

# Solid Phase Extraction of Silicate by Sorption on Modified Magnetite Nanoparticles and Spectrophotometric Determination

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**Abstract** A new adsorbent of alumina-coated magnetite nanoparticles (ACMNPs) modified with cetyltrimethyl ammonium bromide (CTAB) was prepared for the separation/preconcentration of trace silicate from water samples and then determined by spectrophotometry method. Silicate was determined based on the molybdenum blue method, which monitored at  $\lambda_{\max}$  of 830 nm. MNPs and ACMNPs characterized by SEM and VSM. Under the optimal experimental conditions, the preconcentration factor, detection limit, linear range and relative standard deviation of silicate were 70 (for 350 mL of sample solution),  $0.040 \mu\text{g mL}^{-1}$ ,  $0.8\text{-}7.0 \mu\text{g mL}^{-1}$  and 2.2 % (for  $5.0 \mu\text{g mL}^{-1}$ ,  $n=7$ ), respectively. The method was applied to the separation/preconcentration and determination of silicate in tap water, river water and seawater samples with satisfactory results.

**Keywords:** separation/preconcentration, silicate, modified alumina-coated magnetite nanoparticles (ACMNPs), molybdenum blue method

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## 1. Introduction

Analytical separation techniques play a central role in analytical chemistry. Among separation/preconcentration methods, solid phase extraction (SPE) is a separation/preconcentration technique of rapidly growing importance in spectrometric determinations of various species [1]. At present, nano-sized materials such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and carbon nanotubes are more important in SPE due to their special property *i.e.* high adsorption capacity [2,3,4,5]. Among most of nanomaterials investigated, adsorbents made from magnetite nanoparticles (MNPs), proved to be useful in separation/preconcentration applications such as SPE [6,7,8]. A distinct advantage of these nanoparticles is that MNPs can be readily isolated from sample solutions by the application of an external magnetic field. The surface modification of MNPs is a challenged key for SPE application. The main advantage of the preparation of alumina-coated magnetite nanoparticles (ACMNPs) in comparison with MNPs is higher stability in acidic and basic solutions. Recently, we also reported the methods for separation and preconcentration of Pb(II), Ag(I), Pd(II), Rh(III) and Ni(II) using ACMNPs [9,10,11,12].

It is well known that silicon is major component of various soils and natural minerals. Silicate has been used in different industries and important environmental contaminant. An increase in concentration of silicate ions in natural water lowers the dissolved oxygen concentration and cause the death of aquatic animals such as fishes due to the suffocation [13]. Therefore, removal of the excessive silicate ions is important to improve the water quality. There are a relatively limited number of studies dealing with the separation/preconcentration of silicate ions in real samples such as water [14,15,16,17]. To our knowledge, this is the first report of using ACMNPs for the SPE and determination of silicate ions from real samples. In this study, ACMNPs were successfully synthesized and modified by a cationic surfactant *i.e.* cetyltrimethylammonium bromide (CTAB). The CTAB@ACMNPs sorbent has proved to be suitable for the extraction of silicate ions from different water samples prior to determination by spectrophotometric technique based on molybdenum blue method.

## 2. Experimental

### 2.1. Chemicals and Solutions

All reagents and standards were of analytical grade, and all dilutions were performed using triply distilled water. The stock standard solutions ( $1000 \mu\text{g mL}^{-1}$ ) of silicate were obtained by dissolving appropriate amounts of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  (Merck) in triple distilled water. Working standard solutions were prepared by appropriate dilution of the stock standard solution. Cetyltrimethyl ammonium bromide (CTAB), ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), aluminum isopropoxide, hydrochloric acid and ammonia were used without further purification processes. Stock solution of molybdate was prepared by dissolution of ammonium molybdate and potassium antimonyl tartarate in 60 mL of  $9 \text{ mol L}^{-1}$  sulfuric acid and diluted by triple distilled water to a final volume of 100 mL in a volumetric flask and it was stable for one month. The pH adjustments of 4-10 were made by using buffer solutions of  $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH}$  and  $\text{NH}_3/\text{NH}_4\text{Cl}$ .

