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Removal of Pb and Cd ions from contaminated water by dithizone-modified cellulose acetate nanosponges

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Abstract

A method for removing Pb(II) and Cd(II) ions from contaminated waters via a batch procedure by dithizone-modified cellulose acetate nanosponges as an adsorbent is proposed. Determination of Pb(II) and Cd(II) ions in the initial and final samples were carried out by flame atomic absorption spectrometry technique. The adsorbent was prepared from waste photographic tapes. The time required for complete adsorption process was 6 seconds. While non-modified cellulose acetate nanosponges can adsorb only about 2.0 % of Pb^{2+} from an aqueous solution of 50 mg L^{-1} and 1.5 % of Cd^{2+} from a solution of 10 mg L^{-1}, dithizone modification improved the efficiency to up to 99.5 and 95.5 %. Maximum adsorption capacities of the dithizone-modified adsorbent were 787mg $g^{-1}$for lead and 195 mg $g^{-1}$for cadmium.

1. Introduction

With the rapid industrial development, environmental pollution due to discharging trace metals into rivers and marine waters is getting worse. Lead and cadmium are two such trace metals enter into the environment. Existence these two trace metals at hazardous levels in watermay attend to accumulate in living bodies thorough the food chain[1, 2].Several techniques have been applied for the removal of lead and cadmium ions from wastewater such as chemical precipitation, coagulation-flocculation, ion exchange, adsorption, evaporation, biosorption and membrane filtration [3-5]. The imperfections of most of the reported methods are high energy consumption, complicated operations and non-selectivity. Nowadays, nano-adsorption techniques have been extended for water treatment. These techniques have some advantages over traditional treatment methods such as high area to volume ratio, flexibility to modify, selectivity, and feasibility to remove trace quantities of hazardous metals [6].

In recent years, nanosponges have been utilized in various fields, such as drug therapy [7-10], environmental studies [11-13] and analysis [14, 15]. Nanosponges have been proposed to be in the most promising adsorbent in wastewater treatment, and specially have been applied to the removal of trace metal ions [16-20].

Nanosponges have been prepared by various chemical and physical techniques; one of them is phase separation [21]. Generally, phase separation comes from the difference in the solubility of polymeric compounds in two different miscible solvent, soluble in one solvent and insoluble in the other one. Phase separation is executable according to four methods including thermally induced phase separation, air-casting of a polymer solution, precipitation from the vapor phase and immersion-precipitation. In this study, an immersion-precipitation method was used to prepare nanosponges due its simplicity of operation without complicated instruments [22].

Cellulose acetate (CA) adsorbent derivatives like silver-loaded CA hollow fiber membranes [23], CA/polyethyleneimine blend microfiltration membranes [24], epoxy functionalized poly (ether-sulfone) incorporated CA ultrafiltration membranes [25], and so on have been recently applied to eliminate noxious compounds from water. Removal of Pb and Cd from contaminated water have been carried out with various modified forms of cellulosic biopolymers, such as ethylenediamine-modified cellulose [26], nitrilotriacetic acid anhydride-modified ligno-cellulosic material [27], or mercerized cellulose chemically modified with succinic anhydride [28].

The objective of the present study was to investigate the adsorption of lead and cadmium ions onto cellulose acetate nanosponges(CANSs) modified with dithizone, an agent that can form strong complexes with lead and cadmium ions. The proposed method shows high potential for effective adsorption of Pb(II) and Cd(II) from aqueous solutions in a short time via a simple process.

