

# A New and Efficient Method for the Adsorption and Separation of Arsenic Metal Ion from Mining Waste Waters of Zarshouran Gold Mine by Magnetic Solid-Phase Extraction with Modified Magnetic Nanoparticles

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## Abstract:

Widespread arsenic contamination of mining wastewater of Zarshouran (West Azerbaijan province) has led to a massive epidemic of arsenic poisoning in the whole of surrounding areas. It is estimated that approximately all agriculture fields are being irrigated with the water that its arsenic concentrations elevated above the World Health Organization's standard of 10 parts per billion. A novel advanced magnetic matter adsorbent using magnetite embedded within nanosized  $Fe_3O_4$  was prepared and applied for separation of arsenic metal ion from aqueous solution. This adsorbent combines the advantages of magnetic nanoparticles with magnetic separability and high affinity toward arsenic metal ions, which provides distinctive merits including easy preparation, high adsorption capacity, and easy isolation from sample solutions by the application of an external magnetic field. The adsorption behaviors of arsenic from an aqueous medium, using iron magnetite nanoparticles were studied by using equilibrium batch and column flow techniques. The effects of pH, contents of loaded magnetic matter nanoparticles, ionic strength, adsorbent dose, contact time, and temperature on adsorption capacity of the magnetic beads were investigated. All the results suggested that the mentioned nanoparticles could be excellent adsorbents for As(II) and As(III) contaminated water treatment.

**Keywords:** Advanced nano-magnetic matter, Adsorption, Arsenic removal, Magnetite nanoparticles, Zarshouran gold mine.

## 1. INTRODUCTION

Widespread arsenic contamination of groundwater has led to a massive epidemic of arsenic poisoning in Bangladesh and neighbouring countries. It is estimated that approximately 57 million people are drinking groundwater with arsenic concentrations elevated above the World Health Organization's standard of 10 parts per billion. Nanometer-sized materials have attracted substantial interest in

the scientific community because of their special properties [1].

Magnetic separation technique, using magnetic polymeric particles, is a quick and easy method for sensitive and reliable capture of inorganic or organic solutions. The magnetic sorbents behave similar to or even better than various commercial adsorbents [2].

After the usage, the magnetic sorbent can be easily separated from the solution by simple magnetic

force. In the literature, iron oxides have been found to be successfully used as composite materials with host materials in fabricating magnetic sorbent [3]. These particles are super paramagnetic, which means that they are attracted to a magnetic field, but retain no residual magnetism after the field is removed [4]. Moreover, these nanometer-sized metal oxides are not target-selective and are unsuitable for samples with complicated matrix [5].

To our knowledge, the adsorption of arsenic metal ions by magnetite nanosized matter prepared by bonding a synthetic Schiff base tail to surface of the magnetite beads with and without extractant has never been investigated.

## 2. EXPERIMENTAL (MODELING)

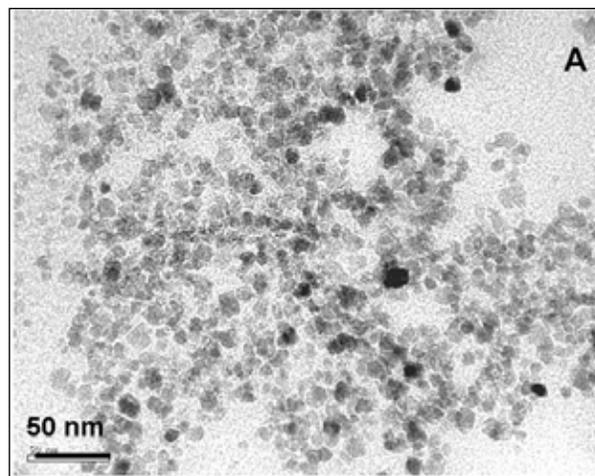
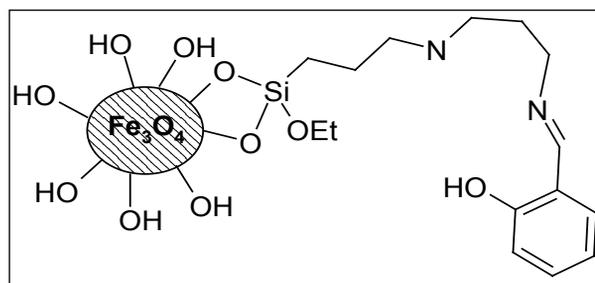
### 2.1. Preparation of magnetite iron oxide nanoparticles