## 2.2. Apparatus

Magnetic properties of the particles were determined by vibrating sample magnetometer (VSM 7400 Model Lake-Shore). The surface morphology of the powders was observed by the scanning electron microscope (LEO 1455VP SEM). A GBC UV-Visible Cintra 6 Spectrophotometer model, attached to a Pentium (IV) computer, with 10-mm glass cells was used to measure the absorbance of silicate ion solution at 830 nm. For magnetic separations, a strong neodymium-iron-boron ( $\text{Nd}_2\text{Fe}_{12}\text{B}$ ) magnet (1.2 T,  $2.5 \text{ cm} \times 5 \text{ cm} \times 10 \text{ cm}$ ) was used.

## 2.3. Preparation of ACMNPs Modified with CTAB

First, ACMNPs were synthesized by chemical co-precipitation procedure [9,10,11,12]. Then, the obtained ACMNPs (100 mg) coated with admicelles of CTAB (40 mg). The pH of this suspension was adjusted to 7.5 by addition of 5 mL of  $\text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH}$  buffer ( $0.1 \text{ mol L}^{-1}$ ) solution. The mixed solution was shaken for 5 min and then CTAB@ACMNPs separated from the reaction medium under the magnetic field, and rinsed with 10 mL pure water. This product was used as sorbent for  $\text{SiO}_3^{2-}$  ions.

## 2.4. Extraction and Determination Procedure

The procedure for the magnetic extraction is demonstrated in Figure 1 and details are as follows: The extraction procedure was carried out in a batch process. A 5 mL  $\text{SiO}_3^{2-}$  standard solution was added to CTAB@ACMNPs from above section. Subsequently the pH value adjusted to 7.5 with ammonium acetate/acetic acid buffer and the solution shaken for 2 min in a beaker to facilitate adsorption of the  $\text{SiO}_3^{2-}$  ions onto the NPs. The beaker was placed on the magnet and nanoparticles were collected. After decanting the supernatant solution, the collected magnetite adsorbents washed with 5 mL of mixture solution of  $0.25 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  and  $0.15 \text{ mol L}^{-1} \text{HNO}_3$  in order to desorb the adsorbed silicate ions by stirring for 3 min. Finally,  $\text{SiO}_3^{2-}$  ions were determined at  $\lambda_{\text{max}}$  of 830 nm using molybdenum blue method.

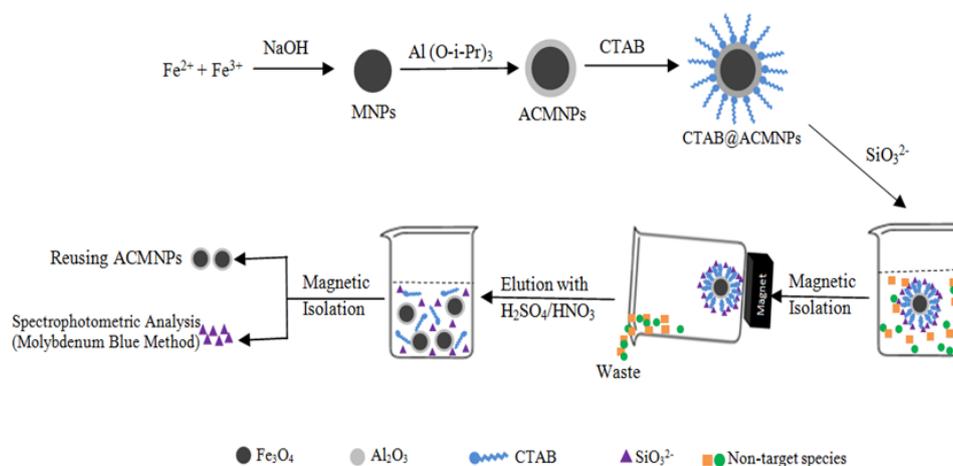


Figure 1. Procedure for the proposed magnetic solid-phase extraction

## 2.5. Sample Preparation

Samples of different waters were filtered through filter paper (Whatman, no. 4) to remove suspended particulate matters after collection and buffered to a pH of 7.5 with ammonium acetate/acetic acid buffer prior to storage in polyethylene container for use. The SPE procedure was carried out as described in general procedure.

