**Iranian Journal of Analytical Chemistry**
Volume 3, Issue 2, September 2016 (137-144)

**مجله ایرانی شیمی تجزیه**
دوره ۳، شماره ۲، مهرماه ۱۳۹۵ ( ۱۴۴-۱۳۷ )

# حذف یون‌های سرب و روی از محلول‌های با استفاده از نفتالین اصلاح‌شده با مشتق مالنونیتریل

**فاطمه صابر ماهانی[۱،*]، فاطمه ضیاالدینی[۱]، زهرا حسنی[۲]**
۱. بخش شیمی، دانشگاه پیام نور، صندوق پستی ۳۶۹۷-۱۹۳۹۵، تهران، ایران
۲. دانشکده علوم و فناوری های نوین، دانشگاه تحصیلات تکمیلی صنعتی و فناوری پیشرفته کرمان، کرمان، ایران

**تاریخ دریافت: ۲۲ فروردین ۱۳۹۵** **تاریخ پذیرش: ۲۸ اردیبهشت ۱۳۹۵**

# Removal of Lead and Zinc Ions from Aqueous Solutions Using Naphthalene Modified with Malononitrile Derivative

**Fatemeh Sabermahani[1,*], Fatemeh Ziaaddini[1] , Zahra Hassani[2]**
1. Department of Chemistry, Payame Noor University (PNU), P.O. BOX 19395-3697, Tehran, IRAN
2. Department of New Materials, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran

**Received:** 10 April 2016 **Accepted:** 17 May 2016

## چکیده

حذف یون‌های سرب و روی از محلول‌های آبی با استفاده از با استفاده از نفتالین اصلاح‌شده با ۲-(۳ و ۴ و ۵ -تری متوکسی بنزیلیدن) مالنونیتریل به عنوان جاذب سنتزی بررسی گردید. سطح جاذب توسط تکنیک FT-IR مشخص گردید. روش ناپیوسته برای بررسی رفتار جذبی مورد استفاده قرار گرفت. آزمایشات جذب سطحی نشان داد که جاذب جدید انتخاب‌پذیری و جذب خوبی را برای حذف یون‌های سرب و روی از محیط‌های آبی دارد. زمان تعادل ۵ دقیقه برای روی و ۱۵ دقیقه برای سرب بود. افزودن نمک اثر کمی بر روی حذف یون‌ها داشت. ماکزیمم ظرفیت جذب برای سرب و روی به ترتیب ۸۸/۵ و ۳۸/۹ میلی‌گرم بر گرم بود. مطالعات ترمودینامیکی نشان داد که فرایند جذب سطحی برای سرب خود به خودی و گرمازا و برای روی گرماگیر می‌باشد.

## واژه‌های کلیدی

جذب؛ سرب؛ مالنونیتریل؛ نفتالین؛ روی.

## Abstract

Removal of Pb(II) and Zn(II) ions from aqueous solutions using naphthalene modified with 2-(3,4,5-trimethoxybenzylidene) malononitrile(TMBM) as synthetic adsorbent was investigated. It was characterized by FT-IR. Batch method was applied for testing of adsorption behavior. Adsorption experiments showed, the new sorbent has high selectivity and good adsorption for removal of lead and zinc ions from aqueous solutions. Equilibration time was 5 min for zinc and 15 min for lead. There was little effect of salt on removal of the ions. The maximum adsorption capacities for Pb(II) and Zn(II) were 88.5 and 38.9 mg $g^{-1}$, respectively. The thermodynamic studies indicated that the adsorption was spontaneous, exothermic and endothermic process for lead and zinc, respectively.

## Keywords

Adsorption; Lead; Malononitrile; Naphthalene; Zinc.

## 1. INTRODUCTION

Increasing concentration of heavy metals in the water constitutes a severe health hazard and harmful effects due to their toxicity, persistent in nature particularly when they exceed the permissible limits. These heavy metals introduced into aquatic ecosystems and natural water resources by waste water discharged from industries. Lead contamination is known as one of the most pervasive and elusive environmental health threats, as considered by the fact that exposure lead(II) has been associated with death and disease in humans, birds, and animals. The lead (II) ions concentration is approximately in the range of 200–500 mg $dm^{-3}$in industrial wastewaters, according to water quality standards; this value is very high and must be reduced to a value of 0.10–0.05 mg $dm^{-3}$[1]. Zinc is an essential trace element for humans, plants and animals. It plays an important role in several biochemical processes and its compounds have bactericidal activity [2]. However, if it is in

---

*Corresponding Author: fatemehsaber2003@yahoo.com

excess, this metal can also play an important role in the progression of damages in human body.