2. Experimental

2.1. *Chemicals*

All solutions were prepared in double distilled water with electric conductivity below 1.5 µS cm^{-1}. All chemicals and reagents used were of analytical grade. Diphenylthiocarbazone (dithizone, Dz), alkyldimethylbenzylammonium chloride (ADBAC), glacial acetic acid, sodium hydroxide, hydrochloric acid (37 %, w/w) and nitric acid (suprapur®, 65 %, w/w) were purchased from Merck (Darmstadt, Germany). CA was obtained from photographic film tape wastes. Sodium hypochlorite solution (5 %, commercial grade, Bojeneh, Ahvaz, Iran) was used to decolorize the CA films. Analytical solutions of lead (0.5-20.0 mg L^{-1}) and cadmium (0.1-2.0 mg L^{-1}) were prepared by stepwise dilution of 1000 mg L^{-1} standard solutions (Romil, Cambridge, UK).

2.2. *Instrumentation*

A flameatomic absorption spectrophotometer (AA240FS, Varian, Melbourne, Australia) equipped with lead and cadmium hallow cathode lamps (Photron, Melbourne, Australia) at the wavelength 283.3 and 228.8 nm was used for determination of lead and cadmium.

A scanning electron microscope (SEM, 1455 VP, Leo, Oberkochen, Germany) was used to study the morphology of the synthesized nanosponges. Structural analysis of modified CANSs was carried out by X-ray diffractometer(XRD, D8 Discover, Bruker, Karlsruhe, Germany). A FTIR spectrometer (Rayleigh WQF-510, Braic, Beijing, China) was used to follow the chemical and physical modification processes via identifying the functional groups and chemical bonding of the coated materials. An orbital shaker (KS 130 Works Basic Model, IKA, Staufen, Germany), a hotplate and stirrer (model 1000, Jenway Staffordshire, UK) and a pH meter (model 827, Metrohm, Herisau, Switzerland) were used during the experiments.

2.3. *Preparation of CA solution*

Photographic film tapes were initially treated with 5 % sodium hypochlorite solution for several seconds in order to remove the gelatinous layers. The transparent films were fragmented with scissors and washed with dishwashing liquid and water several times. The cleaned and discolored CA films were dried in an oven at 50 °C for 1 h. Finally, the fragmented films were dissolved in glacial acetic acid. The prepared CA solution (1 g L^{-1}) was kept in a container prior to use.

2.4. *Preparation of dithizone-modified CANSs*

A volume of 20 mL CA solution (1 g L^{-1}in acetic acid) was injected with a syringe rapidly into 300 mL water while stirring at 500 rpm. Upon injection, the CANSs were formed immediately. They were rinsed with water until the acetic acid in the solution was completely removed. In order to de-esterification exterior CA, the CANSs were poured in 200 mL KOH 5 molL^{-1} and kept in it for 24 h, then washed with water several times. The alkalized CANSs were poured in 200 mL ADBAC solution (0.25 %) and kept at room temperature overnight. The ADBAC-modified CANSs were washed with sufficient water to remove residual ADBACs.Finally, the modified-CANSs were poured into 200 mL of a solution of Dz (1.5 g L^{-1} in ethanol). To complete the functionalization process on modified CANSs, the solution was held one night. The Dz-modified CANSs (Dz@CANSs) were washed with ethanol and water several times. The prepared adsorbent was kept in water prior to use.

From the SEM image of the synthesized Dz@CANSs (**Fig. 1a**), the average size of cavities of hollow fiber structure is concluded to be less than 100 nm.

2.5. *Adsorption procedure*

The adsorption behavior of Pb(II) and Cd(II) onto Dz@CANSs wasinvestigated in a batch process. In a typical experiment, 20 mg ofDz@CANSs was added to 50 mL binary solution of lead (50 mg L^{-1}) and cadmium (10 mg L^{-1}) while stirring on an orbital shaker (200 rpm) at 25 °C and pH 6.0. A short time (approximately 6 seconds) was needed to adsorb lead and cadmium ions, effectively. After injecting adsorbent into lead and cadmium ions solution, the purified solution was passed through Whatmann 41 filter paper and the analytes were determined using FAAS.

