Journal of Elementology ISSN 1644-2296

Amini Z., Hajiaghababaei L., Shahvelayati A.S. 2018.
Removal of Pb^{+2}, Cu^{+2} and Ag^{+} cations from wastewater by modified ZnO nanoparticles with S, N-substituted thiouracil derivative.
J. Elem., 23(4): 1179-1196. DOI: 10.5601/jelem.2018.23.1.1578

RECEIVED: 17 December 2017
ACCEPTED: 4 May 2018

ORIGINAL PAPER

REMOVAL OF Pb^{+2}, Cu^{+2} AND Ag^{+} CATIONS FROM WASTEWATER BY MODIFIED ZnO NANOPARTICLES WITH S, N-SUBSTITUTED THIOURACIL DERIVATIVE

Zahra Amini, Leila Hajiaghababaei*, Asraf Sadat Shahvelayati

Department of Chemistry
Yadegar -e- Imam Khomeini (RAH) Shahre Rey Branch
Islamic Azad University, Tehran, Iran

Abstract

Synthesis of adsorbents for the removal of toxic heavy metal ions is a continuing objective in the research undertaken to control environmental pollution. In this study, the adsorption of Pb^{+2}, Cu^{+2} and Ag^{+} cations was improved by modifying ZnO nanoparticles. For this purpose, the compound 3-hydroxy-3-(4-methoxyphenyl)-7-propyl-2H-thiazolo [3,2-α] pyrimidine-5 (3H)-one was used to modify the surface of the ZnO nanoparticle. Flame atomic absorption spectrometry was used to determine the concentration of cations in a solution. Pb^{+2}, Cu^{+2} and Ag^{+} cations were completely removed at pH ≥4 after stirring 25 mL of 4 mg L^{-1} solution of these three ions with 35 mg of the modified adsorbent for 30 min. Up to an acceptable level of other cations, there is no interference with the cations. The experimental data were analyzed using the Langmuir, Freundlich and Temkin adsorption models. The adsorption isotherms were well described by the Langmuir isotherm model and the maximum capacity of the adsorbent was found to be 115, 210 and 240 μg of Pb^{+2}, Cu^{+2} and Ag^{+} cations per each mg of the adsorbent, respectively. The adsorption of metal ions was studied at three different temperatures and the $\Delta H°$ and $\Delta S°$ were obtained from the Van't Hoff plot. The negative value of the Gibs free energy and the desired value of other thermodynamic parameters show that the removal process is spontaneous and endothermic. Finally, the modified ZnO nanoparticles exhibited an excellent adsorption capacity towards the analyzed cations in water and wastewater samples.

Keywords: removal, Pb^{+2}, Cu^{+2}, Ag^{+}, modified ZnO nanoparticles.

---

* Leila Hajiaghababaei, Associate Professor, Department of Chemistry, Islamic Azad University of Yadegar-e-Imam Khomeini (RAH) Shahre Rey, Km 5 of Tehran- Ghome freeway, Tehran, Iran, phone: +982144360616; Fax:+9821339022, e-mail: lhajiaghababaei@yahoo.com

INTRODUCTION

Heavy metals released into the environment remain a serious problem because of their toxicity and persistence (Seiler et al. 1998). They pose a significant threat to ecosystems and public health. For example, Pb is a cumulative poison and a possible human carcinogen. It can induce autoimmunity, where a person's immune system attacks own cells. Lead can be implicated as a cause of joint diseases and an ailment of the kidneys, circulatory system and neurons. At higher concentrations, Pb can cause irreversible brain damage (Naseem, Tahir 2001, Bakare-Odunola 2005, Sreejalekshmi et al. 2009). Copper is required for the proper functioning of many important enzyme systems. Copper-containing enzymes include ceruloplasmin, cytochrome-c oxidase, tyrosinase, monoamine oxidase, lysyl oxidase and phenylalanine hydroxylase (Linder, Hazegh-Azam 1996). On the other hand, an excess of Cu is toxic. For example, Wilson's disease is an autosomal recessive disorder that leads to copper toxicity because copper accumulates in the liver, brain and eyes (Harris, Gitlin 1996). Wilson's disease affects the hepatic intracellular transport of copper and its subsequent inclusion into ceruloplasmin and bile. Finally, a solution containing Ag may cause a severe corneal injury if it comes in contact with the eyes, or the metal may result in skin irritation. Exposure to high concentrations of this element may cause drowsiness, staggering, confusion, unconsciousness, coma or death.

It is therefore obvious that excess heavy metals need to be removed from the environment. Nowadays, numerous methods have been proposed for efficient heavy metal removal from water, including but not limited to chemical precipitation, ion exchange, adsorption, membrane filtration and electrochemical technologies (Wang et al. 2003, Kurniawan et al. 2006, O'connell et al. 2008, Fu, Wang 2011, Femina Carolin et al. 2017, Rodriguez-Narvaez et al. 2017). Among these techniques, adsorption offers flexibility of a design and operation, while often generating high-quality treated effluent. Synthesis of adsorbents for the removal of toxic heavy metal ions is a continuing objective in the research undertaken to control environmental pollution (Kurniawan et al. 2006, Burham 2009, Ciftci et al. 2010, Chakravarty et al. 2010, Mahmoud et al. 2010*a*,*b*,*c*, Lim, Aris 2014). On the other hand, nanostructure materials have some important physicochemical properties which make them particularly attractive as separation media for water purification, such as a larger surface area than that of bulk particles, which enables them to function with different chemical groups so as to increase the affinity towards target compounds (Ma et al. 2010, Hajiaghababaei et al. 2011, Hajiaghababaei et al. 2012*a*,*b*, Hajiaghababaei et al. 2013, Dubey et al. 2017).

ZnO has many unique advantages, for example it is simple and inexpensive to prepare. It is also convenient to tailor morphologically, which can be utilized to enhance the removal efficiency of toxic heavy metal ions and to develop some advanced functional composites (Ma et al. 2010, Sheela et al.

2012, Zhao, Qi 2012). Therefore, in the present work, the compound 3-hydroxy-3-(4-methoxyphenyl)-7-propyl-2H-thiazolo [3,2-*a*] pyrimidine-5 (3H) -one was synthesized and used for modification of the surface of ZnO nanoparticles. Modified ZnO nanoparticles were used as a new adsorbent for extraction of Pb^{+2}, Ag^{+} and Cu^{+2} cations from water and wastewater samples. To the best our knowledge, this is the first application of modified ZnO NPs with 3-hydroxy-3-(4-methoxyphenyl)-7-propyl-2H-thiazolo [3,2-*a*] pyrimidine-5 (3H)-one for simultaneous removal of Pb^{+2}, Cu^{+2} and Ag^{+}.

