature, 25 °C.

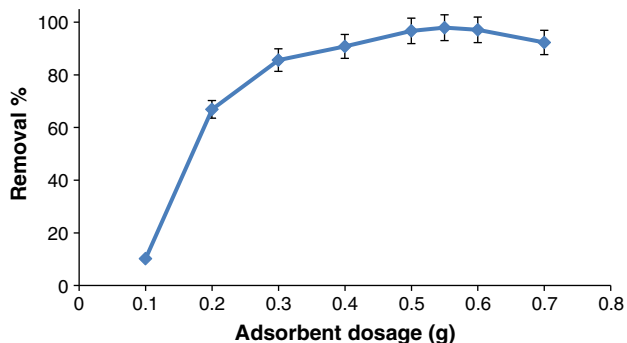


Fig. 5. Effect of C-MIONPs adsorbent amount on the separation of PA. Conditions: 100 mL solution containing fixed amount (50  $\mu\text{g}$ ) of PA; pH 9; volume of buffer solution, 3.0 mL; methanol desorbent solvent, 4 mL; temperature, 25  $^{\circ}\text{C}$ .

### 3.4. Desorbing solvent

In order to desorb the PA from C-MIONPs different organic solvents such as ethanol, acetonitrile and methanol were tested. Desorption of the adsorbed PA was achieved using pure methanol solvent as the desorbing solvent. The amount of the desorbed PA was determined spectrophotometrically at 348 nm. It was observed that the amount of the desorbed PA was increased with increasing the volume of methanol from 2 to 5 mL, and the analyte could be desorbed by 4 mL of pure methanol. This study revealed that more than 98% of the removed/or adsorbed PA could be desorbed and recovered from C-MIONPs by pure methanol.

### 3.5. Effect of electrolyte

The effect of electrolyte concentration (adjusted by  $\text{KNO}_3$ ) on the adsorption and desorption of PA was studied. The results (Fig. 6) show that the adsorption and desorption of PA remained almost constant within the concentration range of 0.00–0.04  $\text{mol L}^{-1}$  of  $\text{KNO}_3$  in the test solution. Electrolyte concentrations more than 0.04  $\text{mol L}^{-1}$  decrease the efficiency of adsorption and desorption processes of PA.

### 3.6. Effect of solution temperature

The effect of temperature on the adsorption of PA was examined in the range of 15–50  $^{\circ}\text{C}$ . The results show that the adsorption of PA (0.50  $\mu\text{g mL}^{-1}$ ) in a 100 mL solution using 0.6 g of damped

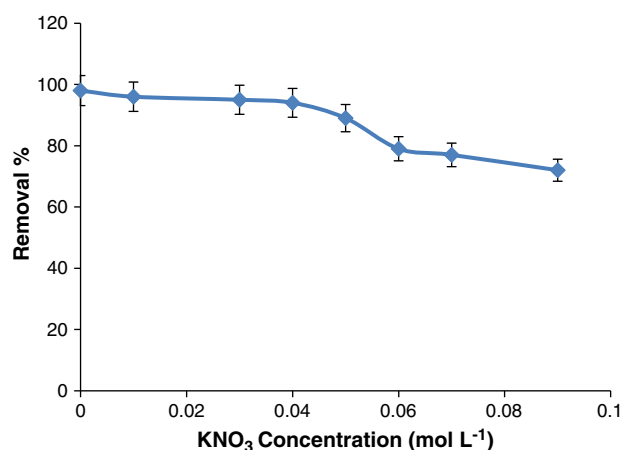


Fig. 6. Effect of electrolyte  $\text{KNO}_3$  concentration on the separation of PA. Conditions: 100 mL solution containing fixed amount (50  $\mu\text{g}$ ) of PA; pH 9; volume of buffer solution, 3.0 mL; methanol desorbent solvent, 4 mL; temperature, 25  $^{\circ}\text{C}$ .

C-MIONPs at pH 9 is decreased with increasing the temperature of the test solution above the room temperature. The removal percent of PA was changed from 99% for 15  $^{\circ}\text{C}$  to 84% for 50  $^{\circ}\text{C}$ . A temperature of 25  $^{\circ}\text{C}$  (99% removal) was used for further works.

### 3.7. Adsorption isotherm

The capacities of C-MIONPs to adsorb PA were examined by measuring the initial and final concentrations of PA in a 0.5  $\text{mol L}^{-1}$  of ammonia buffer solution at pH 9 and 25  $^{\circ}\text{C}$  in batch system. Both Langmuir and Freundlich adsorption isotherms were used to normalize the adsorption data. The results showed that Langmuir model fitted better ( $R^2 = 0.9922$ ) than the Freundlich model ( $R^2 = 0.9635$ ), demonstrating that the adsorption of picrate anion onto CTAB@ $\text{Fe}_3\text{O}_4$  can be considered to be a monolayer adsorption process. This may be due to the formation of a monolayer strong ion pair between the coated CTAB on the surface of MIONPs and picrate anion which covers the surface of MIONPs and no more complex molecules can form on the first layer. The Langmuir isotherm equation [36] was used to describe the relationship between the amount of PA adsorbed and its equilibrium concentration in solutions (Fig. 7).

