

ORIGINAL ARTICLE

# Fluorescence Quenching of CdS Quantum Dots and Its Application to Determination of Copper and Nickel Contamination in Well and Dam Water

Jafar Abolhasani\*, Javad Hassanzadeh, Ebrahim Ghorbani-Kalhor, Zohreh Saeedi

Department of Chemistry, College of Science, Tabriz Branch, Islamic Azad University, Tabriz, Iran

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## KEYWORDS

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**ABSTRACT:** A sensitive and simple method based on the fluorescence quenching CdS quantum dots (QDs) was reported for the determination of copper( $\text{Cu}^{2+}$ ) and nickel ( $\text{Ni}^{2+}$ ) in water samples. Water-soluble and biocompatible thioglycolic acid-capped CdSQDs was synthesized by one step process, then characterized by fluorescence, absorption spectroscopy and transmission electron microscopy (TEM). The fluorescence intensity of synthesized QDs remarkably decreased in the presence of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions. The emission of CdSQDs had a linear decreasing relationship with  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  concentration in the range of 0.6 to 200 and 1 to 250  $\text{ng mL}^{-1}$  with detection limits of 0.15 and 0.4  $\text{ng mL}^{-1}$ , respectively. Other potentially interfering ions such as iron, sodium, potassium, calcium, and magnesium ions did not affect the luminescence. The method showed good sensitivity and was satisfactorily applied to the determination of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  contamination in real water samples, obtained from Nahand dam, Karkaj and Azarshahr well, tab and mineral waters.

## INTRODUCTION

Heavy metals are considered as one of the most dangerous group of contaminants in water supplies, due to non-biodegradation, toxicity, widespread water pollution and fish diseases. Heavy metals are the most toxic pollutants in environment. Because of the nature of non-degradable in the environment, high solubility in water and their potential to accumulate in different parts

of the body, they have serious side effects for human health. They have carcinogenic effects and can damage liver, nerve and bone [1].

In the meantime, monitoring of copper and nickel ions in environmental samples is very important because they are essential elements for human health and toxic in high concentrations [1, 2]. Copper acts as micronutrient

\* Corresponding author: abolhasani@iaut.ac.ir (J. Abolhasani).

in living systems in trace concentrations. It is closely bound up with many physiological functions, such as anti-oxidation, anti-tumor and keeping normal immune functions. However, violent tendencies in males, depression, schizophrenia and hereditary diseases with critical results, like liver damage, are connected to excessive amounts of copper in the body [3]. Ni<sup>2+</sup> bound to ribonucleic acid have a special affinity for bone and skin and play an important role in pigmentation. Normal human plasma contains 0.012-0.085 ppm of Ni<sup>2+</sup> [2]. The high concentration of the nickel does show serious health hazards. The high incident of respiratory trackmoplacia and dermatitis has been observed when exposed by nickel refineries.

Therefore, an economical, sensitive, and rapid analytical method is of great importance for trace determination of copper and nickel. Many techniques are exploited for this purpose including spectrophotometry [2, 4-7], atomic absorption spectrometry [3, 8-13], spectrofluorimetry [14, 15], quantum dots as fluorescent sensor [16], chemiluminescence [17, 18], inductively coupled plasma atomic emission spectrometry [19, 20] and electrochemical methods [21, 22]. Most of these methods often require complex and expensive equipment, skilled labor, high time for preparation of samples. Among these methods, fluorescence has attracted much attention, because of its high sensitivity. Specially, fluorescence of quantum dots (QDs) is more attractive because of their superior luminescence properties and stability in aqueous solutions [23]. Determination of ions by QDs is often based on the interaction between the analyte and QDs, which change their physical and photochemical features. The first report was presented by Chen and Rosen Zweig. They showed that fluorescence intensity of thioglycerol-coated CdS QDs was reduced selectively in the presence of Cu<sup>2+</sup> [24]. Then, several research groups have applied different types of quantum dots as luminescence probe

for Hg<sup>2+</sup> [25-27], Cu<sup>2+</sup> [28-31], Ag<sup>+</sup> [28, 32], Pb<sup>2+</sup> [33, 34].