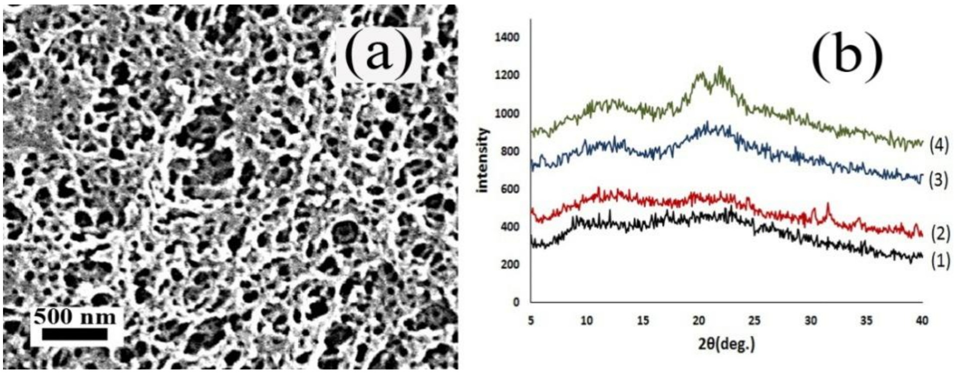

Figure 1: (a) SEM of Dz@CANSs, (b) XRD pattern of (1) cellulose acetate nanosponges, (2) alkalized cellulose acetate nanosponges, (3) ADBAC modified cellulose acetate nanosponges and (4) Dz@CANSs.

2.6. Sampling

The proposed method was applied to different water samples including (1) Karoon river (Ahvaz, Iran) water, (2) Caspian Sea (northern Iran) and (3) Persian Gulf (southern Iran). All the samples were filtered through a 0.45 µm CA membrane filter and preserved at pH 2 with $HNO_3$0.1 mol L^{-1}. Before analysis, pH of the sample solution was adjusted at 6±1 by NaOH 0.1 mol L^{-1}. The adsorption process was performed on the samples according to described procedure in this study.

3. Results and discussion

3.1. Characterization of the CANSs and Dz@CANSs

According to investigations, non-modified CANSs did not have good efficiency to adsorb high amounts of Pb(II) and Cd(II) (Pb 50 mg L^{-1} : 2% and Cd 10 mg L^{-1}: 1.5%). To enhance the capability of CANSs to adsorb the Pb(II) and Cd(II), a strong ligand must be chosen. One of the best options to accomplish this purpose was dithizone. Since the surface of the cellulose acetate is not suitable for direct modification with dithizone due to high tendency of dithizone molecules to adhere on CA through electrostatic forces between N and S of dithizone and –OH groups of CA, pretreatment of cellulose acetate seems to be necessary before modification. For this purpose, a cationic surfactant like benzalkonium chloride was chosen.

XRD patterns of CANSs (**Fig. 1b**) did not reveal any crystallinity. It seems that de-esterification of CA did not improve the crystal structure. After modification of cellulose surface with ADBAC, two special peaks related to cellulose at 20.1° and 22.4° appeared [29]. At the final step, the crystallinity of cellulose was formed due to the modification with dithizone.

To pursue the effect of chemical and physical modification on the operation of preparing adsorbent, FTIR spectrums of cellulose acetate and dithizone-modified cellulose acetate were applied (**Fig. 2**). The spectrum 2A (cellulose acetate) contains strong peaks at 1040 (stretching C-O, alkoxy group), 1237 (stretching C-O, acyl group), 1377 (bending C-H sp3) and 1756 cm^{-1} (stretching C=O). De-esterification of cellulose acetate with KOH removed the acetate groups of cellulose acetate and converted the surface layer of this structure to cellulose. Elimination of the peaks at 1237 and 1756 cm^{-1} in spectrum 2A is strong evidence to the presented hypothesis (spectrum 2B). The surface of alkalized CA was modified by benzalkonium chloride. It seems that the macromolecules of ADBAC were snapped on the surfaces of CA through electrostatic attractions between the nitrogen of ADBAC and –OH of cellulose. Appearance of peaks at 725 (C-H aromatic) and 1468 cm^{-1} (C-C stretching in plane, aromatic) and three peaks at 2855, 2926 and 2956 cm^{-1} (C-H stretching, alkanes) demonstrates the existence of ADBAC on the surfaces cellulose (spectrum 2C). In spectrum 2D, relatively strong peaks at 1064 (N-N) and 1389 cm^{-1} (C=S) related to the dithizone are available that are not observed in spectrum 2C.