Magnetite was prepared by using the modified Massart method [6]. Firstly, ferric and ferrous chloride solutions were mixed at 60°C for 30 min. Then, ammonia solution was added dropwise to the above solution under vigorous stirring.

A black precipitate was formed which was allowed to crystallize for another 30 min under stirring at 90°C. The molar ratio of  $\text{FeCl}_2:\text{FeCl}_3:\text{NH}_3\cdot\text{H}_2\text{O}$  was 1:2:16. All the above processes were run under total  $\text{N}_2$  protection. At last, the precipitate was filtered off and washed with deoxygenated water through magnetic decantation until the pH of the suspension became below 7.5.

### 2.2. Preparation of the target nanobeads

The modified magnetic nanoparticles functionalized with salicylaldehyde groups prepared by previous produce in the literature [7]. The Schiff base tail was firstly synthesized by general methods and then the magnetite nanoparticles and Schiff-base substance were refluxed in methanol solution during 24 h. The solid was separated with magnet and finally, they were washed several times with distilled water and dried in the vacuum drying chamber at 55°C for 24 h (Scheme 1).



*Scheme 1: Up) Target advanced material, Down) SEM image of magnetite nanoparticles*

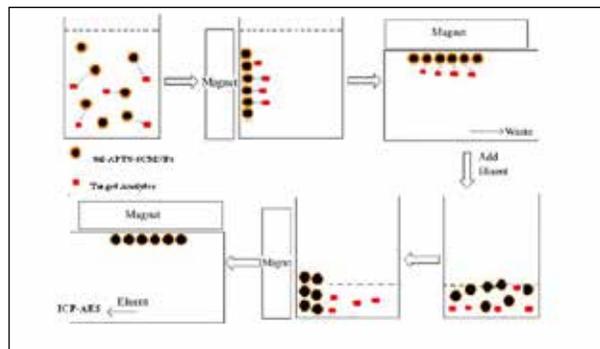
### 2.3. Procedure

The procedure for the magnetic solid-phase extraction is presented in Figure 1 and the details are as follows: a portion of sample solution containing  $10 \text{ ng}\cdot\text{ml}^{-1}$  analyte ions was transferred to a 200-mL beaker; the pH value was adjusted to 8 with  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$  and  $0.1 \text{ mol}\cdot\text{L}^{-1}$  aqueous ammonia.

Then, 100 mg of sample was added, and the solution was stirred for 15 min to facilitate adsorption of the metal ions onto the nanoparticles. Then the magnetic adsorbent was separated easily and quickly using a magnet and the supernatant was decanted directly. The magnet was removed, and a solution containing  $1.0 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$  was added as eluent and stirred again for 2min.

Finally, the magnet was used again to settle the magnetic nanoparticles, and the eluate was pipetted into a test tube for subsequent ICP-AES analysis.

Highly pure deionized water was chosen as the blank solution and subjected to SPE. In this way the blank values were determined.