Precipitation, solvent extraction, concentration, evaporation, and biosorption are the conventional methods for the removal of heavy metals from aqueous solutions [3-6]. These methods suffer from cost effectiveness and ineffectiveness when the metals with low concentration are dissolved in large volume of solution. Adsorption process seems to be most effective and versatile method for removal of heavy metal if combined with regeneration steps. It solves the problem of sludge disposal and renders the system more viable. In the last few years, several methods have been applied in this area. The literatures suggested the use of various synthetic and natural adsorbents for removal of heavy metals from waste water [7- 11] but, most of them are not selective, have long contact time, and some of them low capacity for adsorption.

The present work deals with a series of batch experiments to investigate the adsorption behavior of naphthalene modified with 2-(3,4,5-trimethoxybenzylidene) malononitrile (TMBM) (Fig. 1) as an adsorbent with high selectivity, short contact time for removal of Pb(II)) and Zn(II) from aqueous solutions.

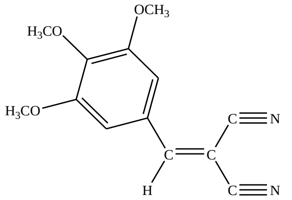

**Fig. 1**. 2-(3,4,5-trimethoxybenzylidene) malononitrile (TMBM).

## 2. EXPERIMENTAL

### *2.1. Apparatus and Reagents*

An atomic absorption spectrometer model Sens AA (Dandenong, Victoria, Australia) equipped with deuterium lamp background corrector was used for determination of Pb and Zn in air-acetylene flame. A mechanical shaker KS 130 basic (Deutschland, Germany) having speed control and timer was used for preparation of the sorbent. A 691 Metrohm pH meter (Herisau, Switzerland) was employed for pH measurements.

The stock solutions of lead (II) and zinc (II) ions used in this work was prepared by dissolving an accurate quantity of $Pb(NO_3)_2$ 99.99% (Merck, Darmstadt, Germany) and $Zn(NO_3)_2$ 99.99% (Merck, Darmstadt, Germany) in deionized water. Naphthalene 99% (Merck, Darmstadt, Germany) was used as sorbent. The ligand TMBM solution was prepared by dissolving 0.10 g of the 2-(3,4,5-trimethoxybenzylidene) malononitrile in acetone and diluting to 50 mL.

### *2.2. Preparation of the ligand TMBM*

The ligand TMBM was prepared using a procedure proposed in the literature [12]. To the mixture of 3,4,5-trimethoxybenzaldehyde (2.0 mmole) in a solution of 10-15 mL water, in the presence of (0.1-0.3) g hard coral as a catalyst, malononitrile (2.0 mmole) was added. Mixture was stirred at room temperature. The reaction progress was determined by TLC. Solid products were immediately formed. Finally reaction mixture was filtered and precipitated by recrystallization using hot water and ethanol meanwhile separated from the catalyst. Yellow pure product was formed in high yield.

mp 146-148 °C (literature29 147-148 °C) (from ethanol). IR (KBr) $cm^{-1}$: 2225.6 (CN). NMR data: δ H ($CDCl_3$) 3.91 (6H, s, 2 $OCH_3$), 3.98 (3H, s, $OCH_3$), 7.19 (2H, s, H-2, H-6), 7.65 (1H, s, CH). The FT-IR spectrum of 2-(3,4,5-trimethoxybenzylidene) malononitrile is given in Fig. 2.

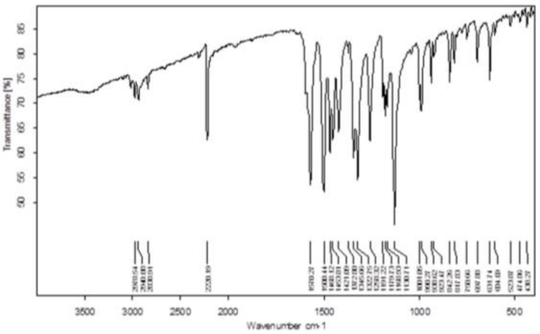

**Fig. 2**. FT-IR spectrum of 2-(3,4,5-trimethoxybenzylidene) malononitrile.

### *2.3. Preparation of the adsorbent*

The naphthalene adsorbent solution was prepared by dissolving 10 g of naphthalene and 0.1 g of 2-(3,4,5-trimethoxybenzylidene) malononitrile in 50 mL of acetone and stirring on a hot plate at 40 $^{0}$C. This solution was added to into 500 mL of water while stirring the solution at room temperature for 1 h. After allowing it to stand for 30 min the supernatant solution containing naphthalene coprecipitated with ligand was drained off by decantation and washed twice with deionized water. This adsorbent was stored in a bottle for further use.

The new adsorbent was confirmed by IR analysis (Fig. 3).

