ORIGINAL ARTICLE

Ultrasensitive determination of lead and chromium contamination in well and dam water based on fluorescence quenching of CdS quantum dots

Jafar Abolhasani · Javad Hassanzadeh · Elnaz Seyed Jalali

Abstract We report lead (Pb^{2+}) and chromium (Cr^{3+}) determination in several water samples obtained from Nahand dam, Karkaj and Azarshahr well, tab and mineral waters to study their contamination in these systems. Determination method is based on the characteristic aggregation and fluorescence quenching of synthesized CdS quantum dots (QDs) at 555 nm by considered cations. Water-soluble and biocompatible CdS QDs modified with thioglycolic acid have been synthesized in one step and characterized by fluorescence and absorption spectroscopy. The fluorescence intensity of CdS QDs is linearly proportional to Pb^{2+} and Cr^{3+} concentration from 0.8 to 100 and 3 to 400 ng mL^{-1} with a detection limit of 0.3 and 1.2 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 lower detection blank and higher sensitivity.

Keywords Lead · Chromium · Contamination · Fluorescence quenching · CdS quantum dots

Introduction

Pollution by heavy metal ions, particularly lead (Pb^{2+}) and chromium (Cr^{3+}), causes a serious hazard to human life and the environment. Pb^{2+}, the heaviest stable element, is one of the four metals that have the greatest effects on human health. Due to its characteristics as a very toxic poison to humans, even at low concentrations, Pb^{2+} has been studied extensively. Many diseases are spread because of the toxic effects of Pb^{2+}, such as respiratory diseases like asthma and allergies, lowered IQ and other nervous system disorders, impaired biosynthesis of hemoglobin and anemia, high blood pressure, kidney damage and brain [1]. The use of Pb^{2+} in electronics has been restricted by European Parliament to reduce unsafe chemical waste leakage to the groundwater [2]. Also Environmental Protection Agency (EPA) set the allowed limit of Pb^{2+} in drinking water as 15 ng mL^{-1}. Unfortunately, Pb^{2+} is still used in refineries to increase gasoline octane number. Cigarette smoke has also a small amount of Pb^{2+}. Also, Pb^{2+} enters drinking water and soil due to corrosion of water lead pipes.

Non-degradable and bio-fermentation Cr^{3+} in nature as well as its extensive usage is the main reason that it is considered a serious environmental pollutant. Cr^{3+} is one of the main pollutants in water, because of its lower storage requirements in some industrial activities. Chromium is known to be toxic to plants and animals because of its potentially carcinogenic effect duo to permeability of cell membranes.

Therefore, due to health concerns and legal restrictions, rapid and sensitive methods are critical for evaluation of heavy metals. Several methods have been reported for Pb^{2+} and Cr^{3+} determination based on electrothermal atomic absorption spectrometry [3, 4], X-ray fluorescence [5], chromatography [6], electrochemical methods [7–9], mass spectroscopy [10, 11] and photometric methods [12]. These methods often require complex and expensive equipment, skilled labor, and high time for preparation of samples. Also, it is necessary to further improve their sensitivity and selectivity. In the meantime, fluorescence recently has attracted much attention, because of its high sensitivity.

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Several fluorescent probes based on organic luminescent dyes [13–16] have been reported for detection of Pb^{2+} or Cr^{3+}. These methods generally displayed relatively high detection limits. In contrast, quantum dots (QDs) displayed superior luminescence properties and stability in aqueous solutions [17, 18]. There are several reports for ion detection based on the fluorescence intensity of quantum dots. Since, Chen and Rosenzweig showed that fluorescence intensity of thioglycerol-coated CdS QDs was reduced selectively in the presence of Cu^{2+} [19], several research groups have applied different types of quantum dots as luminescence probe for Hg^{2+} [20–24], Cu^{2+} [25–29], Ag^+ [25, 30], Pb^{2+} [31–33] based on their fluorescence quenching effect. All the reports show the interaction between the analyte and quantum dots which change their physical and photochemical features.

This paper describes a sensitive method for the determination of Pb^{2+} and Cr^{3+} contaminations in several environmental water samples, based on fluorescence quenching of thioglycolic acid (TGA) capped cadmium sulfide (CdS) quantum dots (QDs). The quenched intensity of fluorescence was proportional to the concentration of Pb^{2+} and Cr^{3+} in different conditions. The procedure is simple, convenient and sensitive with a detection limit of 0.3 and 1.2 ng mL^{-1} for Pb^{2+} and Cr^{3+}, respectively. It does not need any pretreatments for samples. The proposed method was successfully applied to the determination of Pb^{2+} and Cr^{3+} in real samples including Nahand dam, Karkaj and Azarshahr well, tab and mineral waters.