EXPERIMENTAL DESIGN

Apparatus

IR spectra were recorded with a Shimadzu IR-460 spectrometer. 1H and ^{13}C NMR spectra were recorded with a Bruker DRX-300Avance instrument using $CDCl_3$ as the deuterated solvent containing tetramethylsilane as internal standard, at 300 and 75 MHz, respectively, in parts per million, and J in hertz. Aanlyses of the elements (C, H, N) were made on a Heraeus CHN -O-Rapid analyzer. Electron impact ionization-mass spectroscopy (EI-MS) (70 eV): mass spectra were obtained with a Finnigan-MAT-8430 mass spectrometer (in m/z).

The determination of Pb^{2+}, Cu^{2+} and Ag^{+} cations was carried out on a PG-900 (England PG Company) flame atomic absorption spectrometer (FAAS). The flow rates of air and acetylene were set as recommended by the manufacturer. The FAAS determination of other cations was performed under the recommended conditions for each metal cation. The following conditions were used:

Pb: adsorption line: 273.38 nm, slit width: 0.4 nm, lamp current: 5 mA;

Cu: adsorption line: 324.7 nm, slit width: 0.4 nm, lamp current: 5 mA;

Ag: adsorption line: 328.1 nm, slit width: 0.4 nm, lamp current: 5 mA.

Reagents

Zinc acetate dehydrate was purchased from Aldrich. All organic solvents (HPLC grade), nitrate salts, HNO_3 and NaOH were bought from the Merck chemical company. Double distilled deionized water was used throughout. Stock metal cation solutions (1000 mg L^{-1}) were prepared by dissolving an appropriate amount of nitrate salts of metals. Working standard solutions were prepared by diluting the stock standard solutions appropriately.

Synthesis of 3-hydroxy-3-(4-methoxyphenyl)-7-propyl-2H-thiazolo [3,2-*α*] pyrimidine-5 (3H)-one

4-methoxy phenacyl bromide (1 mmol) was added to 4-propyl thiouracil (1 mmol) suspended in 1mL of [bmim]Br and the mixture was stirred at 50°C. After stirring for 3 h, 5 mL of water was added and the mixture was extracted with EtOAc (3×10 mL). The solvent from the mixture was evaporated under reduced pressure to leave solid residue, which was purified by recrystallization from a mixture of EtOAc/n-hexane to afford pure.

Pale yellow powder, m.p. 152-153°C; yield: 0.32 g (79%). IR (KBr): 3432, 1702, 1643, 1583, 1442 cm^{-1}. ^{1}H NMR: δ = 0.94 (3 H, t, ^3J 7.2, Me), 1.66 (2 H, sextet, ^3J 7.2,CH$_2$), 2.573 (2 H, t, ^3J7.2, Me), 3.06 (1 H, d, ^2J 12.1,CH$_2$),3.59 (1 H, d, ^2J 12.1,CH$_2$), 3.93 (3 H, s, OMe), 5.45 (1H, br s, OH), 6.45 (1 H, s, CH-*vinylic*), 6.91 (2 H, d, ^3J 8.8, 2 CH),7.91 (2 H, d, ^3J 8.8, 2 CH)ppm. ^{13}C NMR: δ 13.8 (Me), 21.4 (CH$_2$), 37.4 (CH$_2$), 43.1 (CH$_2$), 55.3 (OMe), 97.6 (COH), 108.1 (CH), 114.5 (2 CH), 125.2 (C), 130.0 (2 CH), 154.1 (C), 162.7 (C), 168.5 (C), 170.2 (C=O) ppm. EI-MS: *m/z* (%) = 318 (M$^+$, 3), 211 (28), 183 (100), 169 (25), 107 (30), 76 (32), 57 (23). Anal.Calcd for $C_{16}H_{18}N_2O_3S$ (318.4): C, 60.36; H, 5.70; N, 8.80; S, 10.07. Found: C, 59.76; H, 5.52; N, 8.03; S, 10.43.

Modification of the surface of ZnO nanoparticles

ZnO NPs were prepared according to the literature procedure (Sabbaghan et al. 2012). An adequate amount of 3-hydroxy-3-(4-methoxyphenyl)-7-propyl-2H-thiazolo [3,2-α] pyrimidine-5 (3H)-one was dissolved in chloroform. Subsequently, ZnO nanoparticles were added. The mixture was maintained at room temperature under vacuum. After evaporation of the solvent (chloroform), modified ZnO NPs with a ligand of 3-hydroxy-3-(4-methoxyphenyl)-7-propyl-2H-thiazolo [3,2-*α*] pyrimidine-5 (3H)-one were obtained. 4-Propylthiouracil and 4-methoxy phenacyl bromide were used without further purification. The modified adsorbent was used to remove Pb^{2+}, Cu^{2+} and Ag$^+$ cations.

Optimum amount of the ligand for modification of ZnO nanoparticles

In order to assess an optimum amount of the ligand for modification of ZnO nanoparticles, the extraction was conducted at varying weight ratios of ZnO/ligand amounts in 25 mL of samples containing 100 μg lead, 100 μg copper and 100 μg silver.

Metal adsorption experiment

The general procedure for Pb^{+2}, Cu^{+2} and Ag$^+$ cation removal by modified ZnO NPs with 3-hydroxy-3-(4-methoxyphenyl)-7-propyl-2H-thiazolo [3,2-*α*] pyrimidine-5 (3H)-one was as follows. To a solution of 25 mL of the sample containing 100 μg each cation (Pb^{2+}, Cu^{2+} and Ag$^+$), 35 mg of modified ZnO

NPs were added and the mixture was stirred for at least 30 min. Then, the resulting mixture was filtered. Finally, the content of Pb^{2+}, Cu^{2+} and Ag^{+} cations in the extracted solution was determined by FAAS.

Equilibrium isotherm studies

An equilibrium isotherm is described by the sorption isotherm characterized by certain constants, whose values express the surface properties and affinity of the sorbent towards the target compound. Popular isotherm models such as ones proposed by Langmuir, Freundlich and Temkin were used to analyze the experimental equilibrium data obtained from the sorption process at room temperature over the concentration range of 2-1000 mg L^{-1}. The Langmuir adsorption model was used to explain the adsorption capacity of the substance by the sorbent. According to the Langmuir adsorption isotherm, adsorption takes place at specific homogeneous sites of the adsorbent's surface and no transmigration of the adsorbate in the surface plane occurs (GUPTA et al. 1997). The Langmuir adsorption is represented by equation 1:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \tag{1}$$

where q_{max} is the maximum amount of a metal ion adsorbed per unit weight of modified ZnO NPs to form a complete monolayer on the surface (mg g^{-1}), K_L is a constant related to the affinity of the binding sites towards the metal ions (L mg^{-1}), and C_e (mg L^{-1}) and q_e (mg g^{-1}) are the equilibrium liquid phase and solid phase metal ion concentrations, respectively.

