Original Research Article

Removal of Aqueous Thiocyanate Anions by Titanium Dioxide Nanoparticles

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## ABSTRACT

Dissolved Thiocyanate in drinking water is a source of global health concern. The purpose of the present study was to remove aqueous Thiocyanate anions by using the titanium dioxide nanoparticles (TiO$_2$ NPs). Titanium dioxide is inexpensive and non-toxic, making it an attractive choice for drinking water purification. Thiocyanate was adsorbed by the surface of nanoparticles into Fe-SCN complex and a filter was used for removing the nanoparticles. The effect of different parameters such as pH, buffer, time of stirring, the number of nanoparticles, concentration of the aqueous iron, and concentration of the electrolyte and its optimal amounts were investigated. Removal of the aqueous SCN$^-$ showed the best performance at the pH of 9, 0.5 mL of buffer, stirring for 15 min, and 0.5 g of TiO$_2$. It was analyzed by means of spectrophotometry at λ=456.8 nm. Langmuir adsorption isotherm and Freundlich adsorption isotherm explained the best correlation between the Thiocyanate adsorption and equilibrium data. Langmuir adsorption isotherm showed more adaptability and the its sorption capacity was 11.6 mg/g^{-1} for nanoparticles. This method was tested for removing Thiocyanate from some real samples including tape water, Karoon River water, and water from petrochemical wastewater. Majority of the TiO$_2$ NPs revealed an acceptable sorption capacity and reuse-ability in Thiocyanate anions removal in water solution.

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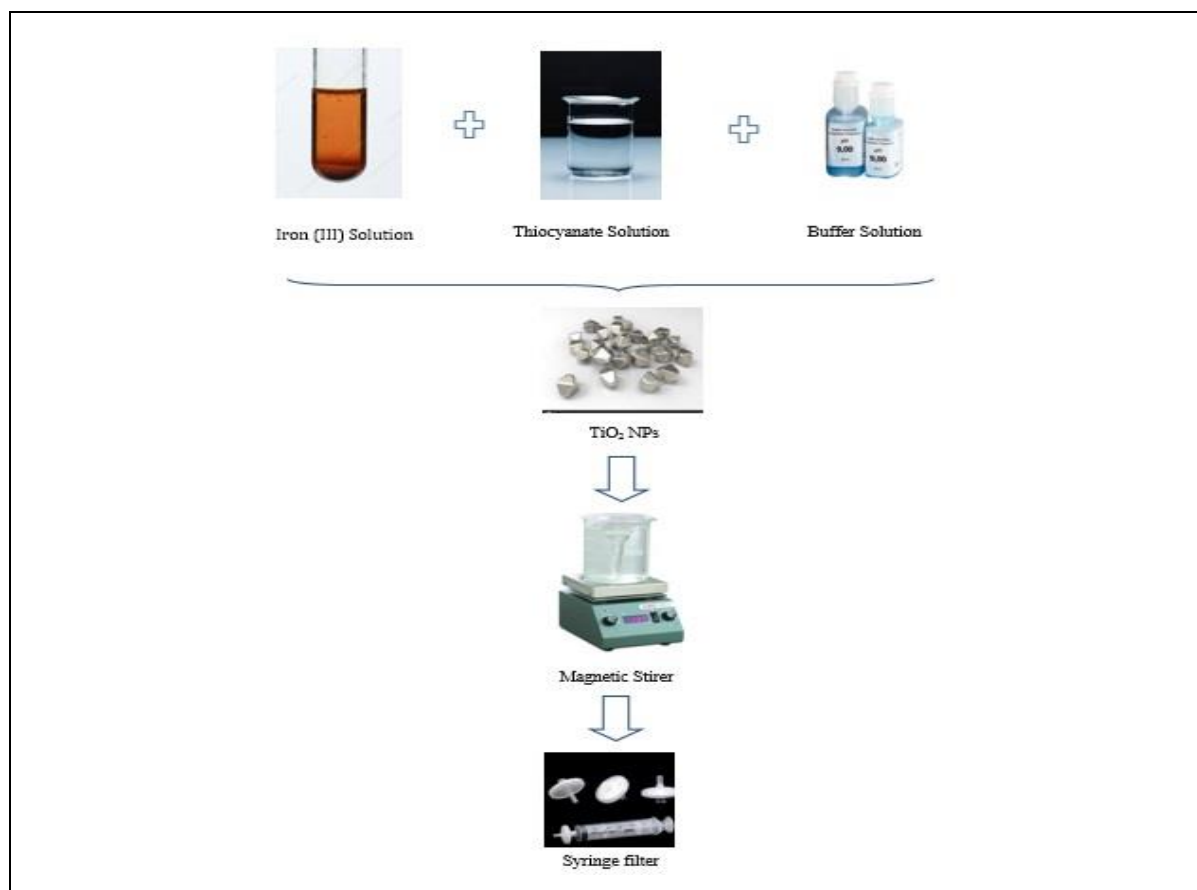
Introduction

Determination of the Thiocyanate in biomedical fluids is a phenomenon that is of interest in biomedical and toxicology sciences [1,2]. These compounds have some serious effects, especially on the nervous system, such as Alzheimer's disease, nervousness, hallucination, psychosis, delusion, and seizure [3,4]. By increasing the amount of the molecular mass of the Thiocyanate alkyl, its disadvantages decrease. This substance exists in industrial wastewater, pesticide residues, and organic metabolism. Thiocyanate is the product of detoxification, reforming of hydrogen cyanide [5]. This anion distributes its negative charge between Sulfur and Nitrogen almost alike. Thiocyanate can also be considered as a Nucleophile such that two or three metal can connect to it [6,7]. The first research about the determination of Thiocyanate particles in biological fluids was conducted based on spectrophotometric detection and intricacy of colors [8]. After that, colorimetric determination of ions and detection radar of Thiocyanate by UV ray at λ=210 nm, or suppressant heat transfer were used [9]. For determining the adsorption of biological fluids, it is advised to use mass spectroscopy with overuse of liquid colorimetric and gas colorimetric [10-12]. Nanostructures exist in every surface and synthesizing many of them can be inspired by various species in nature. Researchers have enhanced the level of reactivity in nanostructures as the number of molecules and atoms on the surface is more than in the volume, so that they have received much attention for agglomeration applications [13]. Using nanotechnology because of having high removal efficiency for these pollution