## 3. Results and Discussion

### 3.1. Characterization of ACMNPs

Magnetic nanoparticles may exhibit different magnetic properties due to their synthetic conditions [18]. The

hysteresis loops measured for the MNPs and ACMNPs are shown in Figure 2. Typical characteristics of superparamagnetic behavior can be observed. The saturation magnetization values from the magnetization curves in Figure 2a and Figure 2b for the uncoated MNPs and ACMNPs were found to be  $56.8$  and  $9.4 \text{ emu g}^{-1}$ , respectively. The decrease of saturated magnetization was attributed to the formation of the alumina layer. However, the sorbent magnetization of ACMNPs is sufficient for magnetic separation with a normal magnet. SEM images conducted to characterize the surface of the MNPs and ACMNPs are shown in Figure 3. These images confirm highly porous morphology of adsorbent with uniform size distribution of the NPs.

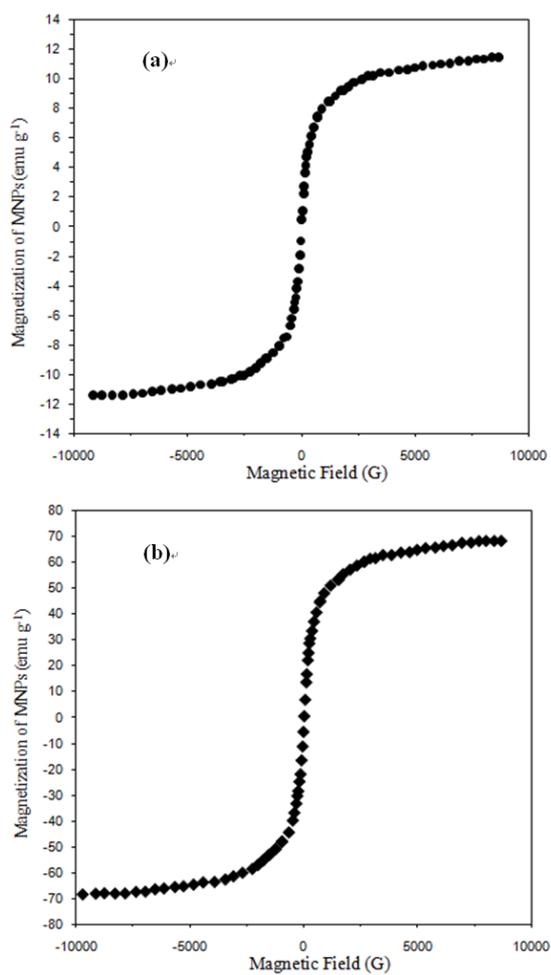


Figure 2. The magnetic behavior of MNPs (a) and ACMNPs (b)

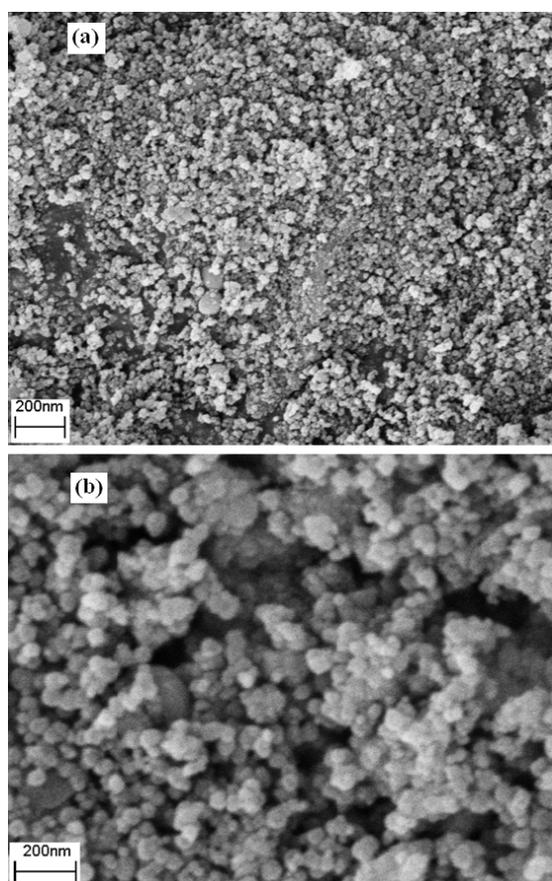


Figure 3. SEM images of MNPs (a) and ACMNPs (b)