Experimental

Apparatus

Fluorescence measurements were performed on a RF-5301 spectrofluorophotometer (Shimadzu, Japan) equipped with a xenon lamp source, using 1.0 cm quartz cell with a cell holder kept in a constant-temperature water circulating device, thermo bath TB-85. The widths of both excitation and emission slits were set at 5 nm. The optimum excitation and emission wavelengths for CdS QDs were found to be 427 and 555 nm, respectively. Absorption spectra were recorded by a UV-1800 spectrophotometer (Shimadzu, Japan).

Materials

All experiments were carried out with analytical grade chemicals and solvents. Doubly distilled deionized water was used for the preparation of all solutions. Cadmium chloride ($CdCl_2 \cdot 5H_2O$), sodium sulfide ($Na_2S \cdot 9H_2O$) and thioglycolic acid (TGA) were all purchased from sigma Aldrich and were used without further purification. Buffer

solutions of acetate and phosphate (0.5 mol L^{-1}) were prepared by dissolving the appropriate amount of sodium acetate (Merck) or $NaH_2PO_4 \cdot 2H_2O$ (Merck) in double distilled water, respectively. The pHs of these buffer was adjusted to 5 and 6, respectively. Stock standard solutions of 100 mg L^{-1} Pb^{2+} and Cr^{3+} were prepared in water from lead nitrate (Merck) and chromium (III) nitrate (Merck), respectively.

Synthesis of TGA-capped CdS quantum dots

TGA-capped CdS QDs were synthesized in aqueous solution using a simple reported procedure [28]. Briefly, 100 ml of TGA (0.05 mol L^{-1}) solution and 100 ml of $CdCl_2$ (0.02 mol L^{-1}) solution were mixed in a round bottom flask. The pH of this solution was adjusted in 8 by NaOH (1 mol L^{-1}) solution. White residue, appear in the solution, was dissolved by adding NaOH solution and finally, the clear solution was obtained. 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. The reaction mixture was then heated up to 90 °C in the argon atmosphere. Then 50 ml of Na_2S (0.02 mol L^{-1}) was added. After refluxing for 2 min, the flask was submerged in the ice-water bath until it cooled to room temperature. After purification, QDs were used as fluorescent nanoparticles.

General procedure

For Pb^{2+} determination, 75 μL synthesized QDs solution and 200 μL phosphate buffer (pH = 5) were transferred to 5 mL volumetric flask. Then an appropriate volume of sample or standard Pb^{2+} solution was added and the final volume was made to 5 mL with distilled water. The fluorescence intensity of the solution was recorded as analytical signal.

For Cr^{3+} determination, 100 μL synthesized QDs solution and 200 μL acetate buffer (pH = 5) were transferred to 5 mL volumetric flask. Then an appropriate volume of sample or standard Cr^{3+} solution was added and the final volume was made to 5 mL with distilled water. The fluorescence intensity of the solution was recorded as analytical signal.

Results and discussion

Characterization of thioglycolic acid-capped CdS quantum dots

Synthesized thioglycolic acid-capped CdS QDs (TGA-capped CdS QDs) are optically characterized by UV–vis absorption spectroscopy and fluorometry. The TGA-capped CdS QDs show long emission wavelengths and a high