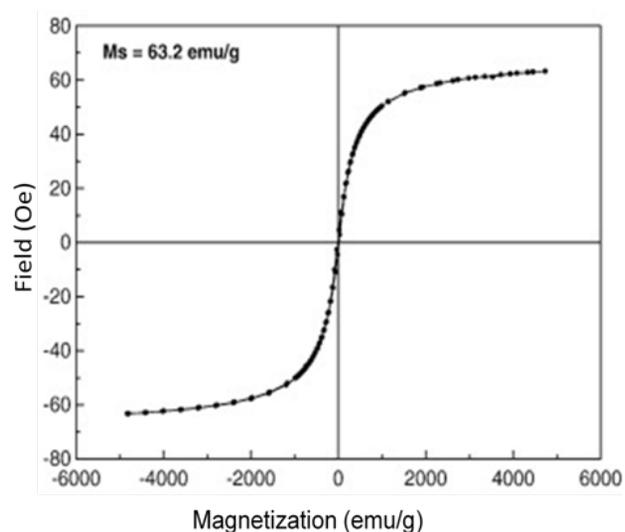
**Figure 1:** Procedure for magnetic solid-phase extraction

### 3. RESULTS AND DISCUSSION

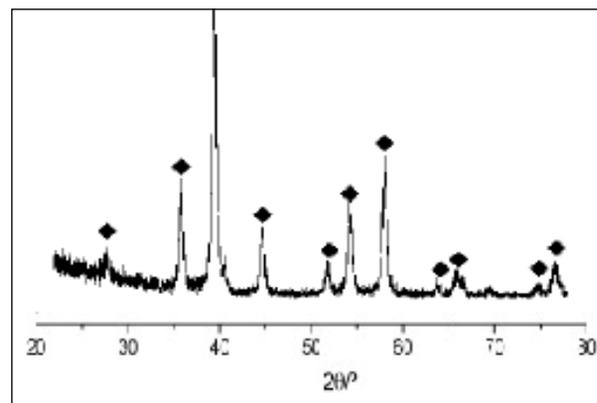
The aim of the present work is to prepare modified nanoparticles of magnetite iron oxide with special ligands as Schiff-bases. The magnetic nanocomposite was used for determination and adsorption capacity of arsenic ion from aqueous medium under batch equilibrium and column flow experimental conditions. The effect of various experimental parameters such as aqueous phase pH, adsorbent dose, ionic strength and temperature, X-ray diffraction (XRD) technique and vibrating sample magnetometer (VSM) were used to determine the crystallographic structure and investigate the magnetic property of the iron oxide, respectively. for investigation the magnetic property of the iron oxide.

As expected, the XRD pattern of iron oxide nanoparticles (Figure 2) is characterized of the inverse spinel structure of  $Fe_3O_4$  and the result is similar to the literature [8]. The magnetic hysteresis loop, obtained by VSM (Figure 3), shows two coincident magnetization curves. No magnetic hysteresis phenomenon is observed, and the coercive force and remanence are close to zero. This reflects an important feature of the magnetic nano-materials, i.e. super-paramagnetic, which is usually

observed when the magnetic particles are less than 10 nm in diameter.



**Figure 2:** The specific saturation magnetization of iron oxide nanoparticles.



**Figure 3:** XRD patterns of  $Fe_3O_4$  nano-particles

#### 3.1. Effect of pH on adsorption

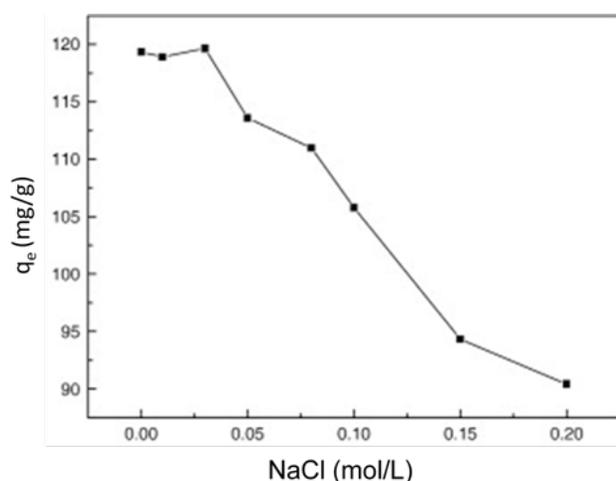
As pH is an important factor affecting the uptake of cations from aqueous solutions, the dependence of arsenic uptake on aqueous pH is studied. The uptake capacity increases from about 1.9 to 9.8 mg/g as pH increases from 2.2 to 3.5. Above pH 3.5, its effect on the uptake becomes insignificant and reaches a plateau. However, with an increase in pH, more negative sites are becoming available