### 3.2. Effect of Amounts of ACMNPs and CTAB

In order to choose the optimum amount of ACMNPs required for quantitative recoveries of 50 mL solution containing  $10.0 \mu\text{g SiO}_3^{2-}$  ions, different quantities of pretreated ACMNPs ranging from 20 to 150 mg were examined. The recovery percentage was increased up to 80 mg. After this, the recovery remained constant. Therefore, 100 mg of ACMNPs was used in all subsequent experiments.

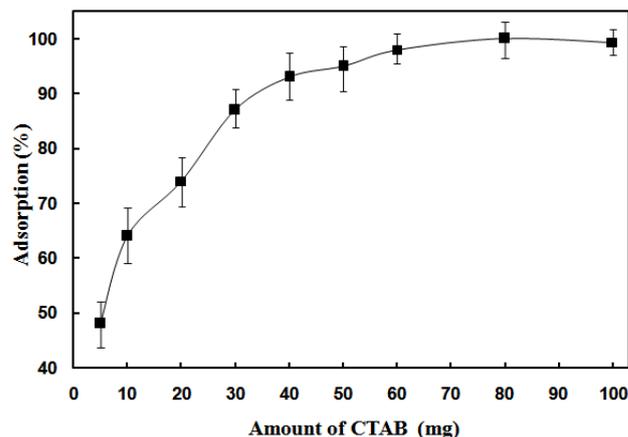


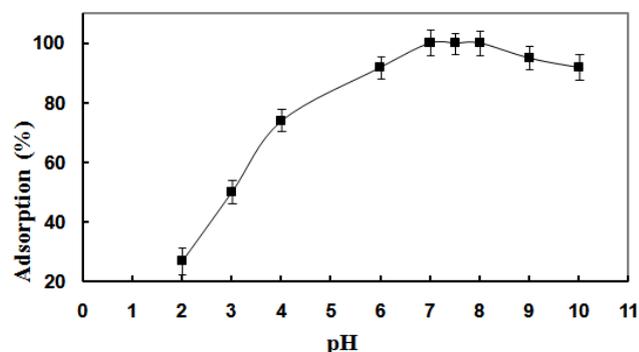
Figure 4. Effect of CTAB concentration on adsorption of  $\text{SiO}_3^{2-}$  ions. Conditions: ACMNPs (100 mg),  $\text{SiO}_3^{2-}$  solution (5 mL,  $5.0 \mu\text{g mL}^{-1}$ , pH 7.5)

Recently, we have been reported the method for separation and preconcentration of palladium and rhodium using magnetite nanoparticles [11]. This method is based on the solid-phase extraction (SPE) of trace amounts of Pd(II) and Rh(III) using MNPs without addition of a chelating agent and modification of NPs. In this paper, we investigate the application of CTAB immobilized on ACMNPs (CTAB@ACMNPs) for the separation/preconcentration of  $\text{SiO}_3^{2-}$  ions. Positively charged CTAB surfactant, can be strongly adsorb on negatively charged surfaces of ACMNPs in basic solutions (Figure 4). Influence of various amounts of 10, 20, 30, 40, 45, 50, 60 and 80 mg CTAB (below its critical micellar concentration,  $1 \times 10^{-3} \text{ mol L}^{-1}$ ) on the adsorption of  $\text{SiO}_3^{2-}$  ions through the ACMNPs substrate was investigated. The results showed that maximum adsorption was obtained when 40 mg of CTAB per 100 mg of ACMNPs used for  $\text{SiO}_3^{2-}$  ions. Thus, this amount was selected as the optimum concentration of CTAB for further studies.