Comparison of the IR spectrum of bare naphthalene with modified naphthalene, showed many new peaks in the spectrum. The infrared spectrum of the ligand showed absorption bands at 2978 - 2838 (C-H), 2220 (CN), 1572 (C=C) and 694 (phenyl bending) (Fig. 2). The naphthalene adsorbent (Fig. 3 (a)), showed the characteristic peaks at 3084 $cm^{-1}$ are assigned to aromatic CH stretching vibration. The C=C stretching vibrations of the molecule have be observed at 1676, 1587 and 1502 $cm^{-1}$. The C-C skeletal vibrations are assigned at 1435 and 1380 $cm^{-1}$ of FTIR. The peaks appeared at 956, 779, 608 $cm^{-1}$ in FTIR confirms the C-H out of plane bending vibrations. The peaks at 1947 and 1847 $cm^{-1}$ are assumed as combination bands while 1733 $cm^{-1}$is assumed as difference band.

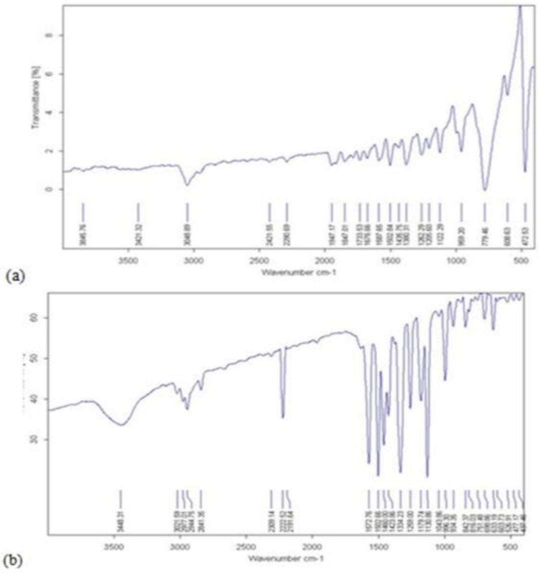

**Fig. 3.** FT-IR spectra of (a) naphthalene (b) naphthalene modified.

However, the IR-spectrum of modified naphthalene adsorbent with ligand is dominated by the peaks corresponding to the naphthalene matrix and some of the band corresponding to ligand, for example at 3021, 2977, 2944 and 2841 (C-H), 2222 (CN) and 1572 (C=C) (Fig. 3 (b)). Consequently, the above experimental results suggest that naphthalene is successfully modified by the ligand.

### 2.4. Adsorption procedure

The adsorption of the cations by modified naphthalene was studied by a batch operation using 250 mL conical flasks at room temperature. 0.05 g of adsorbent was suspended in 40 mL solution of the 30 mg $L^{-1}$ of each Pb(II) and Zn(II) at pH 6 and 8, separately. These samples were stirred for 15 min for lead and 5 min for zinc at 480 rpm. After a time period of agitation, the suspensions were filtered using Whatman filter paper and the remaining concentrations of the lead and zinc were determined by FAAS.

The percent of removed metals ions (R%), and the amount of cation adsorbed ($q_e$) by the adsorbent was calculated by the following equations:

$$R\% = (C_0 - C_e)/C_0 \qquad (1)$$

$$q_e = V(C_0 - C_e/M) \qquad (2)$$

where $q_e$ is the amount adsorbed per gram of the adsorbent, $C_0$ is initial concentration and $C_e$ is the equilibrium concentration of the metal ions (mg/L) that is obtained from calibration curves for each of cations, V is volume of solution (L) and M is the mass of dry adsorbent used (g).

## 3. RESULTS AND DISCUSSION

Naphthalene did not adsorb metal ions from the solution, but it was observed for modified naphthalene with TMBM, the uptake of Pb(II) and Zn(II) took place with high efficiency. It is due to immobilization of the ligand TMBM on naphthalene that can favor the uptake of Pb(II) and Zn(II) by formation of complexes with them. The suggested mechanism of the metal ions adsorption using Naph-ligand is given in Fig. 4. The main parameters affecting on the complexation of Pb(II) and Zn(II) with the chelating agent loaded on microcrystalline naphthalene were studied in detail, and the method was applied to the selective removal of theses cations.