Fig. 1 a Absorption,
b Fluorescence spectra and
c TEM image of synthesized
aqueous TGA-capped CdS QDs
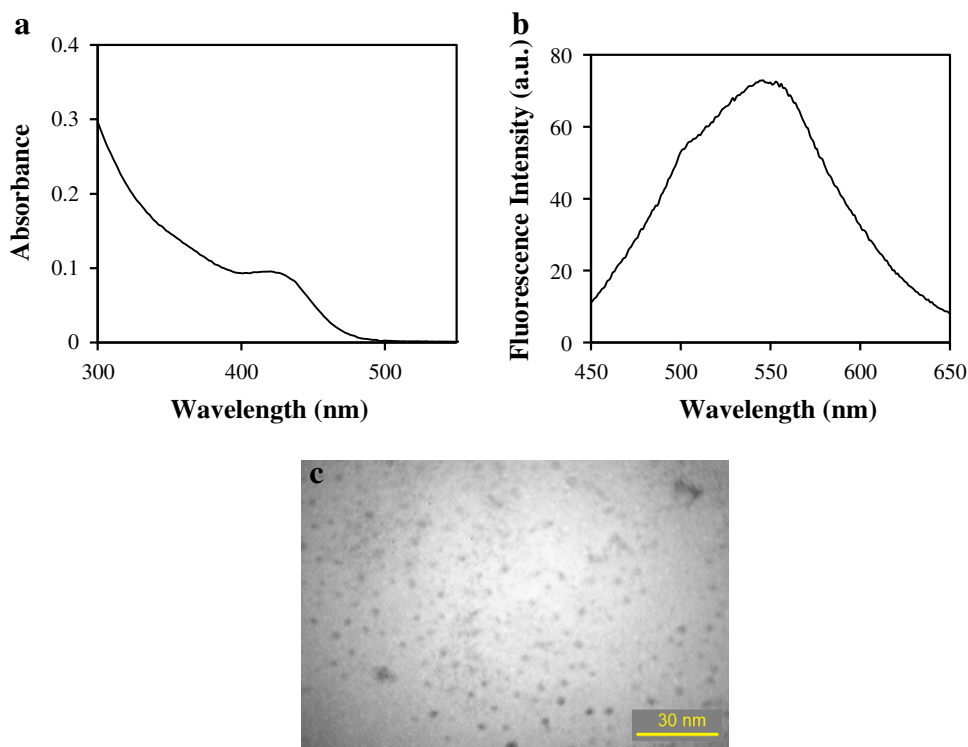
Fig. 2 Fluorescence spectra of
aqueous TGA-capped CdS QDs
in the presence of different
concentrations of **a** Cr^{3+} and
b Pb^{2+}. **a** QDs 75 μL,
phosphate buffer 0.01 M,
pH = 6 (1–7: 0, 25, 50, 100,
200, 300, 400 ng mL^{-1}). **b** QDs
100 μL, acetate buffer 0.01 M,
pH = 5 (1–7: 0, 1, 2.5, 5, 10,
50, 75 ng mL^{-1})
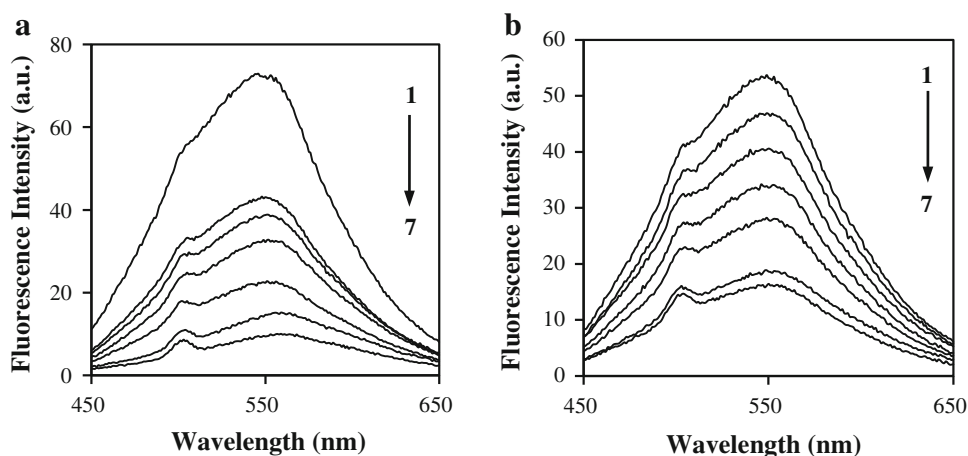
separation between the excitation and emission wave-
lengths (ca. 125 nm) simplifying fluorescence measure-
ments. The absorption spectrum shows well-defined
excitonic absorption peak at wavelength of 427 nm, and a
sharp band edge emission peak ($\lambda = 555$ nm), which was
independent of the excitation wavelength, was obtained in
the FL spectrum (Fig. 1).