particles can be considered as one of the best methods for removal of Thiocyanate. Titanium dioxide nanoparticles (TiO$_2$ NPs) showed good properties such as electrical, optical, and photo catalytical properties [14]. Titanium dioxide, also known as Titanium oxide (IV) or Titania is shown by TiO$_2$. All properties of TiO$_2$ also exists in nano-TiO$_2$ except that its particles size is so smaller, which leads to new properties. Being self-cleaner and photo-catalytic are two important properties of this substance. When the TiO$_2$ particles size decrease to nano scale, the photo-catalytic activity will improve due to increasing the effective surface. TiO$_2$ is used for eliminating organic pollutants such as toluene, surfactants, insecticides, aromatic sulfides, hydrocarbons, and organic dyes [15-17]. Good adsorption, chemical, and physical stability, non-toxicity, resistance to rusting, and low price are some of the advantages of TiO$_2$ [18,19]. By controlling TiO$_2$ nanoparticles through several parameters such as size, form, and porosity, it is possible to use them in thin layers, ceramics, composites, and catalysts [20]. Baorung Li *et al.,* (2003) added Tetra-*n*-butyl Titanate to deionized water and then added ammonium chloride to it to make a gel. Then, after drying, grinding, and calcinating this gel at different temperatures, they gained TiO$_2$ nano-powder [21]. Several hydro-thermal compound models have been used for the synthesis of TiO$_2$ NPs [22]. Thakare *et al.,* (2016) used a mechanochemistry method to make TiO$_2$ nanoparticles with microwave [23]. Ishigaki *et al.,* (2008) applied a thermal plasma method with radio frequency to synthesize TiO$_2$ nanoparticles from an organic precursor [24]. Shiping Xu *et al.,* (2011) used TiO$_2$ nanotubes as a photo-catalyst to separate copper from water and produce hydrogen simultaneously [25]. In this method, 1-D mesoporous tianyum dioxide (TNT) was prepared by a calcination-hydrothermal method. For this purpose, they used photo-

catalytic H$_2$ and Cu^{2+} in the concentration range of 8–800 ppm. After separation, Cu^{2+} in cooperation with TNT, made Cu-TNT, an effective photo-catalytic compound in order to produce H$_2$. Ying Zhao *et al.,* (2013) used restored graphene oxide covered by TiO$_2$ nanoparticles (TiO$_2$-RGO) in order to separate Cr (VI) from aqua solutions [26]. Bao *et al.,* (2016) used TiO$_2$ supported by nano-tubes and carbon walls in order to remove SO$_2$ in a photo-catalytic method [27]. Aghaie and Mohammadi (2016) used hydro-phobic surfaces combined with magnetic iron oxide nanoparticles modified adsorbent to remove and recover metals by magnetic and dispersive solid phase extraction method [28]. They reached this conclusion that the applied extraction method is effective and fast. Also, they observed a low enrichment factor, low detection limit, and high restore level. Precipitate [29], ion exchange [30], severe filtration [31], adsorption [32-35], membrane separation [36], and constructed wetlands [37] are some methods that are used to remove metals. Adsorption is often superior to particle removal because of its cost-effectiveness, easy setup, and flexibility compared with other methods [38,39]. Recently, nano-sorbents have received much attention because of their particle size and surface treatment, which lead to the high chemical reactivity and increase in interference between adsorption and adsorption material [40,41]. The concentration range of nano sorbents for pollutant removal is in the range of 1-1000 ppm [42]. During recent years, different studies have been conducted to remove Thiocyanate. Shukla *et al.,* (2004) measured Thiocyanate anion in wastewater of factories and industries using a spectrophotometry method. The linear range and limit of detection were reported to be $6.3×10^{-7}$ to $1.0×10^{-2}$ mol/L^{-1} and $3.16×10^{-7}$ mol/L^{-1}, respectively [43]. Yujiang Li *et al.,* (2008) studied separating Thiocyanate from aquatic

environments and sorption kinetics by calcinid hydro-catalyst [44]. Yang *et al.,* (2007) measured different concentrations of Thiocyanate using a glassy carbon electrode modified by silver nanoparticles and coated with carbon nanotubes [45]. Niemann and Anderson (2008) examined iodide and Thiocyanate ions in powdered milk and baby milk via ion exchange chromatography [46]. The result demonstrated that, in some of the baby milk samples, the amount of Thiocyanate and iodide ions was 2.0-5.1 mg/Kg[-1] and 0.3-1.3 mg/Kg[-1], respectively. Vitali *et al.,* (2011) successfully measured the nitrate and Thiocyanate in biological samples by a capillary electrophoresis method [47]. Zhang *et al.,* (2012) measured the Thiocyanate anion by using the gold nanoparticles modified with cysteamine by a colorimetric method [48]. Jiang *et al.,* (2008) assessed the effect of crystal phase on the adsorption behavior of the Titania nanoparticles and the correlation between the crystal phase and oxidant capacity. They described the dependence of the physicochemical properties of nanoparticles on their oxidant generating capacity proposed and demonstrated for TiO_2 nanoparticles [49]. In the present study, TiO_2, as an economical and nontoxic sorbent, was used in the adsorption of Thiocyanate anions. Also, the effect of many factors that interfere on adsorption was investigated. The correlation between the Thiocyanate adsorption and equilibrium data was studied by Langmuir adsorption isotherm and Freundlich adsorption isotherm. Finally, the results of the Thiocyanate removal from real samples were represented. The novelty of this research is that the mechanism of removal of Thiocyanate with TiO_2 is based on a reversible physical adsorption while most researches use photocatalytic methods. Furthermore, since the adsorbed Thiocyanate can be easily extracted from adsorbent, there is no need to use a modifier to adjust the surface of the nanoparticles and also nanoparticles are reusable which enhance the performance of the method.

Experimental

Materials and methods

Double beam spectrophotometer (model Lambda 135, manufactured by Perkin-Elmer), and 1 cm TB glass were used for measuring the adsorption of the colored complex of iron-Thiocyanate at λ=456.8 nm and drawing a spectrum. The pH values were adjusted using a pH meter (model F-11) manufactured by Horiba company in Japan. The balance model BP210D (weight capacity=200 g and precision=0.0001 g) manufactured by Sartorius company in Switzerland was used for weighing. A centrifuge *H*-11n manufactured by Kokusan company in Japan was used for the centrifuge. To take the transmission electron microscopy (TEM) photos, Leo 906 device manufactured by Germany was used. To filter the synthesized particles, a syringe filter (Biofil manufactured by China) with a pore size of 0.22 μm and a maximum pressure tolerance of 4.5 bar was used. Iron (III) chloride, solid potassium Thiocyanate, sodium hydroxide, and other materials (all with a high purity) were purchased from Merck. Titanium dioxide adsorbent (purity=99.5-100) was provided by Neutrino, a local company.