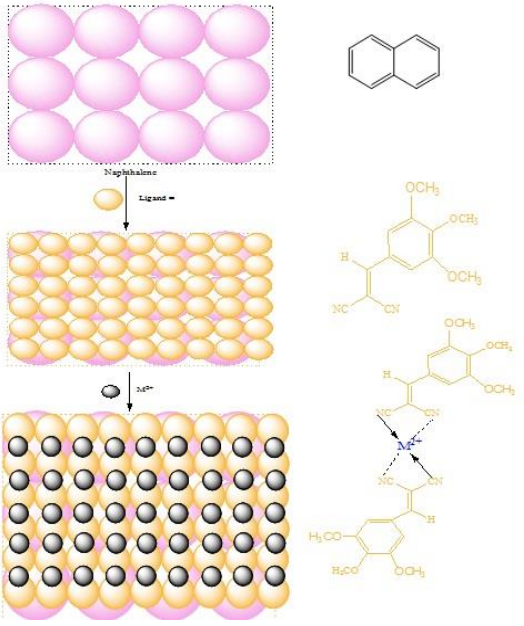

**Fig. 4.** Illustration of suggested mechanism of the metal ions adsorption using Naph-ligand.

### 3.1. Effect of solution pH

The dependence of metal sorption on pH is related to both the metal chemistry in the solution and the ionization state of the functional groups of the sorbent which affects the availability of binding sites. As can be seen from Fig. 5, removal rate increased with increasing the value of pH. Under acidic conditions, the adsorption of the metal ions is low, since the metal binding sites on the adsorbent were closely associated with $H_3O^+$ and restricted the approach of metal cations as a result of the repulsive forces. However, the adsorption increased with increasing solution pH, since more metal binding sites could be exposed with negative charges, with subsequent attraction of metal ions with positive charge and adsorption occurring onto the composite surface. The initial pH was selected 6 for lead and 8 for zinc, in further studies.

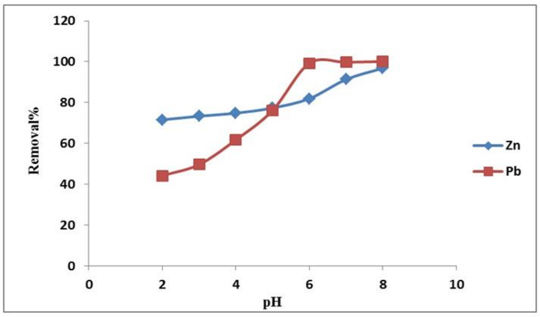

**Fig. 5.** Effect of pH on the adsorption of lead and zinc ions.

### 3.2. Effect of adsorbent dosage

The adsorption studies of Pb(II) and Zn(II) ions were done by varying the quantity of adsorbent from 0.01 to 0.2 g, at room temperature. The R% increased with an increase in the adsorbent dosage, but remained almost constant when adsorbent dosage ranged from 0.05 to 0.2 g for lead and 0.1-0.2 g for zinc (Fig. 6). The increase in R% with an increase in adsorbent dosage is due to the availability of larger surface area and more adsorption sites. At adsorbent dosage more than 0.05 g for lead and 0.1 g for zinc, removal becomes very low as the surface metal ions concentration and the solution metal ions concentration come to equilibrium with each other.

Reusability of the sorbent was also examined. It can be reused after regeneration with 5.0 mL 0.05 M $HNO_3$ and washing with 10 mL distilled water, respectively.

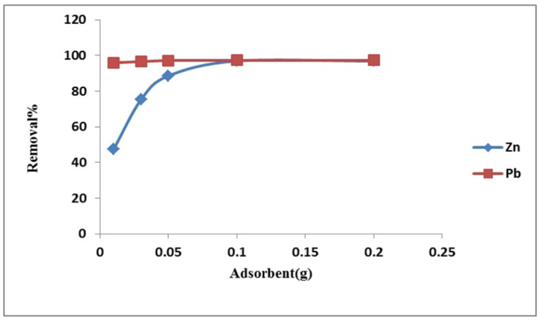

**Fig. 6.** Effect of adsorbent dose on the removal of lead and zinc ions.

### 3.3. Effect of contact time

The data obtained from the adsorption of Zn(II) and Pb(II) ions showed that the adsorption rate was very fast initially; about 96.77% of total Zn (II) and 95.92% Pb(II) was removed within 5 min (Fig. 7). Thereafter, the adsorption capacity remained constant after 5 min for zinc and after 15 min for lead. Thus, these equilibration times were selected for the removal of Zn (II) and Pb (II) ions by the proposed sorbent.