Also TEM (transmission electron microscopy) image of
Synthesized QDs is shown in Fig. 1c.
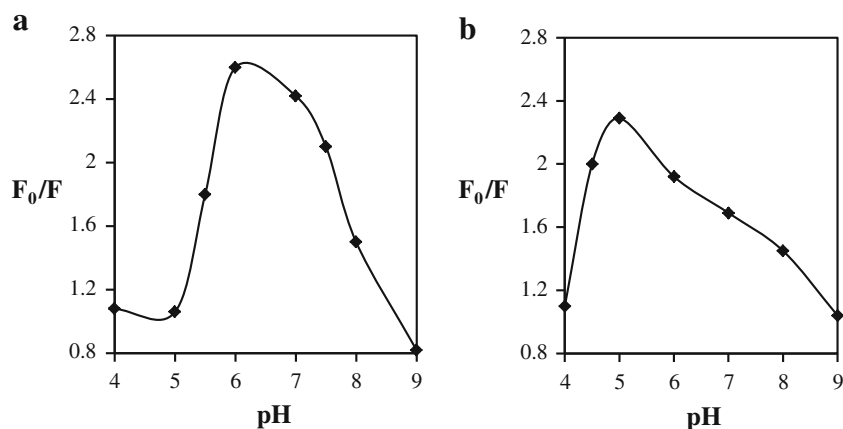
Effect of cations on the fluorescence of QDs

The fluorescence intensity ($\lambda_{ex} = 427$ nm) of quantum
dots drastically decreases with some cations in a certain

condition. It is observed that synthesized QDs have high
tendency for Pb^{2+} and Cr^{3+}. The more the Pb^{2+} or Cr^{+3}
concentration, the lower was the FL intensity obtained.
This decrease was proportional to each cation concentra-
tion (Fig. 2).

Optimization of condition

It is clear that pH influences the fluorescence intensity of
the complex significantly. To investigate the effects of pH
on determinations, the pH ranges between 4 and 9. At
lower pHs, there is no fluorescence intensity because of the
protonation of the thiol groups and aggregation of the QDs
[35]. The maximum value of F_0/F was obtained when pH

Fig. 3 Effects of pH on the F_0/F for **a** Cr^{3+} 10 ng mL^{-1} (QDs = 100 µL, phosphate buffer 0.05 M) and **b** Pb^{2+} 5 ng mL^{-1} (QDs = 75 µL, acetate buffer 0.05 M)

Fig. 4 Effects of QDs amount on the F_0/F for **a** Cr^{3+} 10 ng mL^{-1} (phosphate buffer 0.05 M, pH = 6) and **b** Pb^{2+} 5 ng mL^{-1} (acetate buffer 0.05 M, pH = 5)
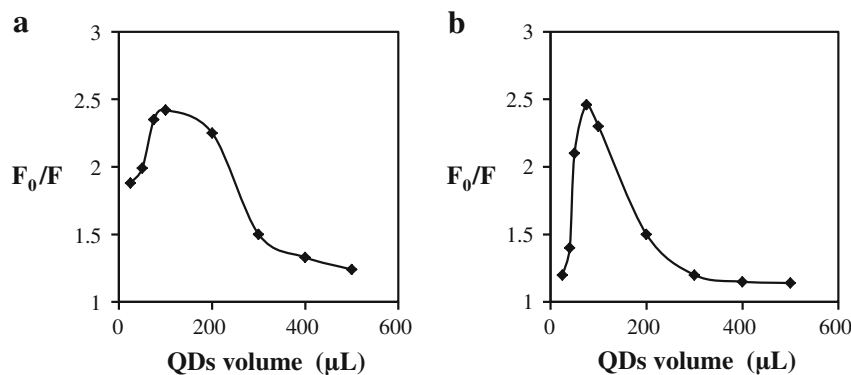
was 6 and 5 for Cr^{3+} and Pb^{2+}, respectively (Fig. 3). (F_0 and F are the fluorescence intensity of the aqueous CdS QDs without and at a given analyte concentration). Therefore, these optimal pH values were chosen to be applied in further experiments.

It was found that the concentration of QDs affected not only the fluorescent intensity but also the sensitivity of the assay. As shown in Fig. 4, high concentration of aqueous QDs decreases the sensitivity and causes self-quenching of the QDs fluorescence. Also, very low concentration of QDs gives very weak fluorescence intensity, which may result in narrow linear range. Thus, 100 and 75 µL of QDs was chosen for Cr^{3+} and Pb^{2+} determinations, respectively. In selected optimal values of the quantum dots, wide linear range and low detection limit concentrations are achieved.