The empirical Freundlich isotherm based upon sorption on heterogeneous surfaces was applied in a linear form (eq. 2):

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{2}$$

where K_f (mg g^{-1}) and $\frac{1}{n}$ (dimensionless) are the Freundlich constants indicating the relative adsorption capacity and the intensity of adsorption, respectively. The adsorption data of lead, copper and silver were also analyzed with the help of the Temkin isotherm. The Temkin isotherm equation (eq. 3) assumes linearly reducing adsorption heat over all adsorbents with a coverage that may be attributed to the adsorbent-adsorbate interactions, up to some maximum binding energy given as below:

$$q_e = B_l \ln K_T + B_l \ln C_e \tag{3}$$

where K_T (Lg^{-1}) is the equilibrium binding constant, corresponding to the maximum binding energy and constant B is related to the heat of adsorption. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B and K_t from the slope and intercept of the straight line plot (OLADOJA et al. 2008).

Removal of metal cations from real and synthetic samples

This method was used for the removal of Pb^{2+}, Cu^{2+} and Ag^{+} cations from a synthetic sample. A dose of 35 mg of modified ZnO NPs was added to 25 ml of an aqueous solution containing 100 µg of lead, copper and silver and 500 µg Co^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Cr^{+3} and Ca^{+2}, after which the mixture was stirred for 30 min. Then, the resulting mixture was filtered on a paper filter. Finally, the Pb^{2+}, Cu^{2+} and Ag^{+} cations in the following solution were determined by FAAS.

The removal of Pb^{2+}, Cu^{2+} and Ag^{+} cations was also examined on wastewater samples obtained from the Islamic Azad University of Yadegar-e-Imam Khomeini (RAH) Shahre Rey Laboratory. They contained organic and inorganic components which had been consumed in the chemistry research laboratory. In addition, the wastewater received effluents from such activities as washing the laboratory glassware with tap and distilled water. Wastewater samples were filtered through a 0.45-µm pore size membrane filter to remove suspended particulate matter, after which pH was adjusted and the wastewater samples were treated with the tested adsorbent under optimal conditions. Because of the matrix effect, the initial concentrations and residual concentrations of Pb^{2+}, Cu^{2+} and Ag^{+} cations in the samples (before and after the removal with the recommended procedure) were determined with the standard addition method.

RESULTS AND DISCUSSION

Effect of modified ZnO NPs

In comparison with the traditional sorbents (micro-sized sorbent), NPs offer a significantly higher surface-to-volume ratio. Therefore, satisfactory results can be obtained with less of NPs. In this study, the optimum amount of the sorbent for the maximum removal was determined by increasing the amount of modified ZnO NPs added into 25 mL of 4 mgL^{-1} Pb^{2+}, Cu^{2+} and Ag^{+} cations. The results are given in Figure 1.

Initially, the percentage of ions adsorbed on modified ZnO NPs increased as the amount of the sorbent was raised, and the complete extraction of Pb^{2+}, Cu^{2+} and Ag^{+} cations (≥99%) was finally achieved using 35 mg of modified ZnO NPs. This was a consequence of a higher number of active sites for the adsorption of metal ions owing to a higher dose of the sorbent. Hence, the subsequent extraction experiments were carried out with 35 mg of modified ZnO NPs applied to remove all of the cations (Pb^{+2}, Cu^{+2} and Ag^{+}).

Moreover, extraction was conducted with various ratios of ZnO/ligand amounts. Remarkably, the removal efficiency of metal ions is relatively low in the absence of the ligand, and it increases with the increasing amoung of the ligand. This shows the effective role of this ligand in the removal process.

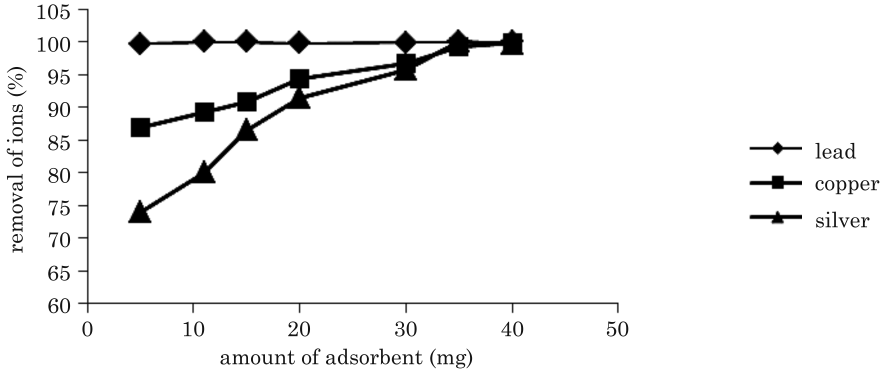

Fig. 1. Effect of the amount of the adsorbent on the percentage of removed Pb^{2+}, Cu^{2+} and Ag^{+} cations

Regarding the results, the ZnO/ligand weight ratio of 1:1 was chosen for preparing a suitable modified adsorbent.

The influence of the pH on the removal of ions

The extraction of Pb^{+2}, Cu^{+2} and Ag^{+} cations by modified ZnO NPs was studied at various pH. The dependence of metal sorption on pH arises from both the metal's chemistry in the solution and the ionization state of the adsorbent's functional groups, which affects the availability of binding sites (HEIDARI et al. 2009) – Figure 2.

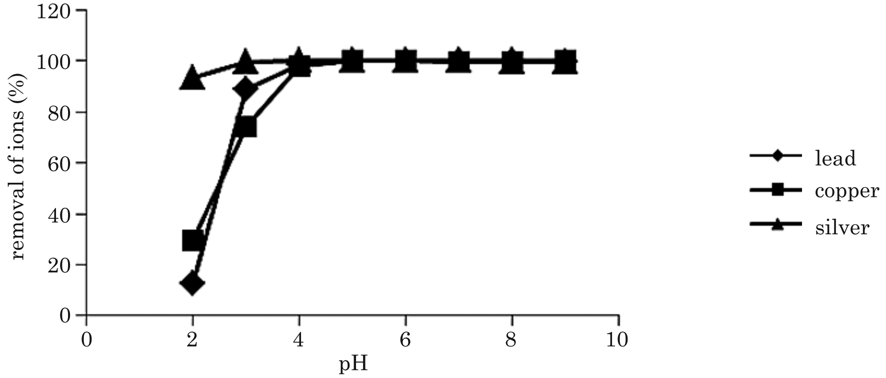

Fig. 2. Effect of pH on the removal efficiency of Pb^{2+}, Cu^{2+} and Ag^{+} cations

The pH of aqueous samples was adjusted to the pH range of 2.0-9.0 (using 1 mol L^{-1} of either nitric acid or sodium hydroxide solution) and the general procedure for ion extraction was carried out. The results are shown in Figure 2. As can be seen, Pb^{2+} and Cu^{2+} can be extracted quantitatively by modified ZnO NPs at pH ≥ 4 and Ag^{+} can be extracted quantitatively at pH ≥ 3. At initial low pH values, the influence of adsorption is the only effect responsible for reducing amounts of heavy metal ions in the solution.

