

Application of Rh(III)-Metalloporphyrin Grafted Fe₃O₄ Nanoparticles for the Extraction of Thiocyanate Ions from Aqueous Solutions

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ABSTRACT: A new sorbent composed of 3-aminopropyltriethoxy-silane-coated magnetic nanoparticles, functionalized with rhodium(III) porphyrin complex was synthesized and characterized by elemental analysis, X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR) and ThermoGravimetric Analysis (TGA). The effect of some co-existing anions present in aqueous solutions, pH, sorbent dosage and contact time on the thiocyanate removal was investigated. Thiocyanate adsorbing material was regenerated with 15 mM NaOH up to 97.0 %. The effectiveness and feasibility of the proposed sorbent for removal of thiocyanate ions from aqueous solutions is proved.

KEY WORDS: Metalloporphyrin, Magnetite, Surface modification, Thiocyanate ion, Water samples.

INTRODUCTION

Thiocyanates are detrimental compounds that produce CN-Cl through chloridization in wastewaters, which is harmful for humans [1,2]. Also with a concentration of more than 5 mg/L, thiocyanates are harmful for plants. Thiocyanate contaminated wastewaters come from different industrial activities such as herbicide and insecticide production plants, electroplating and photofinishing [3,8].

Thiocyanate causes a number of diseases [9]. For example, the effect of thiocyanates on thyroid glands has been proved, and deteriorates the production of the hormones which are a must for normal body function [10]. A little higher than normal values of thiocyanates content affects on the protein dialysis which can even lead to comma [11].

Due to the resistance of thiocyanates toward hydrolysis

and also their nonvolatility, they are toxic for aquatic organisms; thus thiocyanate should be removed before the discharge of contaminated wastewaters [11-13]. Adsorption [12], solvent extraction, oxidation, biodegradation, alkaline chlorination [13-15], electrosorption [15,16], separation through liquid membranes [1, 17-19], Ion exchange, reverse osmosis, electrodialysis, distillation and activated carbon adsorption are processes that have been employed for thiocyanate uptake from drinking water supplies, but there are some disadvantages with these methods [19-21].

Adsorption is one of the most efficient methods for thiocyanates removal from wastewaters. Many adsorbents, such as Fe (III)/Cr (III) hydroxide [22], ZnCl₂ activated coir pith, carbon and calcined hydrotalcite, have been tested for the adsorption of thiocyanates [12-23].

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Metalloporphyrins which have a Lewis acidic metal as the coordinating site have become attractive anion carriers. Design of different anion selective electrodes is the result of selective complexation of anions with metalloporphyrins, which occurs via specific anion coordination with the central metal ion [24-26].

Due to the high surface to volume ratio, nanoparticles have gained interest as sorbents [27-29]. On the other hand their small size produces some difficulties in their separation. By using external magnetic fields, magnetic nanoparticles have overcome this problem and have promising applications for the removal of the environmental pollutants [26, 30-34].

The combination of molecular scale recognition and nano scale surface modification processes has made a powerful tool in the design of selective separation systems. This study points out the selective removal of thiocyanate from aqueous media using a nanosorbent composed of 3-aminopropyltriethoxysilane coated magnetite, functionalized with the Rhodium (III) -tetra (4-carboxyphenyl) porphine chloride complex. The capability of rhodium complexes to bind thiocyanate in a selective way is proved in various anion selective sensors [35-37]. The influence of pH, contact time, sorbent dosage and the effect of some co-existing anions present in aqueous solutions on the thiocyanate removal was investigated.

EXPERIMENTAL SECTION

Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), 3-aminopropyltriethoxysilane (APTES), dichloromethane (DCM), *N,N*-dimethylformamide (DMF), dicyclohexylcarbodiimide (DCHC), methanol, ammonia $\text{Fe}(\text{NO}_3)_3$, sodium salts of indicated anions were all analytical grade from Merck Chemical Co. The sample solutions for all measurements consisted of sodium salts of the indicated anions in 0.05M 4-morpholinoethanesulfonic acid (MES), adjusted to pH 5.5 with NaOH. Free basic porphyrin tetrakis (4-carboxyphenyl) porphine H_2 (TCPP) (Aldrich) was dried under vacuum at 60°C before use. Rhodium (III)-tetra (4-carboxyphenyl) porphine chloride was prepared by methods described in the literature.