The effect of buffer solution on fluorescence intensity system was discussed. To do so, different buffer solutions such as phosphate, tris and acetate were investigated. The results showed that phosphate and acetate have the greatest effect on the fluorescence quenching of TGA-capped CdS QDs in the presence of Cr^{3+} and Pb^{2+}, respectively. Hence, these buffers were selected in all experiments. Optimization of buffer concentration was carried out and the result is showed in Fig. 5. Maximum signal was obtained in 0.01 M for both states.

In results, the best optimal conditions for the measurement of Cr^{3+} are: QDs = 100 µL, phosphate buffer 0.01 M, pH = 6, and for Pb^{2+} are: QDs = 75 µL, acetate buffer 0.01 M, pH = 5.

Quantitative characteristics

Under optimal condition, the ratio of FL intensity (F_0/F) in the absence (F_0) and presence of analyte (F) was plotted versus the concentration of each analyte in ng mL^{-1}. Calibration graphs and corresponding FL spectra are shown in Fig. 6. Obtained analytical characteristics are indicated in Table 1.

The quenching ability of Cr^{3+} and Pb^{2+} can be expressed by Stern–Vollmer equation:

$$\frac{F_0}{F} = 1 + K_{SV}[C]$$

where F and F_0 are fluorescence quantum yield or fluorescence intensity of quantum dots with (F) and without (F_0) extinguishing or analyte. K_{sv} is the Stern–Vollmer constant. Linear equations between concentration and relative fluorescence intensity obtained for Cr^{3+} and Pb^{2+} ($y = 0.0024x + 1.065$ and $y = 0.0098x + 1.057$, respectively) are consistent with Stern–Vollmer equation.

Fig. 5 Effects of buffer concentration on the F_0/F for **a** Cr^{3+} 10 ng mL^{-1} (QDs = 100 μL, phosphate buffer pH = 6) and **b** Pb^{2+} 5 ng mL^{-1} (QDs = 75 μL, acetate buffer pH = 5)
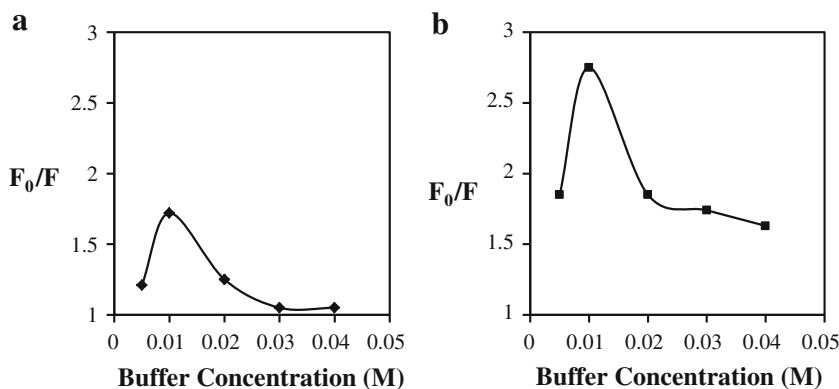
Fig. 6 Calibration curve of the **a** Cr^{3+} and **b** Pb^{2+} in optimum condition
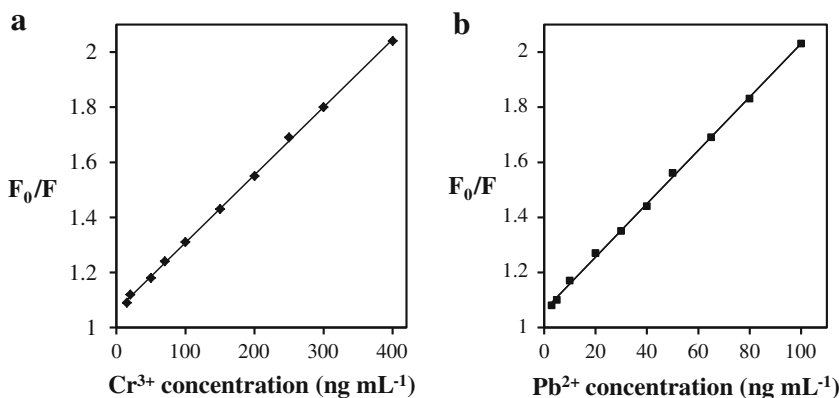
Table 1 Analytical characteristics of the method for the determination of Cr^{3+} and Pb^{2+}