### 3.3. Effect of pH

The pH value plays a key role in the SPE procedure. In order to investigate the effect of pH on the SPE of  $\text{SiO}_3^{2-}$  ions, the pH of aqueous samples was varied from 4 to 10 using buffer solutions of  $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH}$  and  $\text{NH}_3/\text{NH}_4\text{Cl}$ . Negatively charged ACMNPs surfaces effectively adsorb positively charged CTAB at upper pH values. Therefore, retention of  $\text{SiO}_3^{2-}$  ions on CTAB@ACMNPs occurs. It was found that the maximum removal of  $\text{SiO}_3^{2-}$  ions on the CTAB@ACMNPs as adsorbent observed at pH range of 7.0 to 8.0 (Figure 5). At the pH values higher than 8.0 and lower than 7.0, the recovery decreased, due to competition

of OH<sup>-</sup> ions with SiO<sub>3</sub><sup>2-</sup> ions and the formation of negative charges of ACMNPs surfaces (reduction of CTAB adsorption), respectively. Therefore, the pH 7.5 ± 0.5 was selected for the all subsequent works. The pH 7.5 was made by adding an appropriate amount of dilute CH<sub>3</sub>COOH to CH<sub>3</sub>COONH<sub>4</sub> solution.



**Figure 5.** Effect of pH on adsorption of SiO<sub>3</sub><sup>2-</sup> ions. Conditions: CTAB@ACMNPs (100 mg), SiO<sub>3</sub><sup>2-</sup> solution (5.0 µg mL<sup>-1</sup>)

### 3.4. Effect of Standing Time and Eluent

In order to realize complete extraction, the effect of standing time on the adsorption and desorption was investigated. Experimental results showed that 5 min is sufficient for achieving satisfactory adsorption and 1 min for desorption. Meanwhile, in the experiment, CTAB@ACMNPs possessed superparamagnetic properties and large saturation magnetization, which enabled them to be completely isolated in a short amount of time (less than 1 min) by a strong magnet. In a word, analysis time is shortened greatly compared with the traditional column-passing SPE.

Various desorbing eluents were used to find the best desorbing solution for the adsorbed SiO<sub>3</sub><sup>2-</sup> ions. Among different solutions (such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, ethanol and acetonitrile) a mixed solution 0.25 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 0.15 mol L<sup>-1</sup> were used as eluent, HNO<sub>3</sub> provided higher recovery. In addition, the effect of elution volume for quantitative elution of the studied SiO<sub>3</sub><sup>2-</sup> ions was investigated. The minimum volume of a mixed solution of 0.25 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 0.15 mol L<sup>-1</sup> HNO<sub>3</sub> required for a quantitative elution of the retained analytes was found 5.0 mL.

### 3.5. Study of Sample Volume Effect, Adsorption Capacity and Sorbent Regeneration

In order to obtain higher preconcentration factors, a larger volume of sample solution is required. The effect of sample solution volume on the extraction of SiO<sub>3</sub><sup>2-</sup> ions was studied by using different volumes (50–450 mL) of aqueous solution spiked with a fixed 5 µg SiO<sub>3</sub><sup>2-</sup> ions in the optimal conditions. Quantitative recoveries of studied SiO<sub>3</sub><sup>2-</sup> ions (>95%) were obtained when sample volume was less than 350 mL. Hence, sample volume of 350 mL was selected for subsequent experiments. Therefore, a preconcentration factor of 70 could be achieved by this method.

The capacity of the adsorbent is an important factor because it determines how much adsorbent is required to remove a specific amount of SiO<sub>3</sub><sup>2-</sup> ions from the solutions, quantitatively. In order to determinate the adsorption

capacity, 100 mg of CTAB@ACMNPs and 50 mL of solution containing 5.0 mg of SiO<sub>3</sub><sup>2-</sup> ions at pH 7.5 was equilibrated for 30 min. In order to reach the “saturation”, the initial SiO<sub>3</sub><sup>2-</sup> ions’ concentration was increased till the plateau value (adsorption capacity value) obtained. The maximum adsorption capacity of CTAB@ACMNPs has been found to be 8.6 mg g<sup>-1</sup> for SiO<sub>3</sub><sup>2-</sup> ions.

Regeneration is one of the key factors for evaluating the performance of the adsorption material. In this work, it was found that the ACMNPs can be re-used up to three times without loss of analytical performance.