However, at higher pH values (above 6 or 7), both adsorption and aqueous metal hydroxide formation may become significant mechanisms in the metal removal process. The existence of electron donating atoms (nitrogen and sulfur) in the ligand's structure was expected to increase the stability of its transition and heavy metal ion complexes over other metal ions, especially alkali and alkaline earth cations. It was decided to set the pH value at about 5 as a compromise for the sake of simultaneous extraction of all target species.

The effect of the stirring time on removal yield

To investigate the effect of stirring time on the removal of Pb^{2+}, Cu^{2+} and Ag^{+} cations, a series of solutions 25 mL containing 100 µg of each of these cations were prepared. The general procedure for ion extraction in various contact time setups was done. The results are illustrated in Figure 3.

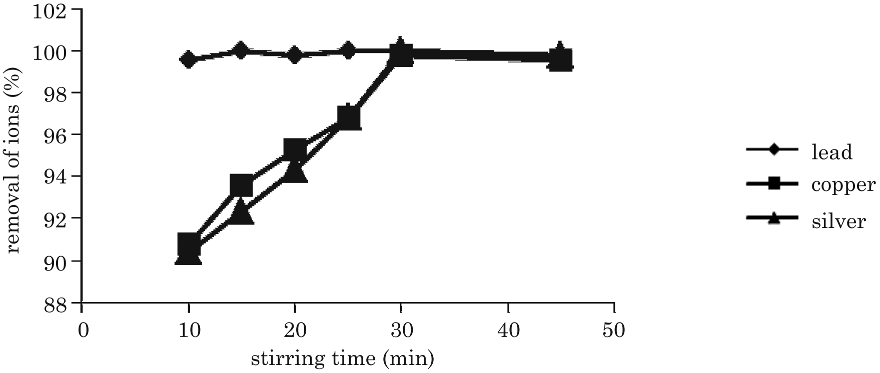

Fig. 3. Effect of the stirring time on the removal of Pb^{2+}, Cu^{2+} and Ag^{+} cations

As it is, Cu^{2+} and Ag^{+} cations can be removed by modified ZnO NPs at the stirring time of 30 min and more, while Pb^{2+} cations can be removed at the stirring time of 10 min and more. For the simultaneous removal of all the three cations, mixtures were stirred for 30 min in all of the experiments.

Equilibrium adsorption of metal ions on modified ZnO NPs

The general procedure for extraction with different initial concentrations was implemented. The amounts of adsorbed metals by the adsorbent, q_e (mg g^{-1}) were calculated from the following mass balance relationship (eq. 1):

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and Ce (mg L^{-1}) are the initial and equilibrium concentrations of the metal cation solution, respectively, V is the volume of the solution (L), and W is the mass (g) of the adsorbent used.

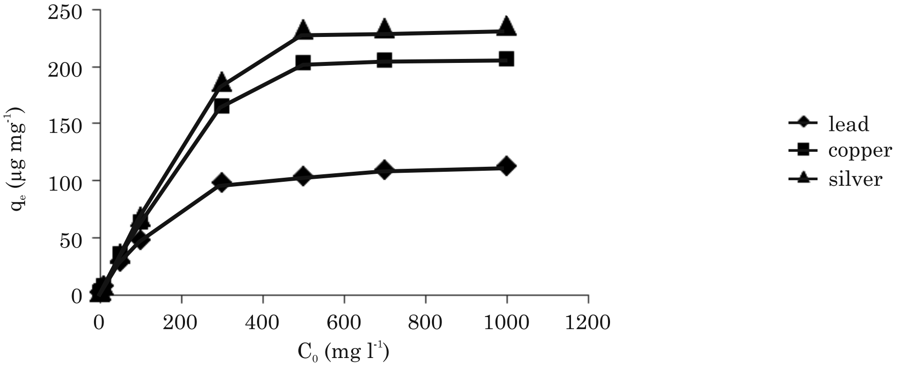

Fig. 4. Equilibrium adsorption of Pb^{2+}, Cu^{2+} and Ag^{+} cations on modified ZnO NPs

Figure 4 shows that the actual amounts Pb^{2+}, Cu^{2+} and Ag^{+} cations adsorbed per unit mass of the adsorbent increased up to constant amounts, although the percentage of ions removed decreased with the increasing initial ion concentration. The results show that metal ions have good affinity towards modified ZnO NPs. This can be attributed to the weak Lewis base characteristic of the ligand and to the cationic anionic interaction between the metal ions and the surface moiety. This adsorbent displays higher adsorption capacity for silver ions than for lead or copper ones, which can be attributed to the presence of nitrogen and sulfur atoms in the ligand's structure.

Removal of lead, copper and silver ions in quaternary mixtures

In order to investigate the removal of Pb^{2+}, Cu^{2+} and Ag^{+} cations from water containing diverse metal ions, an aliquot of aqueous solution (25 mL) containing 100 µg of Pb^{2+}, Cu^{2+} and Ag^{+} cations and various amounts of other cations was taken and the recommended procedure was followed. The results are shown in Table 1. As expected, up to an acceptable level of other cations, Pb^{2+}, Cu^{2+} and Ag^{+} cations were completely absorbed by modified ZnO NPs and there was slight interference at higher concentrations of driver cations.

Adsorption isotherms

In order to optimize the use of modified ZnO, it is important to establish the most appropriate adsorption isotherm. The obtained isotherm values are shown in Figure 5. Parameters related to each isotherm for the adsorption of the metal ions on the adsorbent were determined by using linear regression analysis, and squares of the correlation coefficients (R^2) were calculated (Table 2). The results showed that equilibrium data for all metal ions were explained better by the Langmuir isotherm model than by the Freundlich and Temkin ones. Pb^{2+}, Cu^{2+} and Ag^{+} cations formed a homogeneous monolayer on the adsorbent's surface. On the basis of the Langmuir analysis, the

Table 1

Removal of Pb^{2+}, Cu^{2+} and Ag^{+} cations from quaternary mixtures[a]

Divers ions	Amount taken (µg)	Removal of Pb^{2+} (%)	Removal of Cu^{2+} (%)	Removal of Ag^{+} (%)
K^{+}	2500	100.0(0.8)[b]	99.1 (0.9)	99.6 (1.0)
Na^{2+}	2500	100.0(0.7)	98.1 (0.9)	99.2 (0.7)
Mg^{2+}	2500	98.5(1.1)	96.6 (0.8)	97.0 (0.6)
Cr^{3+}	2500	91.3 (0.7)	86.2 (0.7)	93.3 (0.7)
Cr^{3+}	2000	98.4 (0.6)	96.6 (0.6)	100.1 (0.9)
Co^{2+}	2500	98.2 (0.9)	92.5 (0.8)	80.3 (0.8)
Co^{2+}	2000	100.0 (1.0)	98.5 (0.6)	97.0 (0.6)
Ca^{2+}	2500	97.6 (1.0)	96.5 (0.9)	98.1 (0.8)
Ni^{2+}	2500	100.0 (0.9)	96.4 (0.5)	98.6 (1.1)
Zn^{2+}	2500	100.0 (1.0)	95.9 (0.8)	100.0 (0.6)
Zn^{2+}	2000	100.0 (1.1)	97.5 (0.6)	100.0 (0.8)
Cd^{2+}	2500	100.0 (0.9)	97.2 (1.0)	99.2 (0.6)
Mn^{2+}	2500	98.9 (0.7)	97.0 (0.5)	98.6 (0.9)

[a] Initial samples contained 100 µg of lead, copper and silver ions in 25 ml water.