In this study, we report application of thioglycolic acid (TGA) capped cadmium sulfide (CdS) quantum dots (QDs) as a sensitive probe for the determination of Cu<sup>2+</sup> and Ni<sup>2+</sup> contaminations in several environmental water samples. This method is based on fluorescence quenching of QDs, which is proportional to the concentration of Cu<sup>2+</sup> and Ni<sup>2+</sup>, in deferent conditions. The procedure is simple, convenient and sensitive with a detection limit of 0.15 and 0.6ng ml<sup>-1</sup> for Cu<sup>2+</sup> and Ni<sup>2+</sup>, respectively. The proposed method was successfully applied to the determination of Cu<sup>2+</sup> and Ni<sup>2+</sup> in real samples including Nahand dam, Karkaj and Azarshahr well, tab and mineral waters, without any pretreatments.

## MATERIALS AND METHODS

### *Apparatus*

Fluorescence measurements were performed on a RF-5301 spectrofluorophotometer (Shimadzu, Japan) using 1.0 cm quartz cell. The widths of both the excitation and emission slits were set at 5 nm. The optimum excitation and emission wavelengths for CdSQDs were found to be 427 and 555 nm, respectively. Absorption spectra were recorded by a UV-1800 spectrophotometer (Shimadzu, Japan).

### *Materials*

Cadmium chloride (CdCl<sub>2</sub>·5H<sub>2</sub>O), sodium sulfide (Na<sub>2</sub>S·9H<sub>2</sub>O) and thioglycolic acid (TGA) were all purchased from sigma Aldrich. Buffer solutions of acetate and phosphate (0.5 mol L<sup>-1</sup>) were prepared by dissolving the appropriate amount of sodium acetate (Merck) or NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O (Merck) in double distilled water, respectively. The pHs of these buffers was adjusted to 6 and 7, respectively. Stock standard solutions of 100 mg L<sup>-1</sup> Cu<sup>2+</sup> and Ni<sup>2+</sup> were prepared in water from copper nitrate (Merck) and nickel nitrate (Merck),

respectively. Doubly distilled deionized water was used for the preparation of all solutions.

### *Synthesis of TGA- capped CdS quantum dots*

TGA-capped CdSQDs were simply synthesized in aqueous solution according to Ref. 27. Briefly, 100 ml of TGA ( $0.05 \text{ mol L}^{-1}$ ) solution and 100 ml of  $\text{CdCl}_2$  ( $0.02 \text{ mol L}^{-1}$ ) solution were mixed in a round bottom flask, resulting in an opaque blue solution. This was probably due to formation of Cd-thioglycolic complexes with different structures at different pH values because of different dissociation of Carboxylate and sulfhydryl group. Then, NaOH ( $1 \text{ mol L}^{-1}$ ) solution was added drop wise until the pH of solution adjusted in 8, and a clear solution was obtained. The mixture was heated near the boiling point in the argon atmosphere and 50 ml of  $\text{Na}_2\text{S}$  ( $0.02 \text{ mol L}^{-1}$ ) was added suddenly. After refluxing for 2 min, the flask was submerged in the ice-water bath to reach the room temperature. After purification with ethanol, QDs were used as fluorescent probes.

### *General procedure*

Certain amount of synthesized QDs solution and buffer

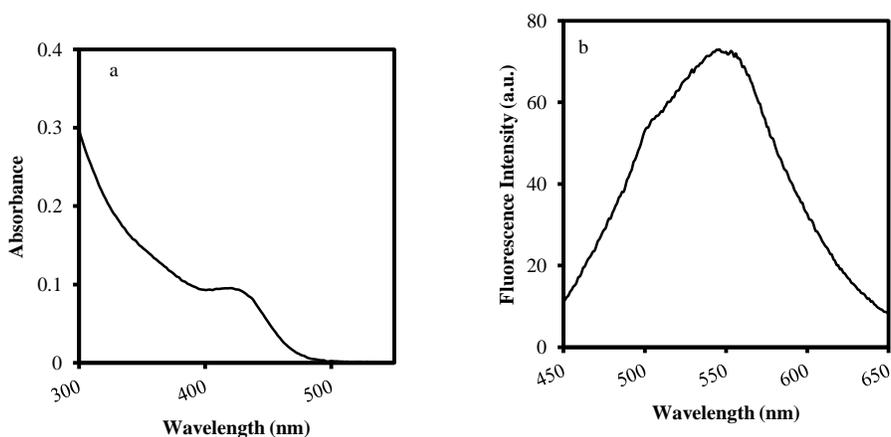
(in optimum amounts and conditions) were transferred to 5 mL volumetric flask. An appropriate volume of sample or standard solutions was added and the final volume was reached to 5 mL with distilled water. The fluorescence intensity of the solution was recorded as analytical signal.