Parameter	Cr^{3+}	Pb^{2+}
Linear range (ng mL^{-1})	3–400	0.8–100
Slope	0.0024	0.0098
Intercept	1.065	1.057
Correlation coefficient (r)	0.9993	0.9979
Number of points	10	10
LOD (ng mL^{-1})	1.2	0.8
RSD% ($n = 5$)	3.2 (8 ng mL^{-1})	2.1 (5 ng mL^{-1})
RSD% ($n = 5$)	3.0 (50 ng mL^{-1})	3.9 (10 ng mL^{-1})
RSD% ($n = 5$)	1.4 (300 ng mL^{-1})	2.4 (50 ng mL^{-1})

Table 2 Interfering effects of some coexisting ions on Cr^{3+} and Pb^{2+} determination

Coexisting ions	Interference ratio for Cr^{3+}	Interference ratio for Pb^{2+}
Hg^{2+}, Fe^{3+}	800	800
Cd^{2+}	300	300
Zn^{2+}	500	300
Na^+	2,000	2,000
Co^{2+}	150	150
Cu^{2+}	200	250
Li^+, Ni^{2+}, K^+, NO_3^-	500	500
CO_3^{2-}	5,000	4,000
SO_4^{2-}	4,000	400
Cl^-	7,000	600

Interference of coexisting foreign substances

In order to investigate the effect of coexisting substances on Cr^{3+} and Pb^{2+} determination in real samples, various concentrations of interfering ions are added to determination solution (1 μg mL^{-1} analyte) and, F/F_0 value is measured versus interference ion concentration. Interference limit is considered 5 % deviation from the initial F/F_0 value (Table 2). The results show that the method for analysis of Cr^{3+} and Pb^{2+} is free from any interference.

Analysis of real samples

The represented method was successfully applied to the quantitative determination of Cr^{3+} and Pb^{2+} in the real samples of various compositions such as Nahand dam, Karkaj and Azarshahr well, tab and mineral waters. The real samples were spiked with standard solution of each analyte, and then were analyzed by standard addition

Table 3 Results for the determination of Pb^{2+} in the real samples

Sample (Pb^{2+})	Add (ng mL^{-1})	Found[a] (ng mL^{-1}) purposed method	Recovery %	Found[a] (ng mL^{-1}) standard method
Karkaj well water	0	4.22 ± 0.2	–	4.51 ± 0.3
	5	9.28 ± 0.1	101 ± 2.0	–
	10	14.40 ± 0.3	102 ± 2.9	–
Nahand dam water	0	0	–	Not detect
	5	4.85 ± 0.11	97.2 ± 2.2	–
	10	10.38 ± 0.21	104 ± 2.3	–
Azarshahr well water	0	Not detect	–	Not detect
	5	5.12 ± 0.1	102 ± 2.1	–
	10	10.14 ± 0.2	101 ± 1.9	–
Mineral water	0	Not detect	–	Not detect
	5	5.21 ± 0.1	104 ± 1.8	–
	10	10.38 ± 0.3	104 ± 2.9	–
Tabriz tab water	0	Not detect	–	Not detect
	5	5.11 ± 0.1	102 ± 1.7	–
	10	10.09 ± 0.3	101 ± 2.5	–

[a] Mean of three determinations $\pm$ standard deviation

Table 4 Results for the determination of Cr^{3+} in the real samples

Sample (Cr^{3+})	Add (ng mL^{-1})	Found[a] (ng mL^{-1}) purposed method	Recovery %	Found[a] (ng mL^{-1}) standard method
Karkaj well water	0	5.81 ± 0.12	–	5.48 ± 0.31
	5	10.72 ± 0.18	97.2 ± 3.6	–
	10	15.58 ± 0.25	97.7 ± 2.4	–
Nahand dam water	0	12.50 ± 0.20	–	4.51 ± 0.14
	5	17.70 ± 0.15	104 ± 2.8	–
	10	22.29 ± 0.32	97.9 ± 3.3	–
Azarshahr well water	0	9.16 ± 0.11	–	4.51 ± 0.22
	5	14.37 ± 0.15	104 ± 3.1	–
	10	19.00 ± 0.30	98.4 ± 3.2	–
Mineral water	0	Not detect	–	Not detect
	5	5.13 ± 0.14	103 ± 2.8	–
	10	10.05 ± 0.12	101 ± 1.1	–
Tabriz tab water	0	Not detect	–	Not detect
	5	4.88 ± 0.19	97.6 ± 3.7	–
	10	9.72 ± 0.30	97.2 ± 2.9	–

[a] Mean of three determinations $\pm$ standard deviation

method. In Tables 3 and 4, the obtained recovery values in real samples are listed.