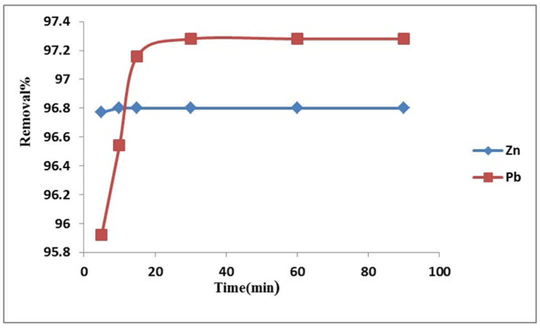

**Fig. 7.** Effect of the contact time on the adsorption of lead and zinc ions.

### 3.4. Effect of initial concentration and adsorption isotherms

The effect of initial concentration on the adsorption of lead (II) and zinc(II) ions by proposed sorbent was investigated with varying solution concentrations (20, 40, 60, and 100 mg/L). As can be seen from Fig. 8, with increasing concentration of the solution, qe increased, while R% decreased. At low initial solution concentration, the surface area and the availability of adsorption sites were relatively high, and the metals ions were easily adsorbed and removed. At high initial solution concentration, the total available sites are limited, thus resulting in a decrease in percentage removal of the ions. The increased $q_e$ at high initial concentration can be attributed to enhanced driving force.

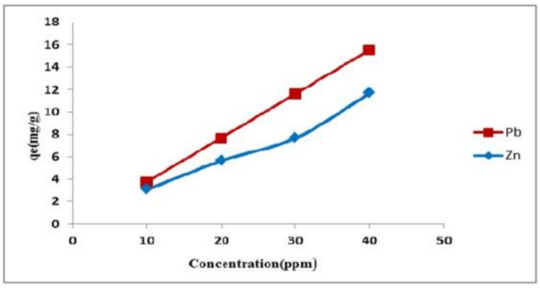

**Fig. 8.** Effect of initial concentration on the adsorption of lead and zinc ions.

Langmuir and Freundlich isotherms have been used to describe observed adsorption phenomena on the adsorbent. The sorption data of two cations have been analyzed according to the linear form of the Langmuir isotherm, as represented in Eq. (3):

$$C_e/q_e = (1/Q_m b) + (1/Q_m)\,C_e \qquad (3)$$

b is Langmuir constant which is a measure of energy of adsorption and $Q_m$ is adsorption capacity expressed in mg/g. The Freundlich equation predicts that the concentration of metal ions on the adsorbent will increase as long as there is an increase in the metal ion concentration in liquid, as represented in Eq. (4):

$$q_e = K_f \; C_e^{1/n} \qquad (4)$$

where 1/n is the constant related to adsorption capacity, and $K_f$ is the constant related to adsorption capacity of the adsorbent and $q_e$ is the weight adsorbed per unit weight of adsorbent. Taking logs gives Eq. (5):

$$\log q_e = \log K_f + {}^{1}/_{n}\log C_e \qquad (5)$$

To compare the obtained results with other adsorbents, the Freundlich and Langmuir constants should be determined from Langmuir and Freundlich isotherms. As can be seen from the Figs. 9 and 10, Freundlich model best fit the equilibrium isotherm data for the both cations. The values of constants obtained from intercepted and slope of plots and values of calculated according to Eqs. (3) and (5) are given in Table 1.

**Table 1.** Langmuir and Freundlich isotherm constants for zinc and lead.

| | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|
| Element | Q(mg.g$^{-1}$) | b( L. mg$^{-1}$) | $R^2$ | $K_f$ | 1/n | $R^2$ |
| Zn | 38.90 | 0.085 | 0.99 | 3.22 | 0.79 | 0.99 |
| Pb | 88.49 | 0.025 | 0.95 | 3.02 | 0.74 | 0.99 |