## RESULTS AND DISCUSSION

### *Synthesis of thioglycolic acid-capped CdSQuantum Dots*

Thioglycolic acid-capped CdSQDs (TGA- capped CdSQDs) were synthesized via a simple chemical method and characterized by UV–vis absorption spectroscopy and fluorometry. The synthesized CdSQDs showed long emission wavelengths and a high separation between the excitation and emission wavelengths (ca. 125 nm) simplifying fluorescence measurements. The exciting wavelength was at 427 nm, and a sharp band edge emission peak ( $\lambda=555 \text{ nm}$ ) was obtained in the fluorescence spectrum, which was independent of the excitation wavelength (Figure 1).

In addition, TEM (transmission electron microscopy) image of Synthesized QDs is shown in Figure 1c.



**Figure 1.** (a) Absorption and (b) Fluorescence spectra of synthesized aqueous TGA-capped CdSQDs,

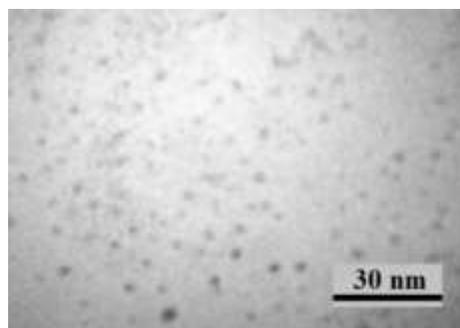


Figure 1 Continued. (c) TEM image of synthesized aqueous TGA-capped CdS QDs.

### Quenching of the fluorescence of QDs by $\text{Cu}^{2+}$ and $\text{Ni}^{2+}$

Trace amount of some cations could remarkably quench the emission of quantum dots. Synthesized QDs had high tendency for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in a certain condition.

The fluorescence emission intensity was decreased with increasing  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  concentration. This decrease was proportional to each cation concentration (Figure 2), and was base of their determinations

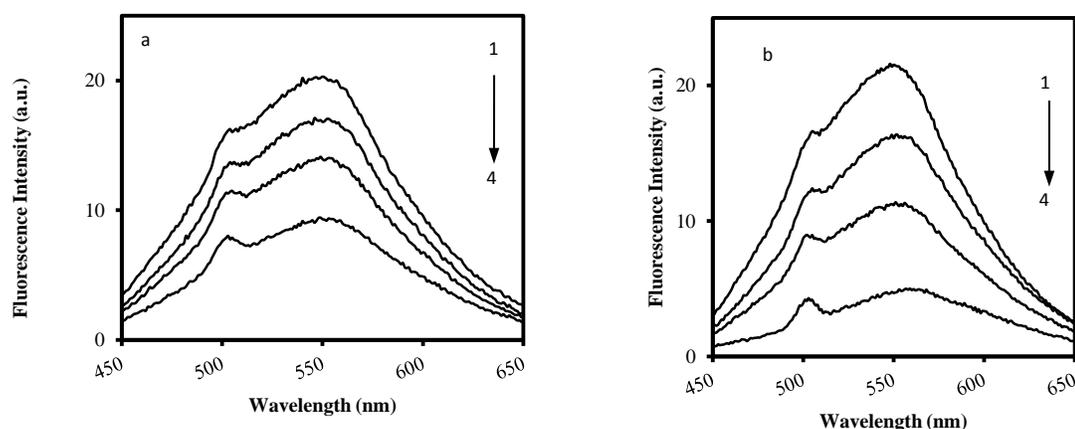


Figure 2. Fluorescence spectra of aqueous TGA-capped CdS QDs in the presence different concentration of (a)  $\text{Ni}^{2+}$  and (b)  $\text{Cu}^{2+}$  (in optimum condition), [1 to 4: 0, 20, 50, 80ng mL<sup>-1</sup>].