Preparation of samples for analysis

First, 2.70 g of iron (III) chloride hexahydrate was carefully weighed by a digital balance and transferred to a 100 mL volumetric flask. Next, it was dissolved in a small amount of water and then was brought to volume by adding fresh distilled water. In the next step, 0.169 g of solid potassium Thiocyanate was carefully weighed by a digital balance and put in a 100 mL volumetric flask. It was dissolved in a small amount of water and then was brought to volume by

adding fresh distilled water. Afterward, 0.75 mL of 13.38 mol/L^{-1} ammonia solution (0.91 g/mL^{-1}, 25% W/W) was put in a 500 mL volumetric flask by micropipette and was brought to volume. The pH of the solution was adjusted with 0.1 mol/L^{-1} hydrochloric acid solution. About 8.33 mL of 12 mol/L^{-1} hydrochloric acid solution (1.19 g/mL^{-1}, 37% W/W) was put in a 1000 mL volumetric flask and then was brought to 1000 mL volume by adding distilled water. For the synthesis of sodium hydroxide solution with a concentration of 0.1 mol/L^{-1}, 1.00 g solid sodium hydroxide with high purity was taken. Finally, after dissolving in a small amount of water, it was brought to volume by adding distilled water in a 250 mL balloon.

General procedure

For adsorbing and removing Thiocyanate by TiO$_2$ NPs, 1 mL of 100 μg/mL^{-1} Thiocyanate solution, 1 mL of 0.1 mol/L^{-1} iron (III) solution, and 0.5 mL buffer (pH=9) were placed in a 10 mL volumetric flask. Next, by adding distilled water, it was brought to volume and the resulting solution was moved to a 50 mL volumetric flask containing 0.5 g TiO$_2$ NPs. The mixture was placed on a magnetic stirrer for 15 min and then nanoparticles were removed by the filter. To measure the amount of residual Thiocyanate after removal, the resulting solution was drawn into the syringe, filtered using the syringe filter, and moved to a 1 cm glass cell. Next, the adsorption of this solution was determined in contrast with the control solution by spectrophotometric in the maximum wavelength of 456.8 nm. The remaining Thiocyanate was measured using the calibration curve. It is noteworthy that the control solution had the same texture materials with sample solutions, except Thiocyanate, and underwent all stages of separation. The results show that

in all stages, the absorbance of the solution occured in the maximum wavelength and Thiocyanate was removed by nanoparticles.

Results and discussion

SEM analysis

Scanning electron microscopy (SEM) was used to study the prepared TiO$_2$ NPs. The average particle size of the adsorbent was 21 nm and their specific surface area was 50±15 m^2/g^{-1}. The obtained pictures showed a drop in the size of prepared TiO$_2$ NPs (Figure 1a).

Determining the maximum wavelength (λ_{Max})

The maximum wavelength can be considered as an important controller in quantitative and qualitative measurements. For this reason, the spectrum of Thiocyanate-iron complex was drawn in the wavelength range of 350-700 nm (Figure 1b). In order to draw the spectrum, 1 mL of 100 μg/mL^{-1} Thiocyanate solution and 1 mL of 0.1 mol/L^{-1} iron (III) solution were put in a 10 mL volumetric flask and brought to volume by adding distilled water. Next, some of this solution was moved to a 1 cm glass cell and its visible continuous spectrum against distilled water was obtained by spectrophotometer machine. Since the maximum adsorption of the resulting solution was observed at λ=456.8 nm, this wavelength was used for measuring the adsorption and concentration of Thiocyanate in all stages of measurement and extraction.

Studying the optimization of parameters affecting the adsorption of thiocyanate

To achieve the highest Thiocyanate adsorption and acceptable repeatability, pH, adsorbent weight, electrolyte, temperature, solution volume, and concentration of acid required for elution were studied.
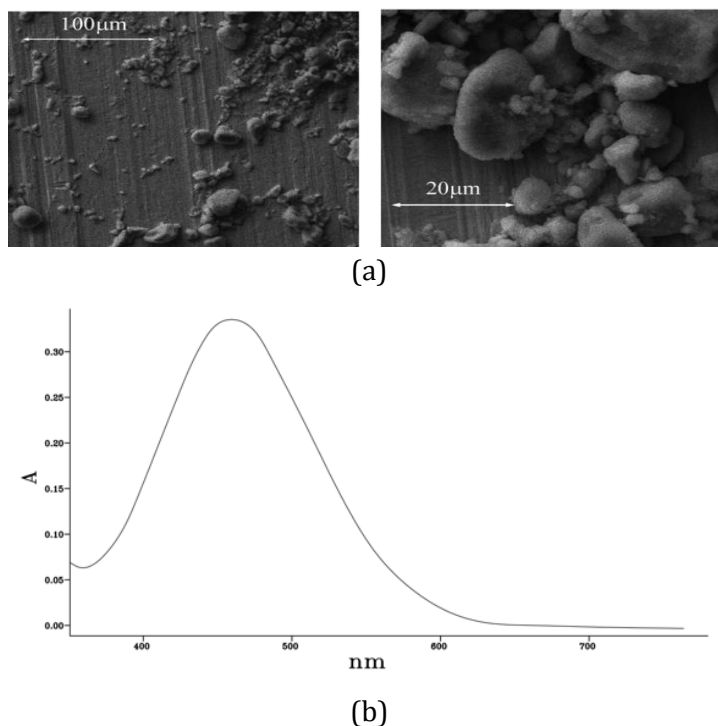
(a)

(b)

Figure 1. (a) SEM images of TiO_2 NPs; and (b) adsorption spectrum of Thiocyanate-iron complex

Studying pH effect

One of the most important parameters especially at the beginning of the study results is studying the effect of pH of the sample solution during testing. The pH of the sample solution plays an effective role in keeping the metal ions in the solid phase extraction method [50]. To study the pH effects, 5 mL of 1000 mg/L^{-1} Thiocyanate solution was added to 50 mL volumetric flasks. Each solution was added a different amount of sodium hydroxide and hydrochloric acid to prepare solutions with pH in the range of 4 to 10. After that, 5 mL of 0.1 mol/L^{-1} iron (III) solution was added to each solution and was brought to volume by adding distilled water. Each of these solutions was moved to a volumetric flask, placed in contact with 0.5 g adsorbent of TiO_2 NPs, and then placed on a magnetic stirrer for 20 min. Next, a part of the solution was drawn into the syringe and cleared by syringe filter. The adsorption of each solution was determined by spectrophotometry at λ=456.8 nm and in contrast with the control solution and

removal percentage of Thiocyanate was calculated (Figure 2a). It was observed that the removal percentage did not change significantly in this range of pH, however the highest amount of removal was seen at pH=9, so it was selected as the optimal amount. Then, the ammonia buffer was used to adjust the pH.