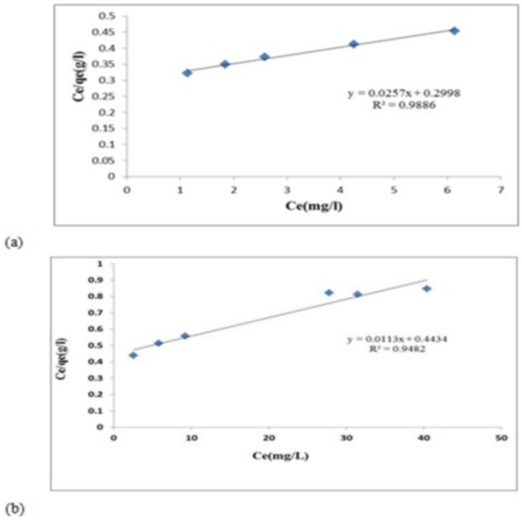

**Fig. 9.** Langmuir isotherms for adsorption of (a) Zn and (b) Pb ions.

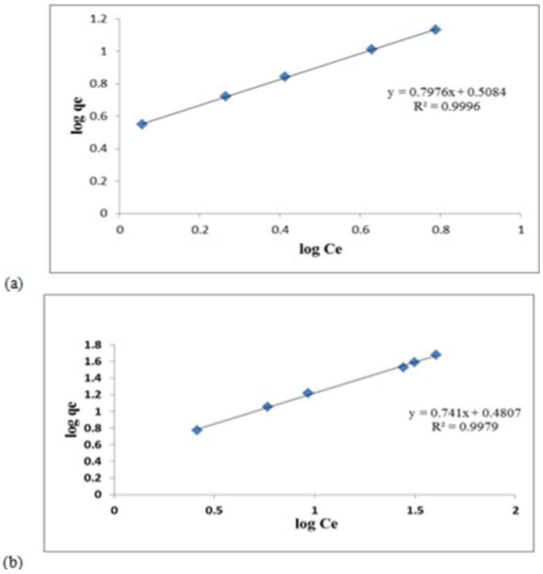

**Fig. 10.** Freundlich isotherms for adsorption of (a) Zn and (b) Pb ions.

### 3.5. Effect of ionic strength

Ionic strength is one of the important parameters influencing aqueous phase equilibrium. Inorganic salts such as NaCl and $CaCl_2$ often exist in industrial wastewater with a comparatively high concentration, and NaCl is often used a stimulator in adsorption processes. The Fig. 11 and 12 show the effect of various amounts of NaCl and $CaCl_2$ on the sorption of lead (II) and zinc (II) ions. As can be seen, there was no serious decrease in the removal of the metal ions. As, even at high concentration of the salt, the new adsorbent still have big percent removal and can be used to removal of zinc and lead from aqueous solutions.

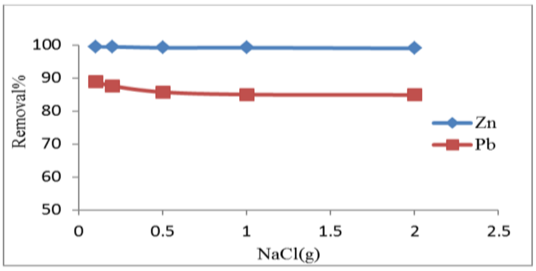

**Fig. 11.** The effect of NaCl on the adsorption of lead and zinc ions.

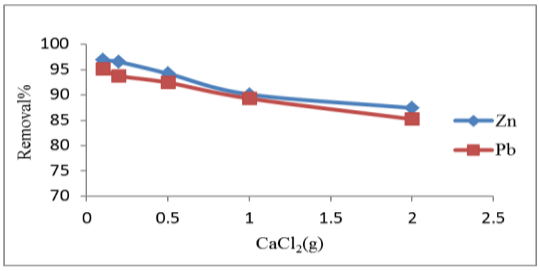

**Fig. 12.** The effect of $CaCl_2$ on the adsorption of lead and zinc ions.

### *3.6. Effect of temperature and thermodynamic parameters*

The removal of of lead (II) and zinc(II) ions onto the new sorbent was examined at 308, 311, 313, 323 and 331 K. Adsorption ability decreased for lead ions and increased for zinc ions with increasing temperature, illustrating that adsorption of lead and zinc onto the sorbent is an exothermic and endothermic process, respectively. The apparent equilibrium constant ($K_c$) of the sorption is defined as:

$$K_c = (C_0 - C_e)/C_e \qquad (6)$$

where $C_e$ is the equilibrium concentration. The $K_c$ value is used in the following equation to determine the Gibbs free energy ($\Delta G^0$) of sorption.

$$\Delta G^0 = -RTlnK_c \qquad (7)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (8)$$

R the universal gas constant (8.314 J $mol^{-1}$ $K^{-1}$) and T is the absolute temperature (K). The enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) can be obtained from the slope and intercept of van ’t Hoff equation of $\Delta G^0$ versus T (Table 2). The negative values of $\Delta G^0$ confirm the spontaneous nature of sorption with high performance of metal ions on the sorbent.

## 4. CONCLUSIONS

It is clearly shown that the modified naphthalene with 2-(3,4,5-trimethoxybenzylidene) malononitrile(TMBM) is an effective adsorbent for the removal of Zn(II) and Pb(II) ions from aqueous solution. In comparison with other sorbents it has short equilibrium time (Table 3). Preparation of the sorbent is simple and it is stable up to 100 runs without loss of the ligand.

**Acknowledgements**

The authors would like to express their appreciations to Payame Noor University of Kerman for providing research facilities. This research was supported by the Research Laboratory of Payame Noor University of Kerman.