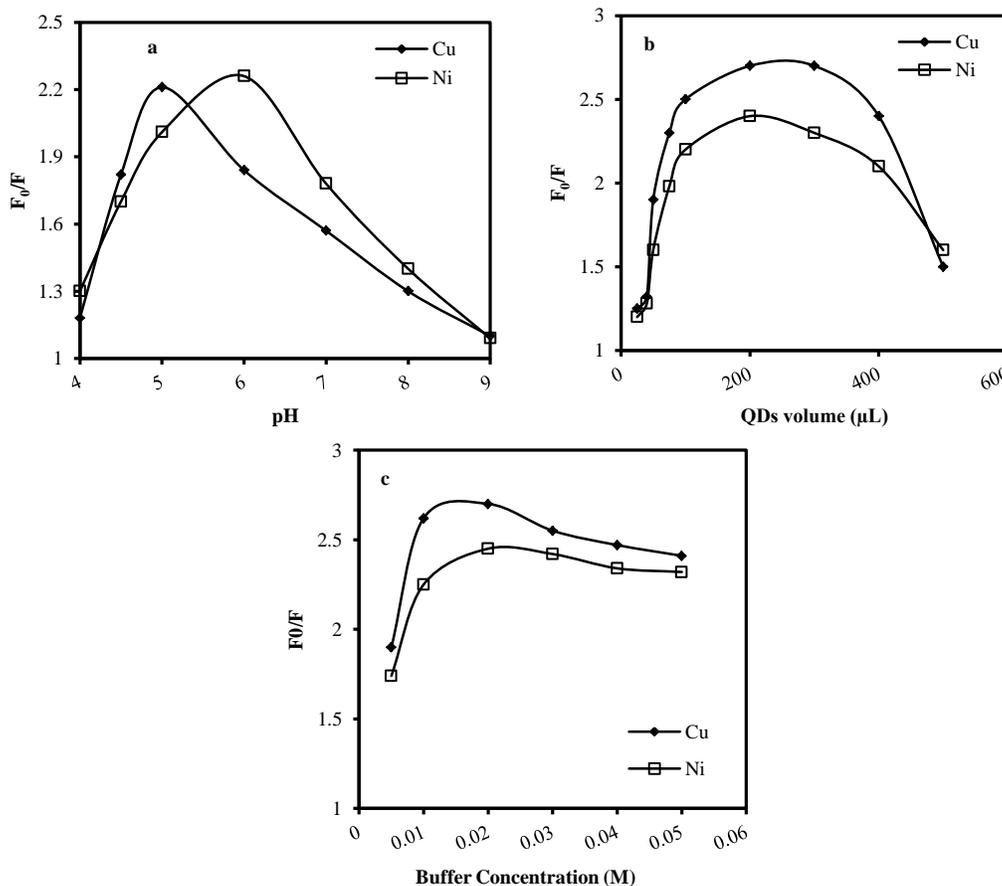
### Optimization of condition

Condition of solution cans significantly affected the fluorescence intensity. Thus, we investigated the effect of pH on determinations, as an important parameter in solution. The pH of QDs solutions was adjusted between 4 and 9. Because, at lower pHs, aggregation of the QDs occur and their emission remarkably decreased [35]. The maximum signal was obtained when pH was 5 and 6 for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , respectively (Figure 3a). Therefore, these optimal pH values were applied in

further experiments. Concentration of QDs in solution could affect the fluorescent intensity and the sensitivity of the assay. At higher concentration of aqueous QDs, self-quenching could decrease the QDs fluorescence and cause low sensitivity (Figure 3b). On the other hand, very low concentrations of QDs caused very weak fluorescence intensity. Overall, 200  $\mu\text{L}$  of QDs was chosen as optimum amount for both  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  determinations. In this condition, wide linear range and low detection limits were obtained.

To study the effect of buffer solution on fluorescence intensity, different buffer solutions such as phosphate, tris and acetate were investigated. Acetate and phosphate had the greatest effect on the fluorescence

quenching behavior of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , respectively. Optimization of buffer concentration was also carried out and maximum signal was obtained in 0.02 M for both cations (Figure 3c).