The recoveries were between 97 and 104 %, showing that the proposed procedure is applicable to the determination of Cr^{3+} and Pb^{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 are no significant differences between the results of two methods.

Conclusion

A simple, sensitive and rapid method for determination of Cr^{3+} and Pb^{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. Also the method does not need any pretreatment steps in analysis. The procedure possesses the advantage of wide dynamic range, selectivity and high sensitivity (expressed by the detection limits)

which may be an incentive to other workers to consider it for determination of Cr^{3+} and Pb^{2+} in traces. Finally, this procedure was successfully applied to determine Cr^{3+} and Pb^{2+} in environmental real samples.

References

1. Landrigan, P.J., Todd, A.C.: Lead poisoning. West. J. Med. **161**, 153–159 (1994)
2. Directive 2002/95/EC: Restriction of the use of certain hazardous substances in electrical and electronic equipment. European Parliament and Council (2003)
3. Sadeghi, S., Mogaddam, A.Z.: Preconcentration and speciation of trace amount of chromium in saline samples using temperature-controlled microextraction based on ionic liquid as extraction solvent and determination by electrothermal atomic absorption spectrometry. Talanta **99**, 758–766 (2012)
4. Sardans, J., Montes, F., Penuelas, J.: Determination of As, Cd, Cu, Hg and Pb in biological samples by modern electrothermal atomic absorption spectrometry. Spectrochim. Acta B **65**, 97–112 (2010)
5. Orescanin, V., Mikelic, L., Lulic, S., Rubcic, M.: Determination of Cr(III) and Cr(VI) in industrial and environmental liquid samples by ED-XRF method. Anal. Chim. Acta **527**, 125–129 (2004)
6. Threeprom, J., Purachaka, S., Potipan, L.: Simultaneus determination of Cr(III)-EDTA and Cr(VI) by ion interaction chromatography using a C_{18} column. J. Chromatogr. A **1073**, 291–295 (2005)
7. Dominguez, O., Arcos, M.J.: Simultaneus determination of chromium(VI) and chromium(III) at trace levels by adsorptive stripping voltammetry. Anal. Chim. Acta **470**, 241–252 (2002)
8. Li, J.J., Zhang, C., Wei, H., Wang, E.K.: Combining chemical reduction with an electrochemical technique for the simultaneous detection of Cr(VI), Pb(II) and Cd(II). Analyst. **134**, 273–277 (2009)
9. Yasri, N.G., Halabi, A.J., Istamboulie, G., Noguer, T.: Chrono-amperometric determination of lead ions using PEDOT: PSS modified carbon electrodes. Talanta **85**, 2528–2533 (2011)
10. Milne, A., Landing, W., Bizimis, M., Morton, P.: Determination of Mn, Fe Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). Anal. Chim. Acta **665**, 200–207 (2010)
11. Beceiro-Gonzalez, E., Guimaraes, A., Alpendurada, M.F.: Optimisation of a headspace-solid-phase micro-extraction method for simultaneous determination of organometallic compounds of mercury, lead and tin in water by gas chromatography–tandem mass spectrometry. J. Chromatogr. A **1216**, 5563–5569 (2009)
12. Chai, F., Wang, C.A., Wang, T.T., Li, L., Su, Z.M.: Colorimetric detection of Pb^{2+} using glutathione functionalized gold nanoparticles. Appl. Mater. Interfaces **2**, 1466–1470 (2010)
13. Hosseini, M.S., Belador, F.: Cr(III)/Cr(VI) speciation determination of chromium in water samples by luminescence quenching of quercetin. J. Hazard. Mater. **165**, 1062–1067 (2009)
14. Kwon, J.Y., Jang, Y.J., Lee, Y.J.: A highly selective fluorescent chemosensor for Pb^{2+}. J. Am. Chem. Soc. **127**, 10107–10111 (2005)
15. Chen, C.T., Huang, W.P.: A highly selective fluoroscent chemosensor for lead ions. J. Am. Chem. Soc. **124**, 6246–6247 (2002)