3.2. Optimization

In higher concentrations of Pb^{2+} and Cd^{2+} in the solution, pH has a determinant effect on adsorption process. With increasing pH, Pb and Cd ions due to the formation of $Pb(OH)_2$ [$K_{sp}=4.0\times10^{-15}$] and $Cd(OH)_2$ [$K_{sp}=4.5\times10^{-15}$] compounds precipitate.The effect of pH on the adsorption of lead and cadmium ions by Dz@CANSs has been studied at pH 2-8 (50 mL, Pb^{2+} 50 and Cd^{2+} 10 mg L^{-1}, 20 mg adsorbent, 25 °C, contact time 30 min., 200 rpm). According to the results (**Fig. 3a**), the best removal efficiencies of Pb^{2+} and Cd^{2+} have been obtained at pH 5.4-8.0 (Pb^{2+}:>99.5 %, Cd^{2+}: >95.8 %). In acidic solutions, removal efficiencies of Pb^{2+} and Cd^{2+}were strongly declined due to strong competition between H^+ and Pb(II) and Cd(II) to bond with nitrogen atoms of dithizone molecules.In further experiments, pH of the sample solutions was fixed at 6.0 using acetate buffer.

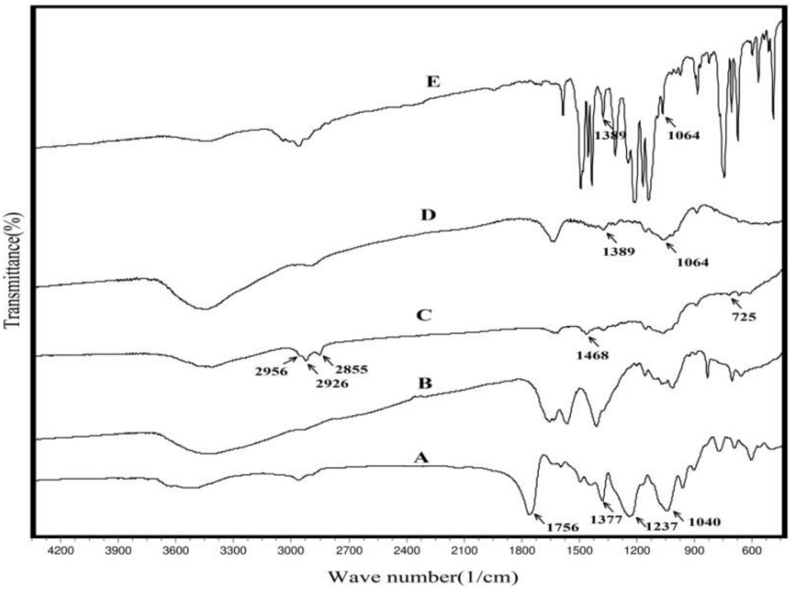

Figure 2: FTIR spectrums of (A) cellulose acetate nanosponges , (B) alkalized cellulose acetate nanosponges , (C) ADBAC modified cellulose acetate nanosponges , (D) Dz@CANSs and (E) dithizone.