**Figure 3.** Effects of (a) pH for  $\text{Cu}^{2+}$  80ng mL<sup>-1</sup> [QDs=100  $\mu\text{L}$ , acetate buffer 0.02 M] and  $\text{Ni}^{2+}$  80ng mL<sup>-1</sup> [QDs=100  $\mu\text{L}$ , phosphate buffer 0.05 M], (b) QDs amount for  $\text{Cu}^{2+}$  [acetate buffer 0.02 M pH=5] and  $\text{Ni}^{2+}$  [phosphate buffer 0.05 M, pH=6], (c) buffer concentration for  $\text{Cu}^{2+}$  [QDs=200  $\mu\text{L}$ , acetate buffer, pH=5] and  $\text{Ni}^{2+}$  [QDs=200  $\mu\text{L}$ , phosphate buffer, pH=6], on the  $F_0/F$ .

### Figure of merits

Under the optimal condition, Calibration graphs, theratioof FL intensity ( $F_0/F$ ) in the absence ( $F_0$ ) and

presence of analyte (F) versus the concentration of each analyte in ngmL<sup>-1</sup>, was plotted (Figure 4). Analytical characteristics of method are indicated in Table 1.

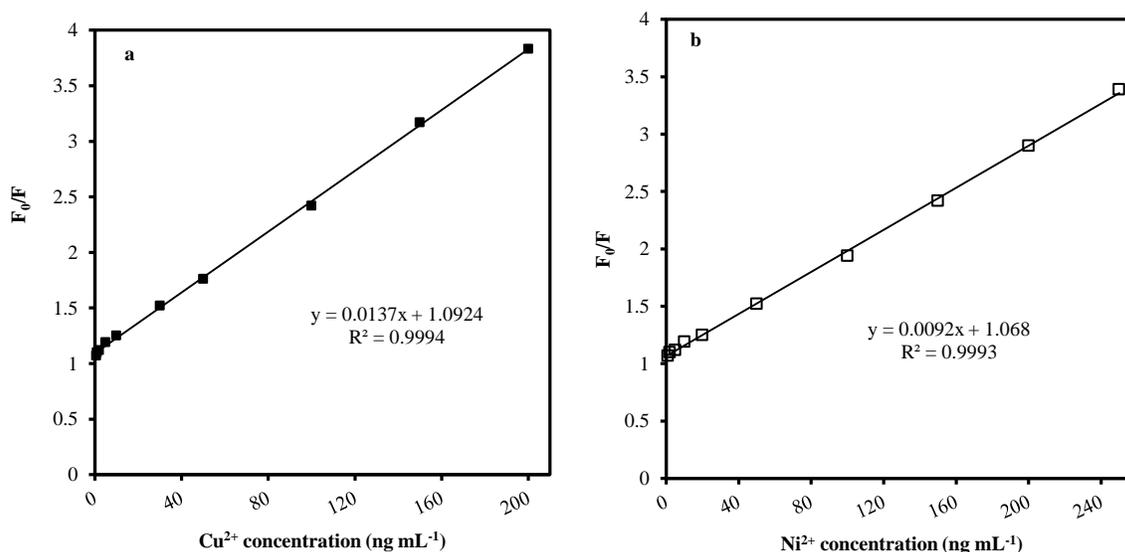


Figure 4. Calibration curve of the (a) Cu<sup>2+</sup> and (b) Ni<sup>2+</sup> in optimum condition

Table 1. Analytical characteristics of the method for the determination of Cu<sup>2+</sup> and Ni<sup>2+</sup>

Parameter	Cu <sup>2+</sup>	Ni <sup>2+</sup>
Linear range, ngmL <sup>-1</sup>	0.6-200	1-250
Slope	0.0137	0.0092
Intercept	1.09	1.06
Correlation coefficient (r)	0.9994	0.9993
Number of points	10	10
LOD, ngmL <sup>-1</sup>	0.15	0.40
RSD% (n=5, 5 ngmL <sup>-1</sup> )	2.1	2.8
RSD% (n=5, 50 ngmL <sup>-1</sup> )	1.8	2.2
RSD% (n=5, 150 ngmL <sup>-1</sup> )	0.9	1.9

#### Interference of co-existing foreign substances

In order to test the interference effect of some potentially interfering substances, increasing amounts of these species was added into a solution of 1 µg mL<sup>-1</sup> Cu<sup>2+</sup> or Ni<sup>2+</sup>. The tolerable concentration ratios for interferences in relative error of <5% were over 5000 for Na<sup>+</sup>, K<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, 2000 for PO<sub>4</sub><sup>3-</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>,

Ca<sup>2+</sup>, Cl<sup>-</sup>, 500 for Cd<sup>2+</sup> and 200 for Zn<sup>2+</sup>, Hg<sup>2+</sup>. Thus, the amounts of most of the potentially interfering species in biological fluids were below their tolerable levels, and there were no interferences from these species in determination of Cu<sup>2+</sup> and Ni<sup>2+</sup>.