Optimizing amount of buffer

The ammonia buffer may destroy the adsorption spectrum and decline λ_{Max} in volumes more than 0.5 mL and concentrations greater than 0.02 mol/L^{-1}. Thus, the optimal amount of buffer was determined as 0.5 mL of ammonia buffer with 0.02 mol/L^{-1} concentration, and added to 1 mL of 100 µg/mL^{-1} Thiocyanate solution and 1 mL of 0.1 mol/L^{-1} iron (III) solution. Then, in a 10 mL volumetric flask, it was brought to 10 mL volume by adding distilled water. The pH of the solution was determined to be 9 by a pH meter.
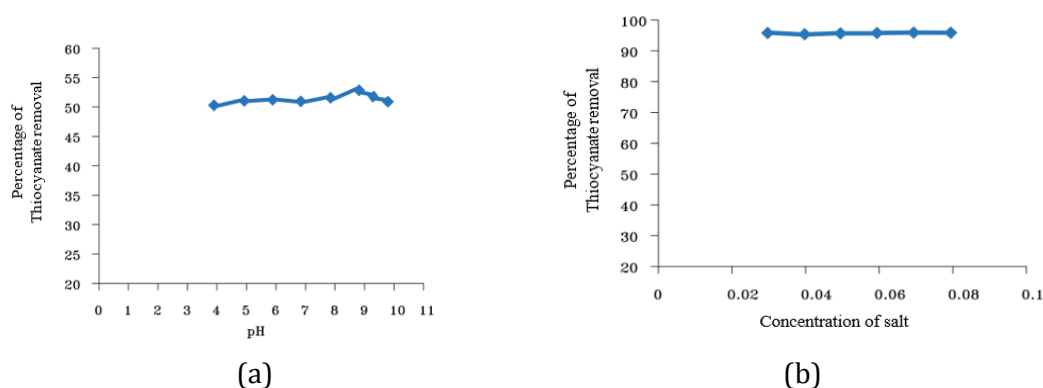
(a)   (b)

Figure 2. (a) Effect of pH on removal percentage of Thiocyanate; and (b) effect of salt concentration on removal percentage of Thiocyanate

Table 1. Effect of salt concentration on Thiocyanate removal

Salt concentration (mol/L^{-1})	Adsorption	R(%)
0.03	.0100	96.20
0.04	0.0098	96.20
0.05	0.0095	96.30
0.06	0.0091	96.40
0.07	0.0089	96.50
0.08	0.0086	96.50

Studying effect of salt concentration

To evaluate the effect of salt concentration, sodium nitrate (NaNO$_3$) was chosen and its 1 mol/L^{-1} solution was prepared. For studying the effect of salt concentration on removing Thiocyanate, 1 mL of 100 μg/mL^{-1} Thiocyanate solution, 1 mL of 0.1 mol/L^{-1} iron (III) solution, and 0.5 mL of ammonia buffer with pH=9 were placed in a 10 mL volumetric flask for every solution. Afterward, it was added with different amounts of salt solution (based on Table 1) and brought to volume by adding distilled water. Each solution was moved to a 50 mL volumetric flask containing 0.5 g TiO$_2$ NPs and was placed on a magnetic stirrer for 15 min. The solutions were cleared by the filter and the adsorption of each solution was determined by spectrophotometry in λ=456.8 nm and in contrast with the control solution (Figure 2b). According to the results, salt concentration

revealed no effect on the removal of Thiocyanate by TiO$_2$ nanoparticles.

Optimizing iron (III) solution volume

For this purpose, 1 mL of 100 μg/mL^{-1} Thiocyanate solution and 0.5 mL of ammonia buffer were added to 10 mL volumetric flasks. Next, different amounts of 0.1 mol/L^{-1} iron (III) solution were added to the solution. After bringing it to volume by distilled water, the solution was moved to a 50 mL volumetric flask containing 0.5 g TiO$_2$ NPs. In the next step, it was placed on magnetic stirrer for 15 min. Then, the solution was drawn into the syringe and cleared by syringe filter. The adsorption of each solution was determined by spectrophotometry at λ=456.8 nm and the removal percentage of Thiocyanate was calculated in contrast with the control solution. Figure 3a, shows the effect of different concentrations of Fe (III) solution on removal percentage of Thiocyanate, where the

optimum amount for the concentration of Fe (III) solution is 0.1 mol/L^{-1}. When solutions containing Fe^{3+} and Thiocyanate ions are mixed, the deep red Thiocyanate iron (III) ion ($[FeSCN]^{2+}$) is formed. As a result of the reaction, the starting concentrations of Fe^{3+} and SCN^- will decrease. For every mole of $[FeSCN]^{2+}$ that is formed, one mole of Fe^{3+} and one mole of SCN^- will react. In this study, the initial amounts of Fe^{3+} and SCN^- are 5×10^{-5} mol and 0.85×10^{-5} mol respectively in 50 mL solution. Since the adsorbent adsorbs Thiocyanate in the complex form, the amount of iron remained in the solution would be 4.5×10^{-5} mol.