Equipments

Powder XRD patterns of nanosorbent were obtained in the 2θ range of 5°-80° using a PW-1840 diffractometer from Philips Co. with Cu-K α radiation ($\lambda=1.54178 \text{ \AA}$). The morphology and dimension of the nanosorbent was obtained from Transmission Electron Microscopy (TEM) using a Zeiss 900 TEM at a voltage of 80 kV. TGA of the sample was obtained using a Mettler Toledo TGA/SDTA 851 instrument, between 20 and 1000 °C at a heating rate of 10 °C/min and FT-IR with IFS 88 FT-IR spectrophotometer from Bruker Co. using standard KBr pellet technique. pH measurements were performed with a Metrohm 691 pH meter. Ion chromatograms were determined by S 1122 Sykam ion chromatograph (IC). A single beam Perkin-Elmer UV-Vis spectrophotometer with a 1 cm cell was used for the measurement of the absorption data.

Synthesis

Synthesis of the Rh(III) - metalloporphyrin grafted Fe_3O_4 nanoparticles was carried out in three stages:

(1) Fe_3O_4 nanoparticles were prepared via improved chemical co-precipitation method [25, 38, 39]. According to this method, 0.016 mol of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.028 mol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 320 mL deionized water. The mixed solution was stirred under N_2 at 80°C for 1 h. Then 40 mL of ammonia solution was added to the mixture drop wise, stirred under N_2 for another 1 h and cooled to room temperature. Finally the precipitated particles were washed with hot water, magnetically separated and were dried.

(2) $\text{Fe}_3\text{O}_4/\text{APTES}$ nanoparticles were synthesized by the reaction between APTES and the surface hydroxyl groups of magnetite. Typically, 0.5 gr Fe_3O_4 nanoparticles were dispersed in 50mL of ethanol by sonication for about 1h, and then under continuous mechanical stirring, 4.2 g of APTES was added to the reaction mixture. The reaction was allowed to proceed for 20 h under nitrogen. The prepared APTES nanoparticles were collected with a magnet, and washed with ethanol and deionized water. $\text{Fe}_3\text{O}_4/\text{APTES}$ nanoparticles were vacuum dried.

(3) For functionalizing the synthesized $\text{Fe}_3\text{O}_4/\text{APTES}$ nanoparticles, they were suspended with DCHC in DMF. Rh (TCPP) was dissolved in DMF and added dropwise to the suspension. The mixture was refluxed at 140 °C for 8 h.