[b] Values in parentheses are RSDs based on three replicate analyses.

Table 2

Values of the isotherm constant for the sorption of Pb^{2+}, Cu^{2+} and Ag^{+} cations

Isotherm	Parameters	Pb^{2+}	Cu^{2+}	Ag^{+}
Langmuir	q_m(mg g^{-1})	115	210	240
	K_L(L mg^{-1})	0.052	0.105	0.280
	R^2	0.9970	0.9990	0.9997
Freundlich	n	2.67	2.06	3.86
	K_f(mg g^{-1})	11.20	14.47	53.10
	R^2	0.9757	0.9399	0.9499
Temkin	B_1	15.286	22.916	28.237
	K_T(L g^{-1})	1.86	11.89	9.97
	R^2	0.9253	0.9342	0.9327

maximum adsorption capacities were determined to be 115, 210 and 240 µg of Pb^{+2}, Cu^{+2} and Ag^{+} cations per each mg of the adsorbent, respectively.

Effect of temperature and thermodynamic parameters

The adsorption of metal ions was studied at three different temperatures in the range 15-35°C and at the concentrations of Pb^{2+}, Cu^{2+} and Ag^{+} cations

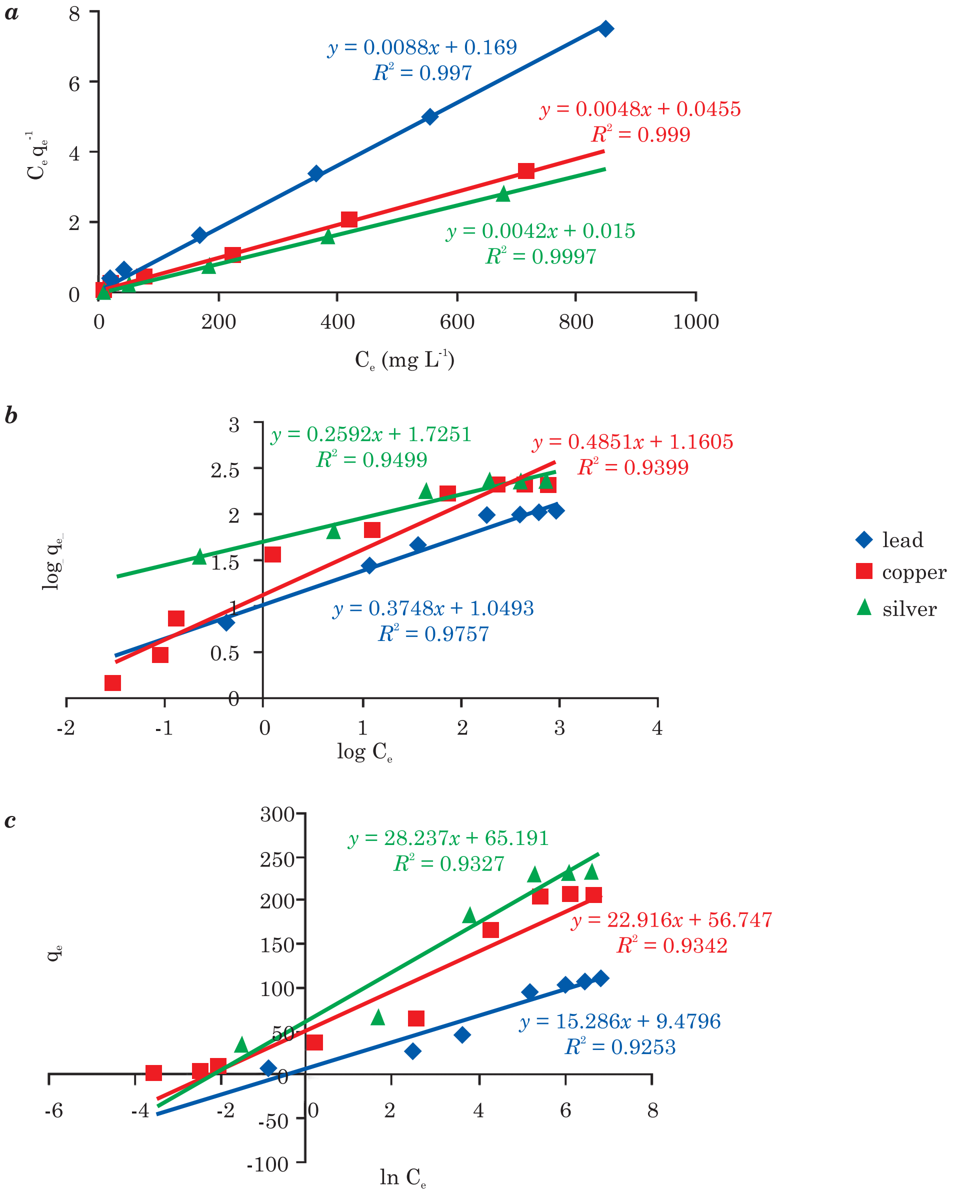

Fig. 5. Linearized Langmuir (*a*), Freundlich (*b*) and Temkin (*c*) isotherms for the adsorption of Pb^{2+}, Cu^{2+} and Ag^{+} cations on modified ZnO NPs

equal 100 mg L^{-1}. Figure 6 shows the effect of temperature on the removal efficiency of these cations using modified ZnO NPs. Adsorption improved with an increasing temperature, indicating it was an endothermic process. This improvement of metal adsorption may arise from a higher diffusion rate

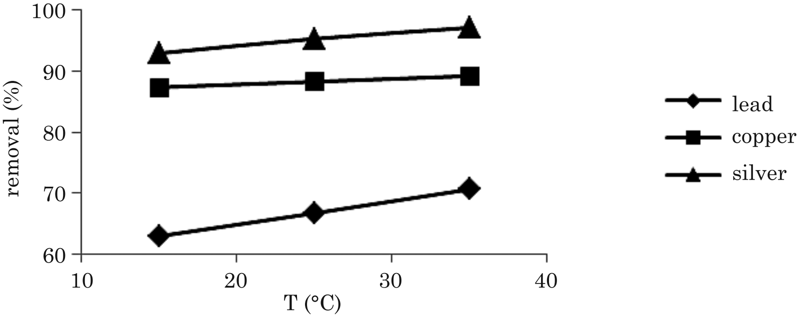

Fig. 6. Effect of temperature on the removal efficiency

of the adsorbate's ions across the external boundary layer and in the surface of the adsorbent's particles (Wong et al. 2009).