Studying amount of adsorbent

To optimize the amount of adsorbent needed for removing Thiocyanate from solutions with the final concentration of 10 µg/mL^{-1} of Thiocyanate in pH=9, different amounts of TiO$_2$ NPs were tested. To prepare the solutions, 1 mL of 100 µg/mL^{-1} Thiocyanate solution, 1 mL of 0.1 mol/L^{-1} iron (III) solution, and 0.5 mL of 0.02 mol/L^{-1} ammonia buffer were placed in a 10 mL volumetric flask and brought to volume by adding distilled water. These solutions were moved to 50 mL volumetric flasks containing different amounts of TiO$_2$ NPs. The amount of these nanoparticles is according to the information in Table 2. After 15 min, the solutions were cleared by the filter and the absorption of each solution was determined by spectrophotometry at λ=456.8 nm and in contrast with the control solution (Figure 3b). According to the results, 0.5 g was chosen as the optimum amount for TiO$_2$ NPs. This amount of adsorbent was economical because after adsorbing Thiocyanate by nanoparticles, around 98% of them can be rinsed by ethanol and nanoparticles can be reused for Thiocyanate adsorption.
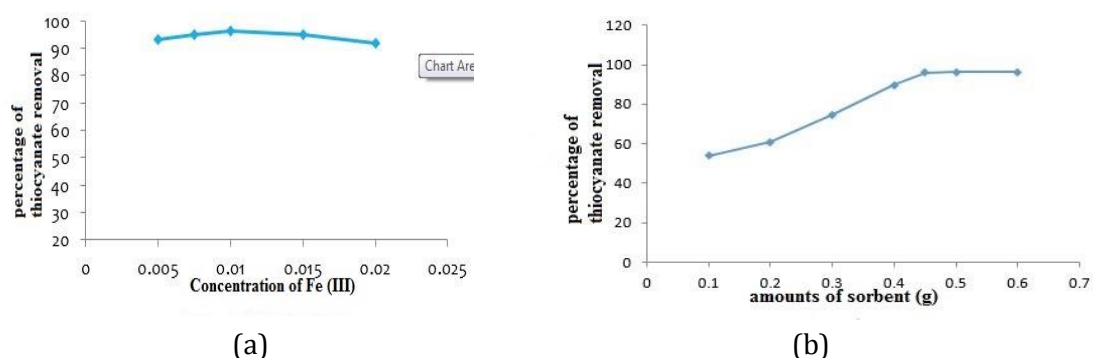

(a) (b)

Figure 3. (a) Concentration of Fe (III) solution effect on removal percentage of Thiocyanate; and (b) effect of salt concentration on removal percentage of Thiocyanate

Table 2. Effect of different amounts of adsorbent on Thiocyanate removal

Mass of adsorbent (g)	Adsorption	R(%)
0.10	0.151	53.98
0.20	0.129	60.69
0.30	0.082	74.60
0.40	0.032	89.59
0.45	0.011	95.92
0.50	0.011	96.20
0.60	0.010	96.20

Studying effect of stirring time

The effect of stirring time was studied on Thiocyanate adsorption on TiO_2 NPs. For this purpose, to every solution, 1 mL of 100 µg/mL^{-1} Thiocyanate solution, 1 mL of 0.1 mol/L^{-1} iron (III) solution, and 0.5 mL of 0.02 mol/L^{-1} ammonia buffer were added in a 10 mL volumetric flask and brought to volume by adding distilled water. Every solution was moved to 50 mL volumetric flask containing 0.1 g of TiO_2 NPs and every volumetric flask was placed in a magnetic stirrer for a specific time. A filter was used for removing nanoparticles. Next, the adsorption of each solution was determined by spectrophotometry at λ=456.8 nm and in contrast with the control solution (Figure 4). According to Figure 4, the removal percentage of Thiocyanate remained constant from the time 15 min. Since less stirring time is an advantage in Thiocyanate adsorption, so this time was chosen as the optimum time.

Studying effect of initial concentration of thiocyanate

Figure 4. Removing Thiocyanate nanoparticles in different stirring times

To evaluate the removal of Thiocyanate in optimal conditions in other concentrations, concentrations of 10 to 200 mg were studied. Thus, to 50 mL volumetric flasks, different amounts of 1000 g/mL^{-1} Thiocyanate solution, 5 mL of 0.1 mol/L^{-1} iron (III) solution, and 2.5 mL of 0.02 mol/L^{-1} ammonia buffer with pH=9 were added and brought to volume by adding distilled water. Next, solutions were moved to 100 mL volumetric flask containing 0.5 g of TiO_2 NPs and every volumetric flask was placed on a magnetic stirrer for 15 min. The solutions were cleared by the filter and the adsorption of each solution was determined by spectrophotometry at λ=456.8 nm and in contrast with the control solution. Finally, removal percentage of Thiocyanate was calculated (Table 3). As can be seen from the results, the removal of Thiocyanate in concentrations more than 40 µg/mL^{-1} was reduced and the removal percentage was about 74% in the final concentration of 200 µg/mL^{-1}. Figure 5 represents error bars for all effective parameters on Thiocyanate removal.
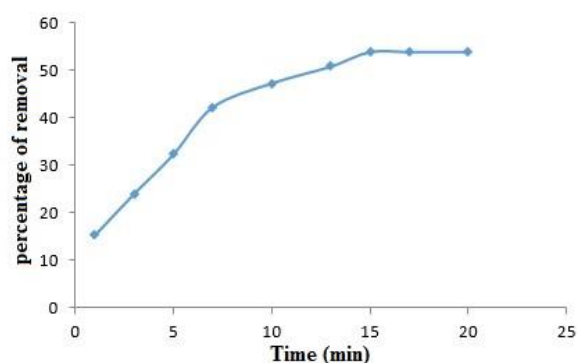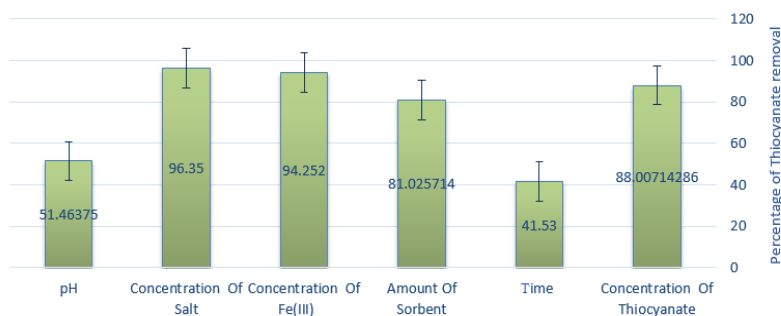

Table 3. Effect of different concentrations of Thiocyanate on Thiocyanate removal

Concentration of Thiocyanate (µg/mL^{-1})	R(%)
10	96.00
20	97.50
30	98.30
40	98.50
100	79.00
150	73.00
200	73.75

Figure 5. Standard error bar for all effective parameters on Thiocyanate removal

Analytical performance of the prepared TiO₂ NP

Calibration curve to determine the amount of thiocyanate

The calibration curve was drawn for Thiocyanate in the range of 0.34 mg/L^{-1} to 50 mg/L^{-1} of Thiocyanate. For this purpose, a suitable amount of Thiocyanate solution was moved to a 10 mL volumetric flask, 1 mL of 0.1 mol/L^{-1} iron (III) solution, and 0.5 mL of 0.02 mol/L^{-1} ammonia buffer with pH=9 and brought to volume by adding distilled water. Some of these solutions were poured into the glass cells, the adsorption of each solution was determined by spectrophotometry at λ=456.8 nm, and the calibration curve was drawn (Figure 6). Line equation based on the data is A=0.0334C-0.0028, where C is the Thiocyanate concentration in milligrams per liter. This calibration curve was used to determine the Thiocyanate concentration remaining in the solution after the removal process by nanoparticles and to calculate the removal of Thiocyanate.