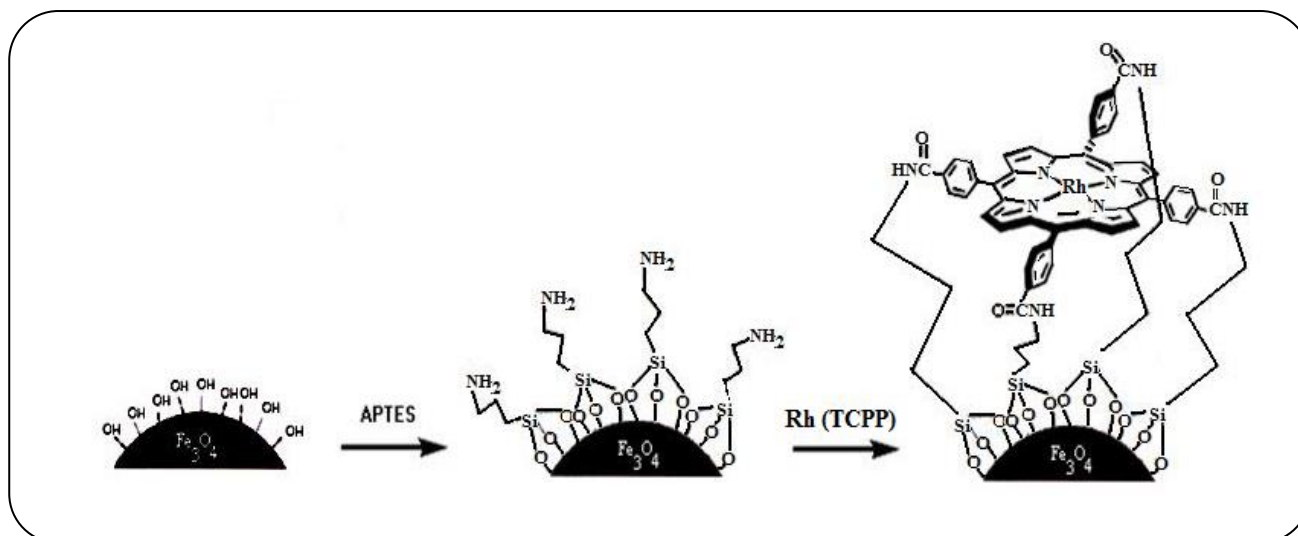


Fig. 1: Chemical functionalization of magnetite surfaces using APTES followed by metalloporphyrin insertion.

In order to prevent the presence of volatile dimethylamine, a product of DMF decomposition, a high flux of nitrogen is recommended. After reaction, the solid Fe₃O₄/APTES/Rh (TCPP) nanoparticles were isolated magnetically and washed with DMF, CH₂Cl₂ and methanol, for the elimination of porphyrins that are electrostatically bonded to Fe₃O₄/APTES. A scheme of the magnetite surface modification process is shown in Fig. 1.

Sorption procedure

Batch-adsorption studies were performed by mixing 10 mL thiocyanate aqueous solution (20 mg/L) and various amounts (25–250 mg) dry powder of the Fe₃O₄/APTES/Rh (TCPP) nanoparticles in a stoppered flask which was shaken at 200 rpm and room temperature for a predefined time. The sorbent was separated before measurement and the residual thiocyanate concentration was determined using standard methods for the examination of water and wastewater. An aliquot of thiocyanate sample was reacted with acidified ferric nitrate reagent to produce a red-colored ferri-thiocyanate complex. The Thiocyanate removal efficiency was calculated according to Eq. (1):

$$\text{Thiocyanate removal efficiency (\%)} = \left[\frac{C_0 - C_r}{C_0} \right] \times 100 \quad (1)$$

where C_0 and C_r are the initial and final concentrations of the thiocyanate ion before and after the sorption, respectively.

RESULT AND DISCUSSION

Characterization of nanomagnets

Structure and particle size determination by XRD and TEM

The XRD patterns of the synthesized nanosorbent and pure magnetite of the Joint Committee on Powder Diffraction Standards (JCPDS No.19-629) were exactly matched (Fig. 2). Another proof for the identity of the black powder and magnetite was the absence of the Fe₂O₃ peaks ranging from 2θ angel of 20° to 30°. The XRD pattern of the synthesized magnetic nanoparticles was in good agreement with that of the standard Fe₃O₄ structure.

The particle size and morphological characteristics of the magnetite nanoparticles, before and after surface modification, were investigated by using TEM (Fig. 3 a,b). The dark nano-Fe₃O₄ cores surrounded by a grey shell could be observed. Moreover, the bare Fe₃O₄ nanoparticles had a mean diameter of about 23 nm, much smaller than the functionalized one (36nm). To analyze the size distribution quantitatively, the particle size distribution was obtained from size histograms. The size distribution histogram (Fig. 3c) shows an average particle size of 45 nm with size distribution standard deviation of 1.28 nm which was obtained by analyzing 300 particles statistically. As can be seen, more than 75 % of the particles are in the range of 40-50 nm. It should be noted that the bare Fe₃O₄ nanoparticles had a mean diameter of about 23 nm and after APTES introduction; particles with an average diameter of 36 nm were observed.

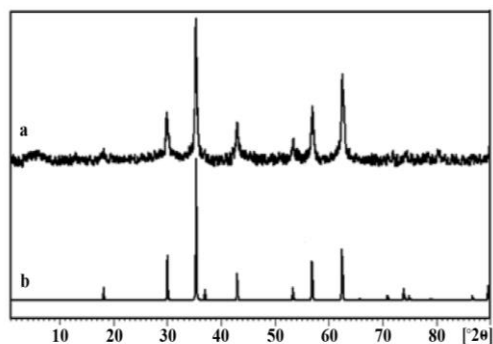


Fig. 2: (a) XRD patterns of $Fe_3O_4/APTES/Rh(TCPP)$ nanoadsorbent and (b) JCPDS No.19-629.