$$\frac{C}{q} = \frac{1}{Kq_m} + \frac{C}{q_m} \quad (1)$$

where  $C$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of the PA in the solution,  $q$  ( $\text{mg PA/g adsorbent}$ ) is the equilibrium adsorption amount of PA,  $q_m$  is the maximum adsorption amount of PA per gram of adsorbent ( $\text{mg/g}$ ) and  $K$  is the Langmuir adsorption equilibrium constant in liter per mg of adsorbent ( $\text{L/mg}$ ). The results show a linear relationship between  $C/q$  and  $C$  using the experimental data obtained, suggesting the applicability of the Langmuir model. Values of  $q_m$  and  $K$  calculated from the least square methods were 46.3 ( $\text{mg/g}$ ) and 2.8 ( $\text{L/mg}$ ), respectively.

### 3.8. Effect of the sample volume

In order to obtain a high removal efficiency of PA from water samples and also preconcentration factor for determination of trace concentrations of PA more diluted solutions of the analyte were examined. Therefore, maximum applicable sample volume was determined by increasing the dilution of the PA solution, while keeping its total amount fixed at 50  $\mu\text{g}$  and also the contact time of 2 min. Different feed volumes between 50 and 250 mL were tested. The obtained results in Fig. 8 show that the removal of PA was quantitative up to 200 mL of sample volume (removal > 95%). At volumes higher than 200 mL, the analyte was not adsorbed effectively probably due to

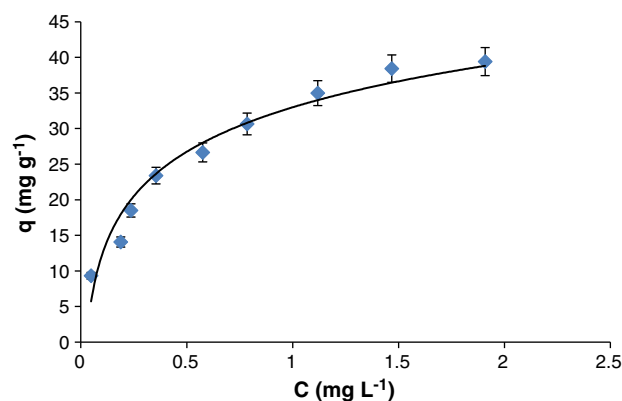
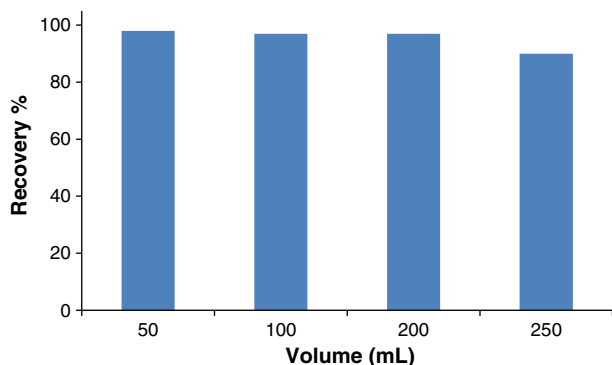


Fig. 7. Adsorption isotherm of PA on C-MIONPs. Conditions: 100 mL solution containing fixed amount (50  $\mu\text{g}$ ) of PA; pH 9; volume of buffer solution, 3.0 mL; methanol desorbent solvent, 4 mL; temperature, 25  $^{\circ}\text{C}$ .



**Fig. 8.** Effect of different feed volumes (50–250 mL) on the removal of PA from sample solution. Conditions: Different volumes of analyte solution containing fixed amount (50  $\mu\text{g}$ ) of PA; pH 9; volume of buffer solution, 3.0 mL; methanol as desorbent, 4 mL; temperature, 25  $^{\circ}\text{C}$ .

lower magnetic field strength at high dilutions. As it was mentioned previously, the final volume of eluting solvent (methanol) after eluting was 4 mL, therefore, the preconcentration factors of 50 was obtained for the analyte.

### 3.9. Effect of interfering ions

The optimum experimental conditions which have been described were used to study the interfering effect of some ions and organic compounds on the separation, preconcentration and determination processes of PA. To this end separation and determination of PA were performed in the presence of co-existing interfering substances. The maximum acceptable error was  $\pm 5\%$ . The obtained results show that most of the investigated ions did not interfere during the separation, preconcentration, and determination. The cations  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  do interfere at concentration ratios more than 5 with respect to PA. The interfering effect of these cations was eliminated by using 1 mL of  $1 \times 10^{-4}$  mol  $\text{L}^{-1}$  of EDTA solution. Organic compounds such as phenol and nitrobenzene do not interfere even at 1000 times higher than PA. Other species such as  $\text{Cl}^{-}$ ,  $\text{Br}^{-}$ ,  $\text{I}^{-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^{-}$ ,  $\text{F}^{-}$ ,  $\text{K}^{+}$ ,  $\text{Na}^{+}$ ,  $\text{NH}_4^{+}$  and acetate ions do not interfere at concentration ratios of 1000 with respect to PA (1  $\mu\text{g mL}^{-1}$ ).