Studying the volume tolerance amount

In this research, the removal percentage of Thiocyanate by TiO₂ NPs in optimum conditions and in different volumes of the sample was studied. For this purpose, 10, 25, and 50 mL volumetric flasks were chosen and 1 mL of 100 µg/mL^{-1} Thiocyanate solution was added to all of them. Then, according to the

data in Table 4, 0.5, 1.25, and 2.5 mL of 0.02 mol/L^{-1} ammonia buffer and also 1, 2.5, and 5 mL of 0.1 mol/L^{-1} iron (III) solution were added to every solution. Eventually, every solution was moved to a 50 mL volumetric flask containing 0.5 g of TiO₂ NPs and every volumetric flask was placed on a magnetic stirrer for 15 min. The solutions were cleared by the filter and the adsorption of each solution was determined by spectrophotometry at λ=456.8 nm and in contrast with the control solution (Table 4). According to the results, in the range of tested volume and in optimized conditions, the volume of the sample solution has no effect on the removal of Thiocyanate.

Adsorption isotherms

The adsorption isotherm shows the adsorption process reaches an equilibrium state and also the distribution of adsorbed types between liquid and solid phases becomes homogenized. In this study, the Langmuir and Freundlich adsorption isotherms were used for investigating the behavior of Thiocyanate on the TiO₂ NPs. These isotherms were used for a range of 10-200 mg/L^{-1} of initial concentrations in the previous optimum conditions. After calculating the remained concentration of Thiocyanate, the amount of q_e was obtained according to Equation (1), where the amount of adsorption Thiocyanate per mass unit of adsorbent is in mg/g^{-1}.

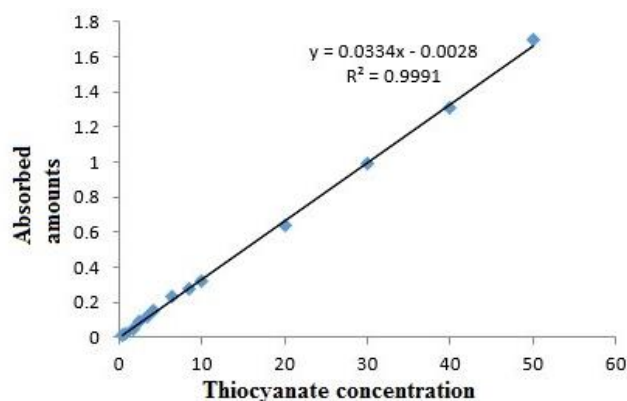**Figure 6.** Calibration curve for determination of the concentration of Thiocyanate

Table 4. Effect of volume tolerance amount of sample on Thiocyanate removal

Volume of primary solution (mL)	Adsorption	R(%)
10	0.01	96.00
25	0.0085	96.60
50	-	>96.60

Also, C_0, C_e, V, and W are the initial concentration of adsorbing, the equilibrium adsorption concentration, the volume of the solution, and the weight of sorbent, respectively.

$$q_e = \frac{(C0 - Ce)v}{w} \tag{1}$$

Langmuir isotherm

Langmuir isotherm is used for adsorption on the quite homogeneous surfaces with slight interaction between adsorbed molecules. Equation (2) was employed to evaluate the adsorption of Thiocyanate based on the Langmuir isotherm. For this purpose, 50 mL solutions were prepared with different concentrations of Thiocyanate and then the removal steps were performed using 0.5 g of TiO_2 adsorbent under the optimized conditions. Finally, the remaining concentration of Thiocyanate (C_e) was calculated and $\left(\frac{1}{qe}\right)$ to $\left(\frac{1}{ce}\right)$ was drawn for Langmuir isotherm. The obtained results are presented in Table 5 and Figure 7. Also, the coefficient of determination (R^2) for this isotherm was obtained to be 0.88. In this equation, q_e, q_m and k_1 are adsorbed Thiocyanate per mass unit of adsorbent, the greatest amount of adsorbed material, and Langmuir constant, respectively.

$$\frac{1}{qe} = \frac{1}{qmk1ce} + \frac{1}{qm} \tag{2}$$

These parameters, which were obtained from the intercept and the slope of the equation of Figure 7, are shown in Table 6. One of the basic characteristics of Langmuir isotherm and suitable adsorption can be expressed by a dimensionless factor called R_L separation factor (Equation (3)). The amounts of this factor are shown in Table 6.

$$R_L = \frac{1}{k1C0 + 1} \tag{3}$$

Based on the R_L, values, the isotherm type is classified as follows: $R_L = 0$: irreversible, $0 < R_L < 1$: suitable, $R_L = 1$: liner, and $R_L > 1$: unsuitable. Parameters obtained for Langmuir isotherm are shown in Table 6.

Table 5. Amounts of $1/q_e$ and $1/C_e$ for different concentration of Thiocyanate

$1/q_e$ (g/mg^{-1})	$1/C_e$ (L/mg^{-1})	q_e (mg/g^{-1})	C_e (mg/L^{-1})	C_0 (mg/L^{-1})
0.51	2.50	1.96	.400	20
0.34	2.00	2.95	0.50	30
0.254	1.590	3.93	0.63	40
0.204	1.00	4.90	1.00	50
0.126	0.048	7.90	21.00	100
0.120	0.027	8.40	36.00	120
0.091	0.025	10.95	40.50	150
0.067	0.019	14.78	52.20	200

Figure 7. Langmuir isotherm Thiocyanate adsorption on TiO$_2$ NPs
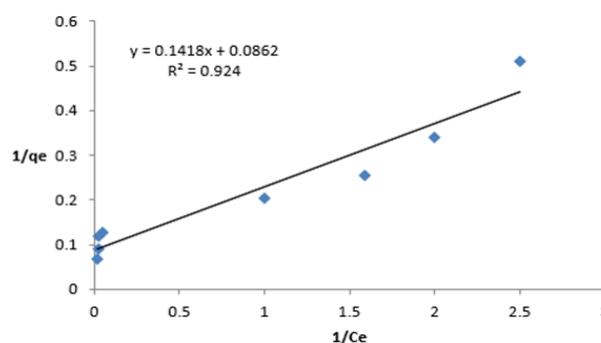
Table 6. Parameters of Langmuir isotherm

q_m (mg/g^{-1})	k_l (L/mg^{-1})	R_L
11.6	0.607	0.0746

Freundlich isotherm

Another important adsorption isotherm is Freundlich isotherm. This empirical model is expressed by Equation (4), where K_f is Freundlich constant, which depends on the adsorption capacity of the adsorbent. To check this isotherm, the log (q_e) was plotted against the log (C_e). The obtained results from the examining Freundlich isotherm are shown in Table 7 and Figure 8. In Freundlich isotherm, 1<n<3 revealed that the Thiocyanate adsorption on the adsorbent is highly desirable. By calculating the line slope (Figure 8), the amount of n was obtained as 63.3. The parameters of Freundlich isotherm are presented in Table 8.