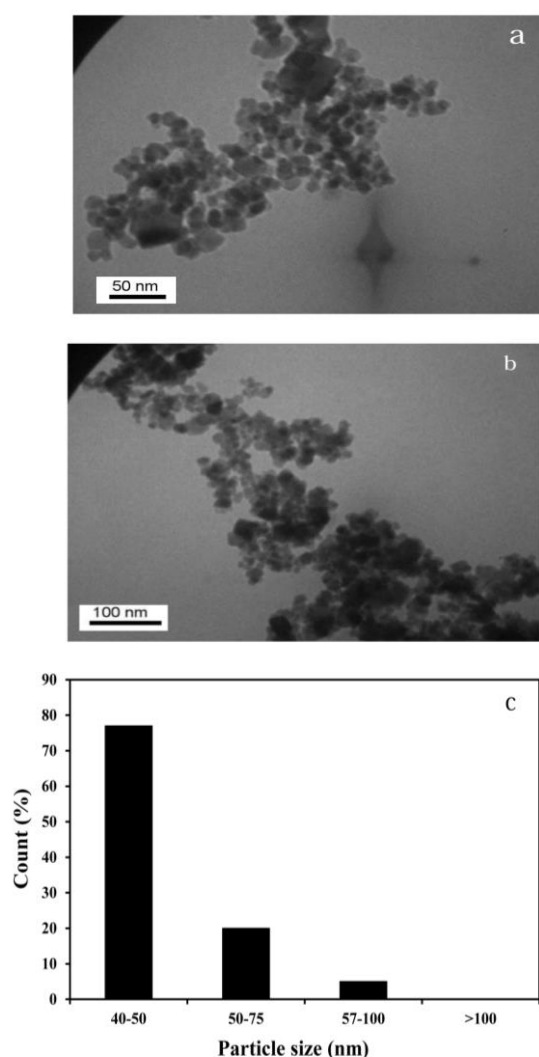


Fig. 3: TEM images of Fe_3O_4 (a), $Fe_3O_4/APTES/Rh(TCPP)$ nanoadsorbent. particle size distribution histogram (c).

FT-IR studies

Structure of the synthesized nanosorbent was characterized by FT-IR spectroscopy (Fig. 4).

The characteristic peak of magnetite is Fe–O stretching band at 580cm^{-1} which confirmed the presence of magnetite nanoparticles (Fig. 4a). The introduction of APTES to the surface of Fe_3O_4 nanoparticles was confirmed by the bands around 1115 and 1030 cm^{-1} from the Si–O–H and Si–O–Si groups. The two bands at 3445 and 1640 cm^{-1} ascribed to the N–H stretching vibration and NH_2 bending mode of free NH_2 groups, respectively and the C–H stretching vibration that appeared at 2930 and 2862 cm^{-1} confirmed (Fig. 4b). Moreover, the FT-IR spectrum revealed the C=C stretching vibrations of the aromatic ring at 1500 cm^{-1} , the stretching band of the amide C–N peak at 1260 cm^{-1} and a peak at 1687 cm^{-1} relating to the amide group stretching band, which prove the covalent attachment of rhodium (III) porphyrin (Fig. 4c).

TGA analysis

The thermal stability of the synthesized nanosorbent was investigated. The relative comparison between weight losses of each sample with the previous one was applied to assess the organic content over the surface of the as-synthesized samples. From the TGA curves, the weight loss or extent of modification reaction (relative to the primary Fe_3O_4 nanoparticles) for $Fe_3O_4/APTES$ nanoparticles, and $Fe_3O_4/APTES/Rh(TCPP)$ nanosorbents were 6 and 5.0,% respectively (Fig 5 a,b,c). The TG curve of the $Fe_3O_4/APTES/Rh(TCPP)$ is shown in Fig. 5c. As can be seen three stages of weight loss are detected: the first weight loss could be explained by the evaporation of the adsorbed solvent attached to the particle surfaces. The second weight-loss stage might result from loss of the APTES layer [40]. The third weight-loss stage may result from the decomposition of metalloporphyrin [41]. These data show that coating and modification of Fe_3O_4 nanoparticles with metalloporphyrin has been performed successfully.