Furthermore, variation in the extent of adsorption with respect to temperature was explained on the basis of thermodynamic parameters, like a change in enthalpy (ΔH°), in entropy (ΔS°), and in free energy (ΔG°), which were determined using the following equations (Sari et al. 2007). The Gibb's free energy change of the process is revealed to the equilibrium constant K_c from the equation (5):

$$K_C = \frac{C_{Ae}}{C_e} \tag{5}$$

where K_C is the equilibrium constant, C_e and C_{Ae} are the equilibrium liquid phase and solid phase concentrations at equilibrium (mg L^{-1}), respectively.

$$\log K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{6}$$

$$\Delta G^\circ = -RT \ln K_C \tag{7}$$

The ΔH° and ΔS° were obtained from the slope and intercept of the Van't Hoff plot (eq. 6) of $\log K_C$ versus 1/T (Figure 7). T is the temperature in Kelvin and *R* is the gas constant. The values of these parameters are presented in Table 3.

The positive values of the standard enthalpy change (ΔH°) for the intervals of temperatures tested proved the endothermic nature of the adsorption process. The low enthalpy values of $\Delta H^\circ < 20$ kJ mol^{-1} indicated that physisorption is involved in the process of adsorption (John et al. 2007).

The estimated values of ΔH° for lead and copper in the present system were 14.5 kJ mol^{-1} and 7.1 kJ mol^{-1}, respectively, but ΔH° for silver in the present system was 39.5 kJ mol^{-1}, which was >20 kJ mol^{-1} and therefore the process may involve a spontaneous sorption mechanism owing to ion exchange. The negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of adsorption of Pb^{2+}, Cu^{2+} and Ag^+ cations onto modified ZnO NPs.

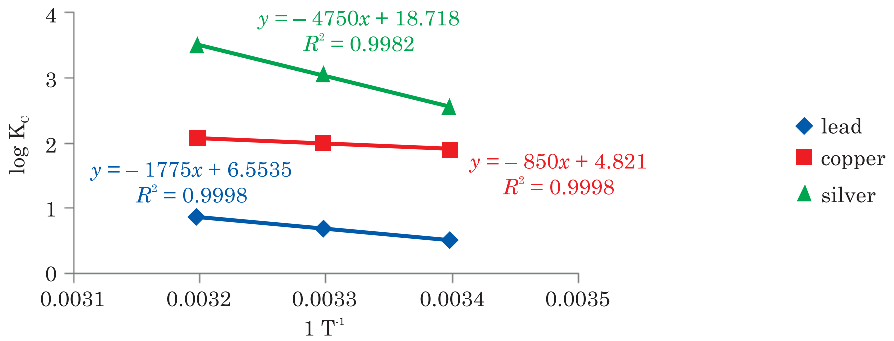

Fig. 7. Van't Hoff Plot for the adsorption of Pb^{2+}, Cu^{2+} and Ag^{+} cations on modified ZnO NPs

Table 3

Thermodynamic parameters for the adsorption of Pb^{2+}, Cu^{2+} and Ag^{+} cations on ZnO NPs

Metal ion	Temperature (°C)	ΔG° (kJ mol^{-1})	ΔS° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	Kc
Pb^{2+}	15	-0.957	0.0536	14.507	1.69
	25	-1.493			2.00
	35	-2.03			2.24
Cu^{2+}	15	-4.48	0.040	7.067	6.91
	25	-4.48			7.53
	35	-5.283			8.27
Ag^{+}	15	-5.350	0.155	39.491	13.20
	25	-6.906			20.45
	35	-8.462			34.33

The effect of the eluents on the stripping of Pb^{2+}, Cu^{2+} and Ag^{+} cations and regeneration of adsorbent

Some preliminary experiments were carried out in order to choose a proper eluent for the retained Pb^{2+}, Cu^{2+} and Ag^{+} cations after the extraction 100 µg ions in 25 mL solution by modified ZnO NPs. Nitric acid (3 mol L^{-1}), nitric acid (4 mol L^{-1}), and sodium thiosulfate (2 mol L^{-1}) were tested for stripping. The results showed that, among the three eluents used, 20 mL of 4M nitric acid can accomplish the quantitative elution of Pb^{2+}, Cu^{2+} cations and 25 mL of 2 M sodium thiosulfate can accomplish the quantitative elution of Ag^{+} cations from the adsorbent.

Then, experiments carried out in order to study the regeneration capacity of modified ZnO NPs. The adsorbent was used in some cycles of the adsorption/desorption process. The results show that the recovery remained constant (96-98%) after five cycles of sorption and desorption and decreased slowly in the consecutive cycles of the adsorption/desorption process.

Removal of Pb^{2+}, Cu^{2+} and Ag^+ cations from wastewater and synthetic samples

The application of the proposed method for removal of Pb^{2+}, Cu^{2+} and Ag^+ cations from wastewater and synthetic samples was examined. The results are given in Table 3 and Table 4. As shown in Table 4, it is quite clear that modified ZnO NPs can completely remove lead, copper and silver ions from a synthetic sample and the removal process is independent from the matrix effects.

Also, as shown in Table 5, the proposed method could be applied successfully for the removal of Pb^{2+}, Cu^{2+} and Ag^+ cations from wastewater samples, ensuring very good efficiency and absence of matrix effects.

Table 4

Removal of Pb^{2+}, Cu^{2+} and Ag^+ cations from a synthetic sample[a]

Divers ions	Amount taken (µg mL^{-1})	Removal of Pb^{2+} (%)	Removal of Cu^{2+} (%)	Removal of Ag^+ (%)
Co^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, Ca^{2+}	20	100.0	98.5	99.5

[a] Initial samples contained 100 µg of lead, copper and silver ions in 25 ml water.

Table 5

Removal of Pb^{2+}, Cu^{2+} and Ag^+ cations from wastewater samples

Samples	Concentration of Pb^{2+} (mg L^1)	Removal of Pb^{2+} (%)	Concentration of Cu^{2+} (mg L^1)	Removal of Cu^{2+} (%)	Concentration of Ag^+ (mg L^1)	Removal of Ag^+ (%)
1	11	98.5	6	99.0	4	99.5
2	16	98.5	8	98.0	5	98.5

Comparison of the proposed method with similar cations retention method reported previously

The results concerning the maximum capacity of the new adsorbent and contact time in the proposed method, compared to ones reported previously, with respect to the retention of Pb^{2+}, Cu^{2+} and Ag^+ cations, are collated in Table 6. The proposed adsorbent is superior to the ones reported previously in terms of the adsorption capacity and contact time. Regarding the contact time, the proposed method achieved effects close to the ones demonstrated earlier with other methods (modified SBA-15 and MCM-41). The adsorption capacity of modified ZnO NPs with 3-hydroxy-3-(4-methoxyphenyl)-7-propyl -2H-thiazolo [3,2-*α*] pyrimidine-5 (3H)-one is better than reported earlier for other methods with respect to Ag^+ and Cu^{2+} cations and is close to the best effects reported previously for Pb^{2+} cations.