for the adsorption of As(III) ion, which leads the uptake to increase at higher pH. Considering the hydroxylation of As(III) at higher pH, the optimum initial pH is defined to be 5.0. In addition, the final pH is obviously higher than the initial pH. The final pH changes only from 5.6 to 5.9 when initial pH ranges from 4.0 to 5.5, demonstrating a buffering ability caused by calcium alginate.

### 3.2. Effect of ionic strength on adsorption

In this study, the effect of initial ionic strength on As(III) sorption is investigated by varying the concentrations of additive sodium chloride from zero to 0.2 mol/L. As shown in Figure 4, the low ionic strength, corresponding to the concentration of sodium chloride less than 0.03 mol/L, has little influence on the As(III) sorption, and above it, the uptake of As(III) obviously decreases with increasing concentrations of sodium chloride.

The uptake capacity changes from 119.3 mg/g to 90.4 mg/g when the concentration of sodium chloride range is from 0.03 mol/L to 0.2 mol/L. A reasonable explanation is that there is a competitive sorption between As(III) and Na<sup>+</sup>. At a lower ionic strength, more function groups are available for As(III) uptake, the effect of Na<sup>+</sup> is insignificant, when the ionic strength is high, competition between As(III) and Na<sup>+</sup> for the available sites becomes important, resulting in the lower As (III) uptake.



**Figure 4:** The effect of ionic strength on uptake capacity of Arsenic using magnetic beads

### 3.3. Effect of temperature on adsorption

By studying the effect of temperature on adsorption of As(III) on magnetic beads, it can be found that the uptake capacity of As(III) increases, as the temperature in solution decreases, suggesting that the adsorption process is exothermic (Finotelli, *et. al.*, 2004).

**Table 1:** The amount of arsenic in wastewater of Zarshouran (ICP-OES by applied research centre of geological survey of Iran)

No.	Sample	Arsenic
1	1 ZGW	80.5 ppb
2	2 ZGW	7.45 ppm
3	3 ZGW	67.4 ppb
4	1 ZGWF	95.3 ppb
5	2 ZGWF	8.22 ppm
6	3 ZGWF	80.6 ppb
7	Z-W-I-Z	31 ppb
8	ZW-G-2	12850 ppb
9	Z-W-O-Z	832 ppb

**Table 2:** The amount of arsenic before and after the experiment (ICP-OES by applied research centre of geological survey of Iran)

No.	Sample	Amount of arsenic before experiment	Amount of arsenic after experiment
1	1ZGW	80.5ppb	<1.00ppb
2	2ZGW	7.45ppm	<1.00 ppb
3	3ZGW	67.4ppb	<1.00 ppb
4	1ZGWF	95.3ppb	<1.00 ppb
5	2ZGWF	8.22ppm	<1.00 ppb
6	3ZGWF	80.6ppb	2.00 ppb
7	Z-W-I-Z	31ppb	<1.00 ppb
8	ZW-G-2	12850ppb	17.00 ppb
9	Z-W-O-Z	832ppb	13.00 ppb

## 4. CONCLUSIONS

In this work, silica coated magnetic nanoparticles was chemically modified by aminopropyl groups

and salicylaldehyde, as a new solid phase extractant was and applied for preconcentration.

Under the optimal experimental conditions, the analytical curve was linear in the range of 2-1000 µg/L and the detection limit was 0.2 ngr/ml. The relative standard deviation (R.S.D.) under optimum conditions was 2.62% ( $n = 10$ ). Common coexisting ions did not interfere with the separation and determination of arsenic at pH 8. The sorbent exhibited excellent stability and its sorption capacity under optimum condition had been found to be 9.2 mg of uranium per gram of sorbent.

#### ACKNOWLEDGMENTS

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