Adsorption experiments

pH, contact time, and sorbent dosage are the main factors which needed to be optimized.

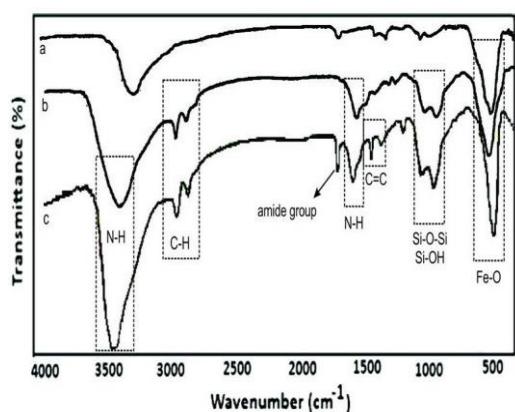


Fig. 4: FT-IR spectra of Fe_3O_4 nanoparticles (a); $Fe_3O_4/APTES$ nanoparticles (b); and $Fe_3O_4/APTES/Rh$ (TCPP) nanoadsorbent (c).

Effect of solution pH

Adsorption of the analyte onto the nanosorbent varies with pH. The sorption studies were carried out using different pH values, in the range of 2 to 11, into 25 mL of solution (20 mg/L, 150 mg MNPs, room temperature) with contact time of 20 min. As presented in Fig. 6 slight variations could be seen of the thiocyanate removal percentage in the 5.0-7.0 pH range. At higher pH values the hydroxyl groups will compete with thiocyanate ions in the active sites of the composite during sorption. On the other hand due to the partial demetallation of the metalloporphyrin complex at lower pH values the thiocyanate removal is decreased. Therefore, pH 5.5 was employed for all subsequent experiments.

Effect of contact time

The effect of contact time on removal efficiency was studied at the range of 0 to 120 min. The experiments were carried out in 25 mL of solution with pH of 5.5 (20 mg/L, 150 mg MNPs, room temperature). The removal of thiocyanate from water with time is shown in Fig. 7. As could be seen the removal of thiocyanate increases in accordance with contact time and after 20 min most of the thiocyanate is removed and reaches a maximum at 1 h and thereafter remains constant. Therefore, 20 min was considered as the optimum value for the subsequent experiments.

Effect of the adsorbent dosage

The amount of adsorbent is an important factor to determine adsorption capacity. For this purpose, some

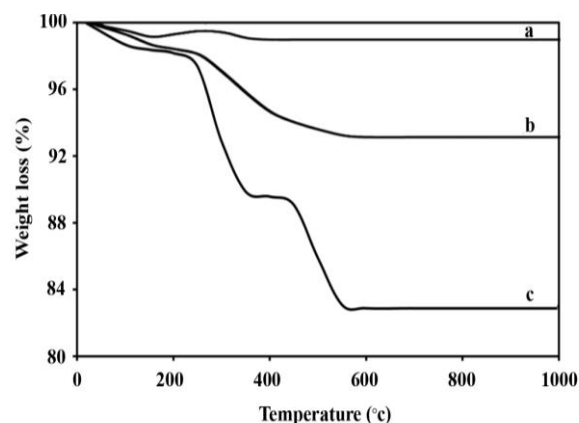


Fig. 5: Thermogravimetric analysis of Fe_3O_4 nanoparticles (a); $Fe_3O_4/APTES$ nanoparticles (b); and $Fe_3O_4/APTES/Rh$ (TCPP) nanoadsorbent (c).

experiments were individually carried out by adding different amounts of MNPs from 25 to 250 mg into 25 mL of solution (20 mg/L, pH = 5.5, room temperature) with contact time of 20 min. As seen in Fig. 8, an increase in adsorbent dosage increased the percent removal of thiocyanate and attained to maximum at 150 mg of nanosorbent and then no further thiocyanate removal is observed by increasing the adsorbent dose. Therefore, in all the experiments, 150 mg of the nanoadsorbents was fixed as the optimum dose.