### 3.6. Interference Study

The effects of interferences from coexisting ions on the preconcentration/separation and determination of SiO<sub>3</sub><sup>2-</sup> ions were examined under the optimum conditions described above. The solutions containing 0.05 µg mL<sup>-1</sup> SiO<sub>3</sub><sup>2-</sup> ions and other ions were prepared and the developed procedure applied in order to determine the selectivity of the sorbent. The following excesses of ions did not interfere (i.e., caused a relative error of less than 5%): less than a 1000-fold (largest amount tested) amount of Na<sup>+</sup>, K<sup>+</sup>, Ag<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>; a 500-fold amount of NH<sub>4</sub><sup>+</sup>, Ba<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>; a 200-fold amount of Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>; a 50-fold amount of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>; and a 1-fold amount of AsO<sub>4</sub><sup>3-</sup> and PO<sub>4</sub><sup>3-</sup>. The results showed that most of the investigated ions do not interfere in the adsorption–desorption and determination of traces of SiO<sub>3</sub><sup>2-</sup> ions in real samples. Only AsO<sub>4</sub><sup>3-</sup> and PO<sub>4</sub><sup>3-</sup> ions appeared to interfere with SiO<sub>3</sub><sup>2-</sup> ions for molybdenum blue method, that these interferences can be eliminated by reduction with thiosulfate in an acidic medium and masking by La<sup>3+</sup> or Ca<sup>2+</sup>, respectively [19,20].

### 3.7. Analytical Performance

The calibration curve for the preconcentration of silicate by the optimized method was found to be linear over the concentration range of 0.8–7.0 µg mL<sup>-1</sup>. The regression equation was  $A = 0.0369C_{\text{silicate}} + 0.1744$  ( $n = 7$ ), where  $A$  is the absorbance and  $C_{\text{silicate}}$  is the concentration of SiO<sub>3</sub><sup>2-</sup> ions in µg mL<sup>-1</sup>. Detection limit (DL) for the target SiO<sub>3</sub><sup>2-</sup> ions based on 3S<sub>b</sub>/m definition (where  $m$  is the slope of the calibration curve and  $S_b$  is the standard deviation for seven blank measurements) was found 0.040 µg mL<sup>-1</sup>. The relative standard deviation (RSD) of 7 replicates was found to be less than ±2.5% at 5.0 µg mL<sup>-1</sup> of SiO<sub>3</sub><sup>2-</sup> ions.

### 3.8. Application of the Method

**Table 1.** Analytical results for real water samples (sample volume: 50 mL, mean ± SD, n=3)

Sample	SiO <sub>3</sub> <sup>2-</sup> (µg mL <sup>-1</sup> )		Recovery (%)
	Added	Found	
Tap water from Ardakan city	0.0	16.3 (±1.25)	---
River water from Hajiabad river	5.0	21.0 (±1.94)	94
Well water from Sirjan city	0.0	21.5 (±1.50)	-----
Mineral water from Iran	5.0	26.9 (±2.30)	108
	0.0	34.4 (±3.20)	-----
	5.0	39.6 (±2.98)	104
	0.0	25.1 (±1.85)	-----
	5.0	30.2 (±2.25)	102

To test the applicability of the optimized method to real water samples, it was applied to the determination of  $\text{SiO}_3^{2-}$  ions in different water samples. The analytical results are shown in Table 1. The accuracy of the method was verified by the analysis of the samples spiked with known amounts of the silicate analyte. As could be seen, recoveries for the target analyte ranged from 94 to 108 %. The results show that the proposed method could be successfully applied to the determination of silicate ions.

## 4. Conclusions

In this study, the synthesized ACMNPs were successfully applied as a new sorbent in solid phase extraction for convenient, fast and efficient enrichment of trace  $\text{SiO}_3^{2-}$  ions from environmental water samples. This new adsorbent was prepared easily and low costly, utilized conveniently and harmless to environment. Magnetic separation in the method shortened analysis times greatly. The results showed that the proposed method is very suitable for the rapid SPE of  $\text{SiO}_3^{2-}$  ions from large volume of water samples.

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