**Table 2.** Thermodynamic Parameters for adsorption of Zn and Pb.

| T(K) | Zn | | | Pb | | |
|---|---|---|---|---|---|---|
| | $\Delta G^0$ (J $mol^{-1}$) | $\Delta S^0$ (J $mol^{-1}$ $K^{-1}$) | $\Delta H^0$ (J $mol^{-1}$) | $\Delta G^0$ (J $mol^{-1}$) | $\Delta S^0$ (J $mol^{-1}$ $K^{-1}$) | $\Delta H^0$ (J $mol^{-1}$) |
| 308 | -2564.71 | 8.43 | 33.51 | -725.61 | 44.54 | -14.37 |
| 311 | -2587.37 | | | -667.65 | | |
| 313 | -2645.99 | | | -450.90 | | |
| 323 | -2690.31 | | | -92.84 | | |
| 331 | -2757.41 | | | 843.77 | | |

**Table 3.** Comparison of various adsorbents for removal of Zn and Pb.

| Adsorbent | Element | Adsorption Capacity (mg $g^{-1}$) | Equilibrium Time (min) | Ref |
|---|---|---|---|---|
| Pinus sylvestris | Pb | 11.38 | 60 | [1] |
| Pinus sylvestris | Zn | 16.97 | 120 | [13] |
| Moringaoleifera Lam. Biomass | Zn | 52.08 | 50 | [14] |
| Activated tea waste | Pb | 81.0 | — | [15] |
| Green alga Ulva lactuca | Zn | 9.48 | 120 | [16] |
| | Pb | 170.70 | 120 | |
| Tea factory waste | Zn | 8.90 | 30 | [17] |
| Marine green activated carbon | Pb | 24.15 | 60 | [18] |
| Hybrid precursor (HP) of silicon and carbon | Zn | 28.76 | 30 | [19] |
| | Pb | 12.5 | 10 | [20] |
| Apple Pomace | Pb | 16.39 | 80 | [21] |
| $Fe_2O_3$-Ceramisite (FOC) | Zn | 7.4 | 300-480 | [22] |
| | Pb | 17.40 | 180-240 | |
| Activated carbon from Polygonum orientale Linn | Pb | 13.05 | 30.0 | [23] |
| Dairy manure compost | Zn | 1549 | 60 | [24] |
| β-$MnO_2$ | Pb | 13.57 | 1440 | [24] |
| Tourmaline | Zn | 18.50 | 1440 | [26] |
| Activated carbon from cow bone | Pb | 42.3 | 360 | [27] |
| Physic seed hull | Zn | 12.28 | 200 | [28] |
| Maghemite nanotubes | Zn | 111.11 | 60 | [29] |
| | Pb | 71.42 | 60 | |
| Modified naphthalene | Zn | 38.9 | 5 | This work |
| | Pb | 88.49 | 15 | |

## REFERENCES

[1] H. Ucun, Y.K. Bayhan, Y. Kaya, A. Cakici and O.F. Algur, Biosorption of lead(II) from aqueous solution by cone biomass of Pinus sylvestris, *Desalination* 154 (2003) 233-238.

[2] V.A. Lemos, W.N.L. Santos, J.S. Santos and M.B. Carvalho, On-line preconcentration system using a mini column of polyurethane foam loaded with Me-BTABr for zinc determination by Flame Atomic Absorption Spectrometry, *Anal. Chim. Acta* 481 (2003) 283-290.

[3] E.J. Kim, S. Park, H. Hong, Y. Choi and J. Yang, Biosorption of chromium (Cr(III)/Cr(VI)) on the residual microalga Nannochloris oculata after lipid extraction for biodiesel production, *Bioresource Technol.* 102 (2011)1155-1160.

[4] C.M. Monteiro, P.M.L. Castro and F.X. Malcata, Biosorption of zinc ions from aqueous solution by the microalga Scenedesmus obliquus, *Environ. Chem. Lett.* 9 (2011) 169-176.

[5] A. Mudhoo, V.K. Garg and S. Wang, Removal of heavy metals by biosorption, *Environ. Chem. Lett.* 10 (2012) 109-117.

[6] H. Kinoshita, Y. Sohma, F. Ohtake, M. Ishida, Y. Kawai, H. Kitazawa, T. Saito and K. Kimura, Biosorption of heavy metals by lactic acid bacteria and identification of mercury binding protein, *Res. Microbiol.* 164 (2013) 701-709.

[7] O.S. Amuda, A.A. Giwa and I.A. Bello, Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon, *Biochem. Eng. J.* 36 (2007)174-181.

[8] M.J. Ayotamuno, R.N. Okparanma, S.O.T. Ogaji and S.D. Probert, Chromium removal from flocculation effluent of liquid-phase oil-based drill-cuttings using powdered activated carbon, *Appl. Energ.* 84 (2007) 1002-1011.

[9] A.K. Bhattacharya, T.K. Naiya, S.N. Mandal and S.K. Das, *Chem. Eng. J.* 137 (2008) 529-541.