Thiocyanate removal study

In this study, synthesis of a nanomagnet encompassing a metalloporphyrin derivative with unique interaction with thiocyanate ion was aimed. Metallocomplexes of Rhodium were evaluated as an ion carrier in construction of thiocyanate selective sensors [42, 43]. To inspect the extracting ability of the proposed nanosorbent towards thiocyanate ion, solid phase extraction was carried out. The extraction result showed that under optimal conditions (contact time: 20 min, pH=5.5, adsorbate 20 mg/L and adsorbent amount 150 mg) the percentage of thiocyanate ions extracted was 92%.

Effect of competing anions

Bi-anion adsorption of nanoadsorbents was examined in the presence of sodium salts of NO_3^- , NO_2^- , F^- , Br^- and Cl^- with a concentration of 20 mg/L and the same concentration of thiocyanate. As seen in Table 1, the removal percentage of SCN^- in the presence of co-existing anion was in the range of 87.1–90.2%.

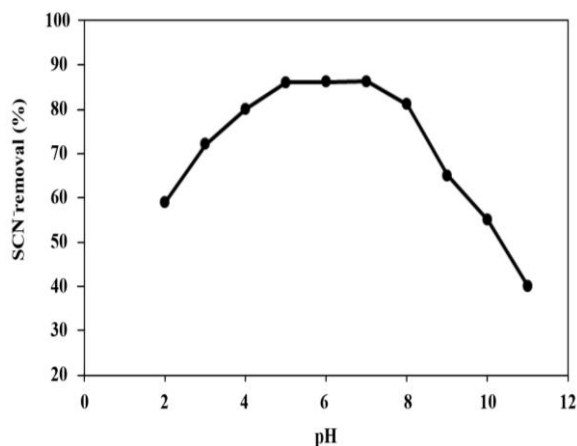


Fig. 6: The pH influence on the removal efficiency of thiocyanate.

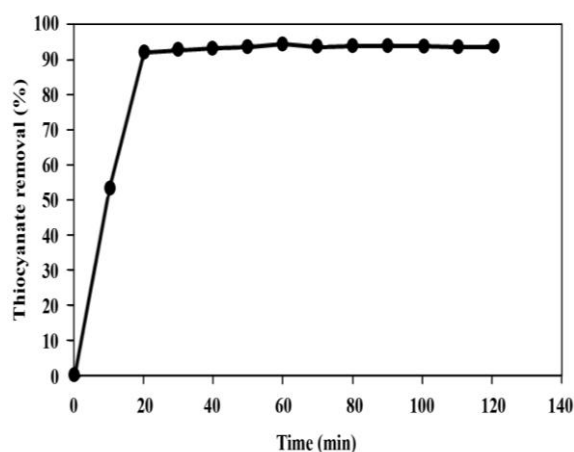


Fig. 7: Effect of contact time on the removal efficiency of thiocyanate.

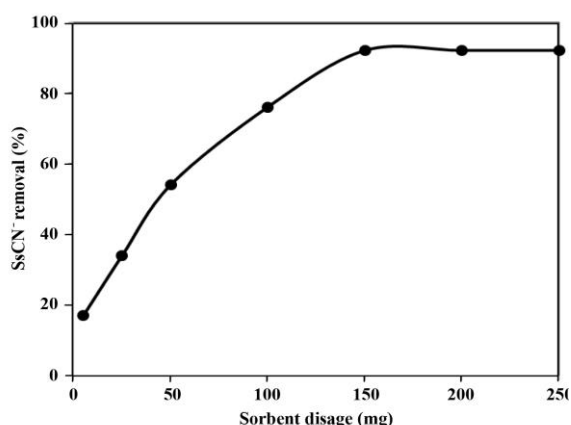


Fig. 8: Effect of nanoadsorbents dosage on the removal efficiency of thiocyanate.

This value was close to the optimized value with no interfering anion; so these anions had little effect on the removal of SCN^- by $\text{Fe}_3\text{O}_4/\text{APTES}/\text{Rh}$ (TCPP) nanosorbents. This observation can be explained by the capability of metalloporphyrins to bind the anions in a selective way which is proved in various anion selective sensors.