**Analysis of real samples**

The represented method was successfully applied to the quantitative determination of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  contamination in some real samples such as Nahand dam, Karkaj and Azarshahr well, tap and mineral waters. Real samples were spiked with standard solution of each analyte, and then analyzed by standard addition method. There were not any pretreatment step for real samples. In Table 2, 3 the obtained recovery values in

real samples are listed. The recoveries were between 96-104%, show that the proposed procedure is applicable to the determination of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in environmental samples. On the other hand, the results were compared with those obtained by a standard method using electrothermal atomic absorption spectroscopy. Statistical analysis using Student *t*-test showed that there were no significant differences between the results of two methods.

**Table 2.** Results for the determination of  $\text{Cu}^{2+}$  in the real samples

Sample ( $\text{Cu}^{2+}$ )	Add ( $\text{ngmL}^{-1}$ )	Found <sup>a</sup> ( $\text{ngmL}^{-1}$ ) purposed method	Recovery %	Found <sup>a</sup> ( $\text{ngmL}^{-1}$ ) Standard method
Karkaj well water	0	11.6±0.5	-	11.8±0.8
	10	22.0±0.4	104±2.1	-
	50	61.8±0.3	101±0.7	-
Nahand dam water	0	15.4±0.4	-	15.2±0.6
	10	25.1±0.4	97.1±1.9	-
	50	64.9±0.9	98.9±1.6	-
Azarshahr well water	0	22.6±0.6	-	21.9±1.0
	10	32.2±0.7	96.2±2.2	-
	50	71.8±1.2	98.3±1.8	-
Mineral water	0	Not Detect	-	Not Detect
	10	10.2±0.1	102±1.1	-
	50	49.1±0.3	98.2±0.7	-
Tabriz tap water	0	8.51±0.4	-	8.99±0.6
	10	18.2±0.4	97.1±2.2	-
	50	57.8±1.3	98.6±1.9	-

<sup>a</sup> Mean of three determinations ± standard deviation

**Table 3.** Results for the determination of  $\text{Ni}^{2+}$  in the real samples

Sample ( $\text{Ni}^{2+}$ )	Add ( $\text{ngmL}^{-1}$ )	Found <sup>a</sup> ( $\text{ngmL}^{-1}$ ) purposed method	Recovery %	Found <sup>a</sup> ( $\text{ngmL}^{-1}$ ) Standard method
Karkaj well water	0	1.62±0.09	-	1.58±0.07
	10	11.7±0.2	100±1.9	-
	50	52.0±1.4	101±2.7	-

**Table 3.** Continued.

<b>Nahand dam water</b>	0	2.10±0.11	-	2.04±0.08
	10	12.4±0.4	103±4.8	-
	50	51.8±0.9	99.4±2.1	-
<b>Azarshahr well water</b>	0	Not Detect	-	Not Detect
	10	10.3±0.2	103±2.1	-
	50	49.7±1.4	99.4±2.7	-
<b>Mineral water</b>	0	Not Detect	-	Not Detect
	10	10.1±0.3	101±3.2	-
	50	50.8±0.9	102±1.9	-
<b>Tabriz tab water</b>	0	Not Detect	-	Not Detect
	10	9.73±0.4	97.4±3.8	-
	50	48.9±0.8	97.8±1.7	-

<sup>a</sup> Mean of three determinations ± standard deviation

## CONCLUSIONS

A simple, sensitive and rapid method for determination of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  contamination has been offered based on the quenching of the fluorescence of TGA-capped CdS quantum dots. The preparation of quantum dots is very simple, fast and economical. The procedure possesses the advantage of wide dynamic range, selectivity and high sensitivity (Detection limit is very low) which may be an incentive to other workers to consider it for determination of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in traces. In addition, the method does not need any pretreatments steps in analysis. Finally, this procedure successfully applied for determination of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in environmental real samples.

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