16. Bozkurt, S.S., Ayata, S., Kaynak, I.: Fluorescence-based sensor for Pb(II) using tetra-(3-bromo-4-hydroxyphenyl) porphyrin in liquid and immobilized medium. Spectrochim. Acta A **72**, 880–883 (2009)
17. Michalet, X., Pinaud, F.F., Bentolila, L.A., Tsay, J.M., Doose, S., Li, J.J., Sundaresan, G., Wu, A.M., Gambhir, S.S., Weiss, S.: Quantum dots for live cells, in vivo imaging, and diagnostics. Science **307**, 538–544 (2005)
18. Alivisatos, P.: The use of nanocrystals in biological detection. Nat. Biotechnol. **22**, 47–52 (2004)
19. Chen, Y., Rosenzweig, Z.: Luminescent CdS quantum dots as selective ion probes. Anal. Chem. **74**, 5132–5138 (2002)
20. Xia, Y.S., Zhu, C.Q.: Use of surface-modified CdTe quantum dots as fluorescent probes in sensing mercury (II). Talanta **75**, 215–221 (2008)
21. Cai, Z.X., Yang, H., Zhang, Y., Yan, X.P.: Preparation, characterisation and evaluation of water-soluble L-cysteine capped CdS nanoparticles as fluorescence probe for detection of Hg(II) in aqueous solution. Anal. Chim. Acta **559**, 234–239 (2006)
22. Li, H., Zhang, Y., Wang, X., Gao, Z.: A luminescent nanosensor for Hg(II) based on functionalised CdSe/ZnS quantum dots. Microchim. Acta **160**, 119–123 (2008)
23. Chen, J., Gao, Y.C.: A novel fluorescent array for mercury (II) ion in aqueous solution with functionalized cadmium selenide nanoclusters. Anal. Chim. Acta **577**, 77–84 (2006)
24. Koneswaran, M., Narayanaswamy, R.: Mercaptoacetic acid capped CdS quantum dots as fluorescence single shot probe for mercury(II). Sens. Actuators. B **139**, 91–96 (2009)
25. Gattas-Asfura, KM., Leblanc, RM.: Peptide-coated CdS quantum dots for the optical detection of copper (II) and silver (I) Chem. Commun. 2684–2685 (2003)
26. Fernandez-Arguelles, M.T., Jin, W.J., Costa-Fernandez, J.M., Pereiro, R., Sanz-Medel, A.: Surface-modified CdSe quantum dots for the sensitive and selective determination of Cu(II) in aqueous solutions by luminescent measurements. Anal. Chim. Acta **549**, 20–25 (2005)
27. Xie, H.Y., Liang, J.G.: Luminescent CdSe- ZnS quantum dots as selective Cu2 + probe. Spectrochim. Acta A **60**, 2527–2530 (2004)
28. Zhang, Y., Zhang, H.: L-Cysteine-coated CdSe/CdS core-shell quantum dots as selective fluorescence probe for copper(II) determination. Microchem. J. **89**, 142–147 (2008)
29. Koneswaran, M., Narayanaswamy, R.: L-Cysteine-capped ZnS quantum dots based fluorescence sensor for Cu^{2+} ion. Sens. Actuators B **139**, 104–109 (2009)
30. Chen, J.L., Zhu, C.Q.: Functionalised cadmium sulfide quantum dots as fluorescence probe for silver ion determination. Anal. Chim. Acta **546**, 147–153 (2005)
31. Ali, E.M., Zheng, Y., Yu, H., Ying, J.Y.: Ultrasensitive Pb^{2+} detection by glutathione capped quantum dots. Anal. Chem. **79**, 9452–9458 (2007)
32. Wu, H., Liang, J., Han, H.: A novel method for the determination of Pb^{2+} based on the quenching of the fluorescence of CdTe quantum dots. Microchim. Acta **161**, 81–86 (2008)
33. Cai, Z., Shi, B., Zhao, L., Ma, M.: Ultrasensitive and rapid lead sensing in water based on environmental friendly and high

luminescent L-glutathione-capped-ZnSe quantum dots. Spectrochim. Acta A **97**, 909–914 (2012)

34. Winter, J.O., Gomez, N., Gatzert, S., Schmidt, C.E., Korgel, B.A.: Variation of cadmium sulfide nanoparticle size and photoluminescence intensity with altered aqueous synthesis conditions. Colloid. Surf. A **254**, 147–157 (2005)

35. Wang, G.L., Dong, Y.M., Yang, H.X., Li, Z.J.: Ultrasensitive cysteine sensing using citrate-capped CdS quantum dots. Talanta **83**, 943–947 (2011)