[10] M. Koroki, S. Saito, H. Hashimoto, T. Yamada and M. Aoyama, Removal of Cr(VI) from aqueous solutions by the culm of bamboo grass treated with concentrated sulfuric acid, *Environ. Chem. Lett*. 8 (2010) 59-61.

[11] C.M. Monteiro, P.M.L. Castro and F.X. Malcata, Capacity of simultaneous removal of zinc and cadmium from contaminated media, by two microalgae isolated from a polluted site, *Environ. Chem. Lett.* 9 (2011) 511-517.

[12] J. Volmajer, R. Toplak, S. Bittner and A.M. Le Marechal, 2-Oxiranecarbonitriles in the synthesis of linked quinono heterocyclic derivatives, *ARKIVOC* 14 (2003) 49-61.

[13] E.I. El-Shafey, Removal of Zn(II) and Hg(II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk, *J. Hazard. Mater.* 175 (2010) 319-327.

[14] H.N. Bhatti, B. Mumtaz, M.A. Hanif and R. Nadeem, Removal of Zn(II) ions from aqueous solution using Moringa oleifera Lam. (horseradish tree) biomass, *Process Biochem.* 42 (2007) 547-553.

[15] M.K. Mondal, Removal of Pb(II) ions from aqueous solution using activated tea waste:Adsorption on a fixed-bed column, *J. Environ.Manage* 90 (2009) 3266-3271.

[16] M.M. Areco, S. Hanela, J. Duran and M.S. Afonso, Biosorption of Cu(II), Zn(II), Cd(II) and Pb(II) by dead biomasses of green alga Ulva lactuca and the development of a sustainable matrix for adsorption implementation *J. Hazard. Mater.* 213-214 (2012) 123-132.

[17] K.L. Wasewar, M. Atif, B. Prasad and I.M. Mishra, Batch adsorption of zinc on tea factory waste, *Desalination* 244 (2009) 66-71.

[18] R.P. Suresh Jeyakumar and V. Chandrasekaran, Adsorption of lead(II) ions by activated carbons prepared from marine green algae: Equilibrium and kinetics studies, *Int. J. Ind. Chem.* 5 (2014) 2-10.

[19] N. Gupta, S.S. Amritphale and N. Chandra, Removal of Zn (II) from aqueous solution by using hybrid precursor of silicon and carbon, *Bioresource Technol.* 101 (2010) 3355-3362.

[20] R. Han, J. Zhang, W. Zou, J. Shi and H. Liu, Equilibrium biosorption isotherm for lead ion on chaff, *J. Hazard. Mater.* 125 (2005) 266-271.

[21] P. Chand and Y.B. Pakade, Removal of Pb from water by adsorption on apple pomace: Equilibrium, kinetics, and thermodynamics studies, *J. Chem.* doi: 10.1155/2013/164575.

[22] L. Yuan and Y. Liu, Removal of Pb(II) and Zn(II) from aqueous solution by ceramisite prepared by sintering bentonite, iron powder and activated carbon, *Chem. Eng. J.* 215-216 (2013) 432-439.

[23] L. Wang, J. Zhang, R. Zhao, Y. Li, C. Li and C. Zhang, Adsorption of Pb(II) on activated carbon prepared from Polygonum orientale Linn.: Kinetics, isotherms, pH, and ionic strength studies, *Bioresource Technol.* 101 (2010) 5808-5814.

[24] M. Zhang, Adsorption study of Pb(II), Cu(II) and Zn(II) from simulated acid mine

drainage using dairy manure compost, *Chem. Eng. J.* 172 (2011) 361-368.
[25] D. Zhao, X. Yang, H. Zhang , C. Chen and X. Wang, Effect of environmental conditions on Pb(II) adsorption on β-$MnO_2$, *Chem. Eng. J.* 164 (2010) 49-55.
[26] H. Liu, C. Wang, J. Liu, B. Wang and H. Sun, Competitive adsorption of Cd(II), Zn(II) and Ni(II) from their binary and ternary acidic systems using tourmaline, *J. Environ. Manage* 128 (2013) 727-734.
[27] M.A. Prado Cechinel, S.M.A.G. Ulson de Souza and A.A. Ulson de Souza, Study of lead(II) adsorption onto activated carbon originating from cow bone, *J. Clean. Proud.* 65 (2014) 342-349.
[28] M. Mohammad, S. Maitra, N. Ahmad, A. Bustam, T.K. Sen and B.K. Dutta, Metal ions removal from aqueous solution using physic seed hull, *J. Hazard. Mater.* 179 (2010) 363-372.
[29] A. Roy and J. Bhattacharya, Removal of Cu(II), Zn(II) and Pb(II) from water using microwave-assisted synthesized maghemite nanotubes, *Chem. Eng. J.* 211-212 (2012) 493-500.