Electrokinetic measurements

Adsorption phenomenon of the sorbent is usually connected to its electrokinetic behavior which is determined by the net surface charge of the particles [44] and zero point of charge (pH_{zpc}) [42]. To investigate the zeta potential behavior of the sorbents as a function of the pH, 1 gr of nanosorbents was conditioned in 100 mL of 10^{-4}M KCl at various pH values for 24 hours, then the suspension was kept still for 10 min to let the larger particles settle down [42]. Fig. 9 shows that pH_{zpc} is about 7.7, i.e. the sorbent surface is positively charged at lower pH values and vice versa. The observed trend is a good solution for the recovery of thiocyanate and regeneration of nanosorbent after extraction.

Reusability of $\text{Fe}_3\text{O}_4/\text{APTES}/\text{Rh}$ (TCPP) nanosorbents

To make an economic process the adsorbent should be regenerable. In this work NaOH was chosen as stripping reagent to recover the thiocyanate ions from the adsorbents. It was found that with a NaOH solution with 5, 10, 15, 20 and 25 mM concentrations, the percentages of thiocyanate released were 55.1, 75.2, 97.0, 97.2 and 97.1, respectively. Therefore, the highest recovery was obtained by using NaOH 15 mM solution.

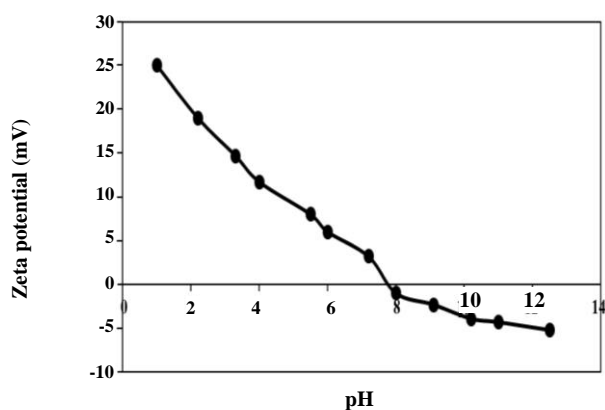
After the first regeneration, the adsorption studies were repeated; the nanosorbents were again regenerated and subjected to further adsorption. In this study, the desorption limit for thiocyanate was four cycles. The desorption efficiencies of the nanoadsorbents from the five cycles were 97.1%, 96.6%, 95.2%, 93.8 and 88.4%, respectively; suggesting that the modified nanoparticles are regenerable and can be used for a couple of times. It should be remind that the chemical bonding between Rh porphyrin and magnetic nanoparticles plays the major role in retaining the capacity of the $\text{Fe}_3\text{O}_4/\text{APTES}/\text{Rh}$ (TCPP) nanosorbents.

CONCLUSIONS

In this study, $\text{Fe}_3\text{O}_4/\text{APTES}/\text{Rh}$ (TCPP) nanoadsorbents is prepared and showed good efficiency

Table 1: Effect of co-existing anions on the removal of SCN⁻ by Fe₃O₄/APTES/Rh (TCPP) nanosorbents.

| Anions in the solution | Removal of SCN ⁻ (%) |
|---|---------------------------------|
| SCN ⁻ only | 92.2 |
| SCN ⁻ + NO ₃ ⁻ | 87.6 |
| SCN ⁻ + NO ₂ ⁻ | 87.1 |
| SCN ⁻ + F ⁻ | 88.2 |
| SCN ⁻ + Br ⁻ | 90.2 |
| SCN ⁻ + Cl ⁻ | 87.3 |

**Fig. 9: The electrokinetic behaviour of Fe₃O₄/APTES/Rh (TCPP) nanoadsorbent.**

towards removal of thiocyanate from water sample. The main conclusions from this study are as follows:

(i) Batch experiments indicate that removal of thiocyanate was very rapid, i.e. most of the thiocyanate was removed during 20 min and reaches to maximum of 94.2% at 1 h.

(ii) The removal of thiocyanate is pH independent in the range of 5.0-7.0; beyond this range the removal efficiency decreases.

(iii) The presence of coexisting anions has little influence on thiocyanate removal efficiency.

(iv) The used nanoadsorbents can be regenerated for four cycles.

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