Table 6

Comparison of the proposed method with the ones reported previously

Adsorbent	Maximum capacity (mg g^{-1})	Contact time	Removed ions	References
ZnO/Granular Activated Carbon	76.7	3 days	Pb^{+2}	Kikuchi et al. (2006)
	16.6		Cu^{+2}	
	12.2		Cd^{+2}	
ZnO-nanosheet	6.7	several hours	Pb^{+2}	Ma et al. (2010*b*)
Nano ZnO	26.1	3 h	Pb^{+2}	Venkatesham et al. (2013)
Diethylenetriamine functionalized SBA-15	183.0	15 min	Pb^{+2}	Hajiaghababaei et al. (2012)
	156.0		Cu^{+2}	
	80.0		Zn^{+2}	
MCM-41-coating with CoFe2O4 and piperazine	238.1	10 min	Pb^{+2}	Kanani et al. (2017)
	208.3		Cu^{+2}	
	178.6		Cd^{+2}	
Waste coffee grounds	49.5	60 min	Ag^{+}	Jeon (2017)
Chitosan/montmorillonite	43.5	150 min	Ag^{+}	Jintakosol et al. (2016)
Modified ZnONPs	115	30 min	Pb^{+2}	this work
	210		Cu^{+2}	
	240		Ag^{+}	

CONCLUSIONS

This research has demonstrated the successful application of modified ZnO NPs with 3-hydroxy-3-(4-methoxyphenyl)-7-propyl-2H-thiazolo [3,2-α] pyrimidine-5 (3H)-one for the effective removal of Pb^{2+}, Cu^{2+} and Ag^{+} cations as a rapid and easy method. The modification of the adsorbent is an efficient tool to improve the efficiency and selectivity of a removal procedure. Pb^{2+}, Cu^{2+} and Ag^{+} cations were completely removed at pH ≥ 4 after stirring for 30 min in 25 mL of 4 mg L^{-1} solution of these three ions and by using 35 mg of modified ZnO NPs. Isotherm studies indicated that the Langmuir model fitted the experimental data better than did the Freundlich and Tempkin models. The maximum adsorption capacity was 115, 210 and 240 μg per mg modified ZnO NPs for Pb^{2+}, Cu^{2+} and Ag^{+} cations, respectively. The negative value of Gibbs free energy and desired values of other thermodynamic parameters show that the tested removal process was spontaneous and endothermic. The application of the present method to real samples indicated that the adsorbent had a good potential to remove Pb^{+2}, Cu^{+2} and Ag^{+} cations from wastewater samples. Finally, it should be mentioned that the proposed method is very rapid and efficient and since the adsorption capacity of modified ZnO nanoparticles is good, even a small amount of the absorbent is enough to ensure high efficiency removal. The proposed modification is easy to perform, and this methodology could be suitable for large scale removal of heavy metal ions from water and wastewater.

ACKNOWLEDGMENT

The authors are grateful to the Islamic Azad University of Yadegar-e-Imam Khomeini (RAH) Shahre-Rey Branch Research Council for the support of this work.

REFERENCES

Bakare-Odunola M.T. 2005. *Analysis of copper, zinc and lead using atomic absorption spectrophotometer in ground water of Jimma town of Southwestern Ethiopia.* Nig. J. Pharm. Res., 4(4): 51-54. DOI: 10.1016/j.ijcas.2013.07.006

Burham N. 2009. *Separation and preconcentration system for lead and cadmium determination in natural samples using 2-aminoacetylthiophenol modified polyurethane foam.* Desalination, 249(3): 1199-1245. DOI: 10.1016/j.desal.2009.04.009

Chakravarty P., Sen Sarma N., Sarma H.P. 2010. *Removal of lead (II) from aqueous solution using heartwood of Areca catechu powder.* Desalination, 256: 16-21. DOI: 10.1016/j.desal.2010.02.029

Ciftci H., Yalcin H., Eren E., Olcucu A., Sekerci M. 2010. *Enrichment and determination of Ni2+ ions in water samples with a diamino-4-(4-nitro-phenylazo)-1H-pyrazole (PDANP) by using FAAS.* Desalination, 256(1-3): 48-53. DOI: 10.1016/j.desal.2010.02.018

Dubey S., Banerjee S., Nath Upadhyay S., Chandra Sharma Y. 2017. *Application of common nano-materials for removal of selected metallic species from water and wastewaters: A critical review.* J. Mol. Liq., 240: 656-677. DOI: 10.1016/j.molliq.2017.05.107

Femina Carolin C., Senthikumar S., Saravanan A., Janetjoshiba G., Naushad M. 2017. *Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review.* J. Environ. Chem. Engin., 5(3): 2782-2799. DOI:10.1016/j.jece.2017.05.029

Fu F.L., Wang Q. 2011. *Removal of heavy metal ions from wastewaters: A review.* J. Environ. Manage, 92(3): 407-418. DOI: 10.1016/j.jenvman.2010.11.011

Gupta V.K., Rastogi A., Dwivedi M.K., Mohan D. 1997. *Process development for the removal and recovery of zinc and cadmium from wastewater using slag, a blast furnace waste material.* Sep. Sci. Technol., 32: 2883-2912.

Hajiaghababaei L., Badiei A., Ganjali M.R., Heydari S., Khaniani Y., Mohammadi Ziarani G. 2011. *Highly efficient removal and preconcentration of lead and cadmium cations from water and wastewater samples using ethylenediamine functionalized SBA-15.* Desalination, 266(1-3): 182-187. DOI:10.1016/j.desal.2010.08.024

Hajiaghababaei L., Ghasemi B., Badiei A., Goldooz H., Ganjali M.R., Mohammadi Ziarani G. 2012. *Aminobenzenesulfonamide functionalized SBA-15 nanoporous molecular sieve: A new and promising adsorbent for preconcentration of lead and copper ions.* J. Environ. Sci., 24(7): 1347-1354. DOI: 10.1016/S1001-0742(11)60892-9

Hajiaghababaei L., Badiei A., Shojaan M., Ganjali M.R., Mohammadi Ziarani G., Zarabadi Poor P.

2012. *A novel method for the simple and simultaneous preconcentration of Pb^{2+}, Cu^{2+} and Zn^{2+} ions with aid of diethylenetriamine functionalized SBA-15 nanoporous silica compound.* Int. J. Environ. Anal. Chem., 92(12): 1352-1364. DOI:10.1080/03067319.2011.585715

Hajiaghababaei L., Tajmiri T., Badiei A., Ganjali M.R., K. Y., Mohammadi Ziarani G. 2013. *Heavy metals determination in water and food samples after preconcentration by a new nanoporous adsorbent.* Food Chem., 141(3): 1916-1922. DOI: 10.1016/j.foodchem.2013.04.096

Harris Z.L., Gitlin J. 1996. *Genetic and molecular basis for copper toxicity*. Am. J. Clin. Nutr., 63(5): 836-841.