$$log\, qe = log\, kf + \frac{1}{n} log\, C_e \qquad (4)$$

*Studying kinetic effects*

Pseudo-first-order kinetic model

The pseudo-first-order kinetic equation is expressed as Equation (5):

$$log(qe - q\, t) = log\, qe - \left(\frac{k1}{2.303}\right)t \qquad (5)$$

Where q_e and q_t are the amount of adsorbed Thiocyanate in milligram per gram per mass unit of adsorbent in time and in equilibrium, respectively. These variables are determined using the Equations (6) and (7), respectively, where C_t (t) is Thiocyanate concentration in the solution phase.

Table 7. Amounts of log q_e and log C_e for different concentrations of Thiocyanate

log q_e	log C_e	q_e (mg/g^{-1})	C_e (mg/L^{-1})	C_0 (mg/L^{-1})
0.292	-0.398	1.96	.400	20
0.470	-0.301	2.95	0.50	30
0.560	0.20	3.93	0.63	40
0.690	0.00	4.90	1.00	50
0.900	1.30	7.90	21.00	100
0.924	1.57	8.40	36.00	120
1.040	1.607	10.95	40.50	150
1.710	1.700	14.78	52.20	200

Figure 8. Freundlich isotherm Thiocyanate adsorption on TiO$_2$ NPs
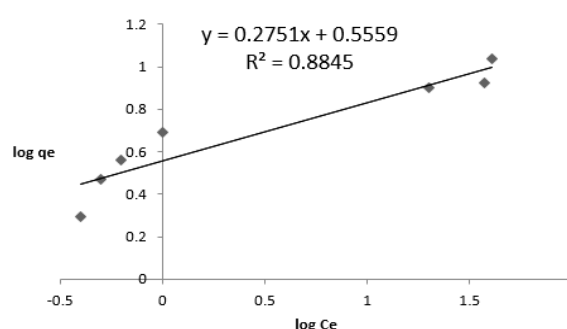
Table 8. Langmuir isotherm parameters

K_f (mg/g^{-1})	n
3.59	3.63

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{6}$$

$$q_t = (C_0 - C_t)\frac{V}{W} \tag{7}$$

The pseudo-first-order kinetic model is obtained by liner graph of log (q_e-q_t) with respect to t. Here, k_1 (1/min) is the rate constant of the pseudo-first-order kinetic model; q_e is the equilibrium adsorption capacity, which is based on the milligrams per gram and is obtained from the slope and intercept of the line of Equations (5-7). In this research study, the pseudo-first-order kinetic model was studied for concentrations of 40 and 50 mg. For this purpose, 50 mL of solution with mentioned concentrations of Thiocyanate was placed in contact with nanoparticles in optimum conditions and at different times. Afterward, the remaining concentration of Thiocyanate and, as a result, q_e and q_t were calculated. The results are shown in Figure 9a, Table 9, and 10. The

amounts of R^2, q_e, and k_1 are shown in Table 10. The calculated values of q_e and its testing are not equal. Hence, it can be concluded that the data do not follow the pseudo-first-order kinetic model.

Pseudo-second-order kinetic model

The linear graph of the pseudo-second-order kinetic equation is based on Equation (8).

$$\frac{t}{kt} = \frac{1}{k2qe2} + \frac{1}{qe}t \tag{8}$$

The pseudo-second-order kinetic model was obtained from the linear graph of t/q_t based on t. In this model, k_2 is the rate constant of the pseudo-second-order kinetic model based on a gram per milligram per minute and q_e is the equilibrium adsorption capacity based on a milligram per gram which are obtained from the intercept and slope of the equation. In this research, the pseudo-second-order kinetic model was studied for concentrations of 40

and 50 mg per liter. The results are shown in Figure 9b, Table 11, and Table 12. The amount of R^2, q_e and k_2 are shown in Table 12. The amount of R^2 is acceptable and the calculated values of q_e and its testing are roughly equal. So, it can be concluded that these data follow the pseudo-second-order kinetic model.

Studying on real samples

To work on real samples, some water samples from tap water, the water of Karun River and Karkheh dam, and water from petrochemical sewage were selected. In all selected samples, the initial amount of Thiocyanate was below the lower limit of measurement by the calibration curve. So, the additional standard method was used for examining tissue samples. About 5 mL of tap water, the water of Karun River and Karkheh dam, and petrochemical sewage were placed in a 10 mL volumetric flask.
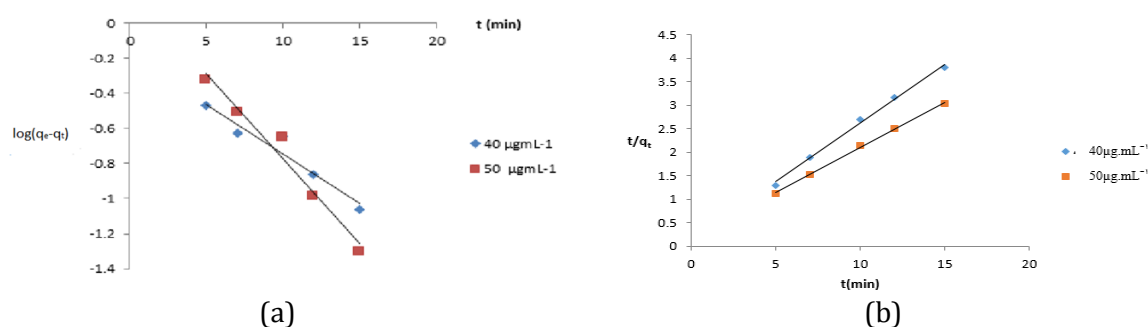

(a)   (b)

Figure 9. (a) pseudo-first-order kinetic model for 40 and 50 mg/L^{-1} concentrations of Thiocyanate; and (b) pseudo-second-order kinetic model of 40 and 50 mg/L^{-1} concentrations of Thiocyanate