### 3.10. Reusability of the C-MIONPs

The ability of reusing the adsorbents in several successive adsorption and desorption processes was tested. The obtained results showed (Table 1) that the modified magnetic nanoparticles can be reused for three times without a considerable loss in their adsorption efficiency.

### 3.11. Analytical characteristics

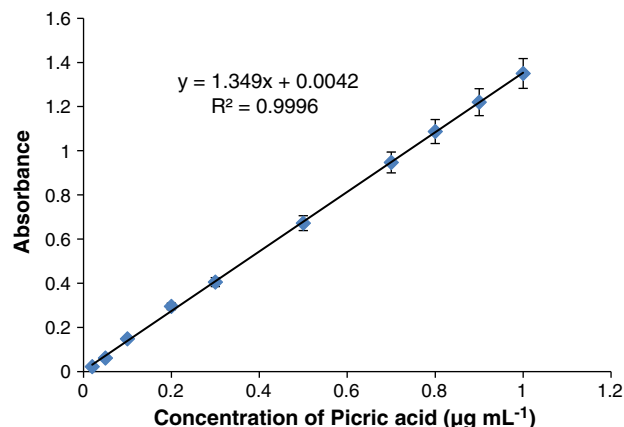
The analytical features of the proposed method such as linear range of the calibration curve, limit of detection and precision were also

**Table 1**

Reusability tests for adsorption–desorption of spiked PA in water samples by using the same C-MIONPs in 5 sequential runs.

Run no.	Added PA ( $\mu\text{g mL}^{-1}$ )	Removal % <sup>a</sup>	Recovery % <sup>a</sup>
1	0.50	98.4	96
2	0.50	98.1	95
3	0.50	97.2	94
4	0.50	90.0	95
5	0.50	81.0	92

<sup>a</sup> n = 3.



**Fig. 9.** Calibration curve for preconcentrated PA under optimum conditions.

examined. The calibration curve (Fig. 9) was linear in the range of 0.02–1.00  $\mu\text{g mL}^{-1}$  of PA. The equation for this calibration graph was  $A = 1.342 C_{\text{PA}} + 0.005$  ( $r = 0.999$ ). The limit of detection (LOD) based on three times the standard deviation of the blank ( $3s_b$ ), under optimal experimental conditions, was  $7.0 \times 10^{-3}$   $\mu\text{g mL}^{-1}$  of PA ( $n = 8$ ). The relative standard deviations for 0.03 and 0.8  $\mu\text{g mL}^{-1}$  of PA ( $n = 8$ ) were 3.98% and 1.97%, respectively.

### 3.12. Analytical applications

The ability and validity of the proposed method for the adsorption and desorption of PA in a real sample were examined using Karoon River water. Different recovery tests were carried out to evaluate the reliability and accuracy of the method. The analytical results, along with the recoveries for the spiked samples, are given in Table 2. The results showed the capability of the proposed method to real sample analysis. Excellent recoveries indicated that the complex matrix of river water samples does not interfere with the separation, preconcentration and determination of PA. In order to eliminate the interfering effect of some cations for separation process, 1 mL of  $1 \times 10^{-4}$  mol  $\text{L}^{-1}$  of EDTA solution was added to the river solutions.

## 4. Conclusions

Picric acid, PA (in anionic form) could be removed from an aqueous solution by (CTAB)-coated magnetic iron oxide nanoparticles (C-MIONPs). The proposed methodology was fast, simple, sensitive and cheap, especially if more sophisticated techniques such as liquid chromatography, spectrofluorometry and polarography are not available. In addition, it is notable that both the adsorption and desorption of PA are fast and could be completed within 2–3 min. The proposed method is recommended for removal and/or determination of PA in different water samples.

**Table 2**

Recovery tests for adsorption–desorption of spiked PA in Karoon river water samples by C-MIONPs.

Sample	Added PA ( $\mu\text{g mL}^{-1}$ )	Found PA <sup>a</sup> ( $\mu\text{g mL}^{-1}$ )	Recovery (%)
Karoon River water <sup>b</sup>	–	ND	–
Karoon River water	0.50	$0.49 \pm 0.01$	98.0
Karoon River water	0.80	$0.77 \pm 0.02$	96.2

<sup>a</sup> n = 3.

<sup>b</sup> Karoon river water main components:  $\text{Ca}^{2+} = 82$ ;  $\text{Mg}^{2+} = 49$ ;  $\text{Na}^{+} = 68$ ;  $\text{CO}_3^{2-} = 91$ ;  $\text{Cl}^{-} = 44$ ;  $\text{SO}_4^{2-} = 35$ ;  $\text{NO}_3^{-} = 9$   $\mu\text{g mL}^{-1}$ ; pH = 7.1; TDS = 387; EC = 1340.

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