Heidari A., Younesi H., Mehraban Z. 2009. *Removal of Ni(ii), Cd(ii), and Pb(ii) from a ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica*. Chem. Eng. J., 153(1-3): 70-79. DOI: 10.1016/j.cej.2009.06.016

Jeon C. 2017. *Adsorption of silver ions from industrial wastewater using waste coffee grounds.* Korean J. Chem. Engin., 34(2): 384-391. DOI: 10.1007/s11814-016-0253-9

Jintakosol T., Nitayaphat W. 2016. *Adsorption of silver (I) from aqueous solution using Chitosan/Montmorillonite composite beads*. Mat. Res., 19(5): 1114-1121. DOI: 10.1590/1980-5373-MR-2015-0738

John Kennedy L., Judith Vijava J., Sekaran G., Kayalvizhi K.J. 2007. *Equilibrium, kinetic and thermodynamic studies on the adsorption of m-cresol onto micro- and mesoporous carbon.* J. Hazard. Mater., 149(1): 134-143. DOI: 10.1016/j.jhazmat.2007.03.061

Kanani N., Bayat M., Shemirani F., Ghasemi J.B., Bahrami Z., Badiei A. 2017. *Synthesis of magnetically modified mesoporous nanoparticles and their application in simultaneous determination of Pb(II), Cd(II) and Cu(II).* Res. Chem. Intermed., 44(3): 1689-1709. DOI: 10.1007/s11164-017-3192-0

Kikuchi Y., Qian Q., Machida M., Tatsumoto H. 2006. *Effect of ZnO loading to activated carbon on Pb(II) adsorption from aqueous solution.* Carbon, 44(2): 195-202. DOI: 10.1016/j.carbon.2005.07.040

Kurniawan T.A., Chan G.Y.S., Lo W.H., Babel S. 2006. *Physico-chemical treatment techniques for wastewater laden with heavy metals*. Chem. Eng. J., 118(1-2): 83-98. DOI: 10.1016/j.cej.2006.01.015

Lim A.P., Aris A.Z. 2014. *A review on economically adsorbents on heavy metals removal in water and wastewater*. Rev. Environ. Sci. Biotech., 13: 163-181.

Linder M.C., Hazegh-Azam M. 1996. *Copper biochemistry and molecular biology*. Am. J. Clin. Nutr., 63(5): 797-811.

Ma X.F., Wang Y.Q., Gao M.J., Xu H.Z., Li G.A. 2010. *A novel strategy to prepare ZnO/PbS heterostructured functional nanocomposite utilizing the surface adsorption property of ZnO nanosheets.* Catal. Today, 158: 459-463. DOI: 10.1016/j.cattod.2010.07.013

Mahmoud M.E., Osman M.M., Hafez O.F., Hegazi A.H., Elmelegy E. 2010. *Removal and preconcentration of lead (II) and other heavy metals from water by alumina adsorbents developed by surface-adsorbed-dithizone.* Desalination, 251(1-3): 123-130. DOI: 10.1016/j.desal.2009.08.008

Mahmoud M.E., Kenawy I.M.M., Hafez M.A.H., Lashein R.R. 2010. *Removal, preconcentration and determination of trace heavy metal ions in water samples by AAS via chemically modified silica gel N-(1-carboxy-6-hydroxy) benzylidenepropylamine ion exchanger.* Desalination, 250(1): 62-70. DOI: 10.1016/j.desal.2009.09.009

Mahmoud M.E., Hafez O.F., Alrefaay A., Osman M.M. 2010. *Performance evaluation of hybrid inorganic/organic adsorbents in removal and preconcentration of heavy metals from drinking and industrial waste water.* Desalination, 253(1-3): 9-15. DOI: 10.1016/j.desal.2009.11

Naseem R., Tahir S.S. 2001. *Removal of Pb(ii) from aqueous/acidic solutions by using bentonite as an adsorbent.* Water Res., 35(16): 3982-3986.

O'connell D.W., Birkinshaw C., O'dwyer T.F. 2008. *Heavy metal adsorbents prepared from the* *modification of cellulose: A review*. Bioresour. Technol., 99(15): 6709-6724. DOI: 10.1016/j.biortech.2008.01.036

Oladoja N.A., Aboluwoye C.O., Oladimei Y.B. 2008. *Kinetics and isotherm studies on methylene blue adsorption onto ground palm kernel coat*. Turkish J. Eng. Env. Sci., 32: 303-312.

Rodriguez-Narvaez O.M., Peralta-Hernandez J.M., Goonetilleke A., Bandala E.R. 2017. *Treatment technologies for emerging contaminants in water: A review*. Chem. Engin. J., 323: 361-380. DOI: 10.1016/j.cej.2017.04.106

Sabbaghan M., Shahvelayati A.S., Bashtani S.E. 2012. *Imidazolium-based Ionic liquids on ... properties of ZnO nanostructures in imidazolium-based ionic liquids*. Solid State Sci., 14(8): 1191-1195.

Sari A., Tuzen M., Citak D., Soylak M. 2007. *Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay*. J. Hazard. Mater., 149(2): 283-291. DOI: 10.1016/j.jhazmat.2007.03.078

Seiler H.G., Sigel A., Sigel H. 1998. *Handbook on toxicity of inorganic compounds*. Marcel--Dekker, New York.

Sheela T., Arthobanayaka Y., Viswanatha R., Basavanna S., Venkatesha T.G. 2012. *Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles*. Powder Technol., 217: 163-170.

Sreejalekshmi K.G., Krishnan K.A., Anirudhan T.S. 2009. *Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: Kinetic and equilibrium isotherm studies*. J. Hazard. Mater., 161(2-3): 1506-1513. DOI: 10.1016/j.jhazmat.2008.05.002

Venkatesham V., Madlhu G.M., Satyanarayana S.V., Preetham H.S. 2013. *Adsorption of lead on gel combustion derived nano ZnO*. Proced. Eng., 51: 308-313. DOI: 1016/j.proeng.2013.01.041

Wang Y.H., Lin S.H., Juang R.S. 2003. *Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents*. J. Hazard. Mater., 102(2-3): 291-302. DOI: 10.1016/S0304-3894(03)00218-8

Wong S.Y., Tan Y.P., Abdullah A.H., ONG S.T. 2009. *The removal of basic and reactive dyes using quartenised sugar cane bagasse*. J. Phys. Sci., 20(1): 59-74.

Zhao X., Qi L. 2012. *Rapid microwave-assisted synthesis of hierarchical ZnO hollow spheres and their application in Cr(VI) removal*. Nanotechnology, 23(23): 235604. DOI: 10.1088/0957-4484/23/23/235604