Table 9. Pseudo-first-order kinetic model of 40 and 50 mg/L^{-1} concentrations of Thiocyanate

Log (q_e-q_t) 50 (mg/L^{-1})	40 (mg/L^{-1})	T (min)
-0.32	-0.47	5
-0.508	-0.625	7
-0.65	-0.644	10
-0.987	-0.863	12
-1.300	-1.060	15

Table 10. Pseudo-first-order kinetic model of 40 and 50 mg/L^{-1} concentrations of Thiocyanate parameters

Kinetic parameters	40 (mg/L^{-1})	50 (mg/L^{-1})
$q_{e,\,exp}$ (mg/g^{-1})	3.397	4.90
K_1 (min^{-1})	7.692	4.540
q_e (mg/g^{-1})	0.569	1.580
R^2	0.935	0.969

Table 11. Pseudo-second-order kinetic model 40 and 50 mg/L^{-1} concentrations of Thiocyanate results

Log (q_e-q_t) 50 (mg/L^{-1})	40 (mg/L^{-1})	T (min)
1.13	1.39	5
1.53	1.89	7
2.14	2.70	10
2.50	3.16	12
3.03	3.80	15

Next, 1 mL of 0.1 mol/L^{-1} iron (III) solution, 0.5 mL of 0.02 mol/L^{-1} ammonia buffer with pH=9, and 0.5 mL of 100 μg/mL^{-1} Thiocyanate solution were added to the solution and brought to volume by adding distilled water. In the next step, the solution was moved to a 50 mL volumetric flask containing 0.5 g of TiO$_2$ NPs and was placed on a magnetic stirrer for 15 min. The solution was cleared by a filter and its adsorption was determined by spectrophotometry at λ=456.8 nm and in contrast with the control solution. These steps were repeated for every four types of water in volumes of 1, 1.5, and 2 mL of 100 μg/mL^{-1} Thiocyanate solution (Table 13).

Studying effect of activated species

To study the method selectivity for the removal of Thiocyanate in real samples, which is actually done by the Efficiency Index, the probable interferences of cationic and anionic species on the removal of Thiocyanate were studied. For this purpose, 1 mL of 100 μg/mL^{-1} Thiocyanate solution, 1 mL of 0.1 mol/L^{-1} iron (III) solution, 0.5 mL of 0.02 mol/L^{-1} ammonia buffer with pH=9 and 1 mL of a solution containing cationic and anionic species with 500 μg/mL^{-1} or 1000 μg/mL^{-1} of concentrations were added in a 10 mL volumetric flask and brought to volume by adding distilled water. In the next step, the solution was moved to a 50 mL volumetric flask containing 0.5 g of TiO$_2$ NPs and placed on a magnetic stirrer for 15 min. The solution was cleared by a filter and its adsorption was determined by spectrophotometry at λ=456.8 nm and in contrast with the control solution. The removal rate of Thiocyanate was compared at presence and absence of other reactive species. Less than 5% difference in the removal rate of Thiocyanate indicates the lack of reactive species. In this study, 11 cations and 7 anions were examined and their interference effects were determined on the removal of Thiocyanate. The results are shown in Table 14.

Table 12. Pseudo-second-order kinetic model 40 and 50 mg/L^{-1} concentrations of Thiocyanate parameters

Kinetic parameters	40 (mg/L^{-1})	50 (mg/L^{-1})
q$_{e, exp}$ (mg/g^{-1})	3.937	4.96
K$_2$ (g/mg^{-1}/min^{-1})	1.87	27.47
q$_e$ (mg/g^{-1})	4	5.24
R^2	0.995	0.998

Table 13. Amounts of removal Thiocyanate in various sample water

Sample	R(%)	Stored Thiocyanate in solution (mg/L^{-1})	Added Thiocyanate (mg/L^{-1})
	96.40	0.18	5
Tap water	96.20	0.38	10
	96.40	0.54	15
	96.00	0.20	5
Karoon water	95.90	0.41	10
	95.33	0.70	15
	96.00	0.20	5
Karkhe water	96.50	0.35	10
	96.33	0.70	15
	96.40	0.18	5
Petrochemical sewage	95.80	0.42	10
	95.28	0.71	15

Table 14. Studying the effect of reactive species on removal Thiocyanate from solution

R(%)	Reactive ions
No interference until concentration of 10	SO_4^{2-} , OAC^- CrO_4^{2-} , HPO_4^{2-} , $Cr_2O_7^{2-}$ BrO_3^-
No interference until concentration of 10	Sn^{2+} , Na^+ , Ca^{2+} Cu^{2+} , Ba^{2+} , Hg^{2+} Zn^{2+} , Mg^{2+} , K^+ , NH_4^+
No interference until concentration of 5	CO_3^{2-} , Co^{2+}

Conclusion

Thiocyanate anion is one of the most dangerous pollutants in many industrial applications. In this regard, several methods have been proposed to remove it. In this research, TiO₂ NPs were used for this purpose. These nanoparticles are cheaper and more accessible compared with many other nanoparticles. Since, the procedure does not need modifying the surface of nanoparticles; this method can be conserved as an efficient method with low cost, short time, and high speed. Iron Thiocyanate complex has a maximum adsorption wavelength at 456.8 nm. Therefore, the absorbance of iron Thiocyanate solutions was studied to find out the concentration of Thiocyanate at this wavelength. The optimum conditions for removal of Thiocyanate anion were found to be pH=9, 0.5 g of adsorbent, and 15 min stirring time. To validate the obtained results, removal of Thiocyanate from real samples such as Ahwaz drinking water, the water of Karun River and Karkheh dam, and petrochemical sewage were studied. In all samples, the removal rate of the Thiocyanate was obtained to be 96%. The test data were analyzed in 20-200 mg/L⁻¹ of concentration, 25 °C of Temperature, and under optimal conditions by Langmuir and Freundlich isotherms. According to the R^2 values obtained for the two Freundlich and Langmuir isotherms, it can be concluded that the adsorption process follows the Langmuir isotherm but it does not match with the Freundlich isotherm. Therefore, the removal of Thiocyanate by TiO₂ NPs follows the Langmuir isotherm model. To study the mechanism of adsorption, the first and second pseudo-kinetic models were studied in 40 and 50 mg of concentrations. Based on the obtained results, the adsorption process would follow the pseudo-second-order model due to the linearity of the kinetic data.

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Disclosure statement

No potential conflict of interest was reported by the author.

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