The effect of contact time on the adsorption of Pb(II) and Cd(II) has been experienced at different times on 50 and 10 mg L^{-1} solutions (50 mL, 20 mg adsorbent, pH 6.0, 25 °C, 200 rpm), respectively. After adsorption process on the test solutions, they have been collected for analysis of heavy metal ions using FAAS. According to the results, adding adsorbent to the test solutions caused to adsorb Pb and Cd ions immediately (Pb^{2+}: ≥99.5 %, Cd^{2+}: ≥95.5 %). The time required to adsorb Pb and Cd ions was less than 0.1 minute. Probably it arises from the high tendency of dithizone to form complex with Pb and Cd ions. Elapsing more time did not have more effect on removal efficiency. The amount ofDz@CANSs adsorbent for quantitative removal of Pb and Cd ions from 50 mL solutions(50 and 10 mg L^{-1}, respectively) hasbeen optimized by varying adsorbent amounts ranging from 1 to 30 mg. Other conditions that might influence the adsorption process have been controlled (pH 6.0, 25 ºC and 200 rpm). Acceptable removal efficiencies (Pb^{2+}:>99.0 %, Cd^{2+}: >95.2 %) have been obtained by using 15 mg of dithizone-modified cellulose acetate nanosponges (**Fig. 3b**). The fixed amount of adsorbent used in entire experiments was chosen to be 20 mg.

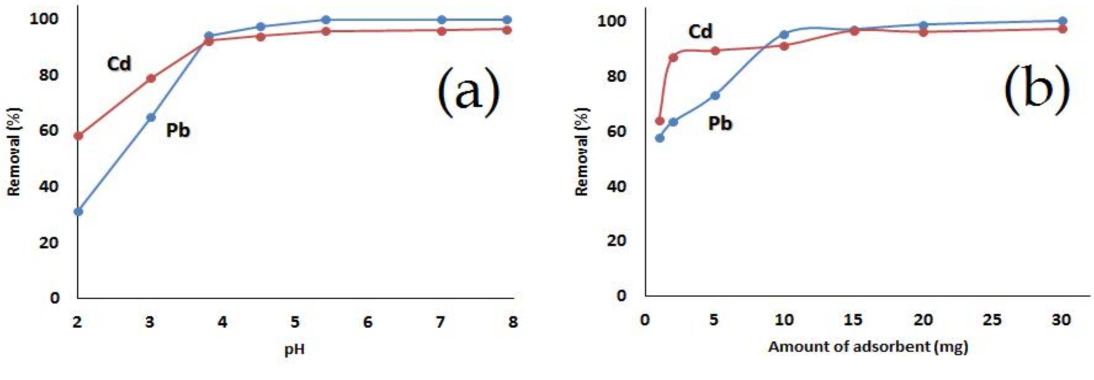

Figure 3: (a) The effect of pH of the solution for quantitative removal of Pb(II) and Cd(II) using Dz@CANSs (50 mL, Pb^{2+} 50 and Cd^{2+} 10 mg L^{-1}, 20 mg adsorbent, 25 °C, contact time 30 min., 200 rpm), (b) The effect of adsorbent amount on removal efficiencies of Pb(II) and Cd(II) at 25 °C (50 mL, Pb^{2+} 50 and Cd^{2+} 10 mg L^{-1}, pH 6.0, 25 °C, contact time 30 min., 200 rpm).

3.3. Adsorption isotherm

To determine the adsorptivity properties of Pb(II) and Cd(II) on Dz@CANSs, Langmuir and Freundlich adsorption isotherms were investigated. The capacity of Dz@CANSs for adsorption of lead and cadmium ions was achieved by measuring the initial and final concentrations of the ions in the solution in a batch system (pH

6.0, 25 °C, stirring speed 200 rpm and contact time 60 min.). Respectively, different concentrations of Pb^{2+} and Cd^{2+} ranging from 50-500 and 10-100 mg L^{-1} in aqueous samples were examined with fix amount of adsorbent (5 mg). Both Langmuir and Freundlich isotherms were computed to realize adsorption behaviors of Pb^{2+} and Cd^{2+} on Dz@CANSs adsorbent. As discussed, the results were collected before and after removal process with respect to calibration curves determined by FAAS system. The results showed that Langmuir model (R^2=0.998) fitted better than Freundlich model (R^2=0.984) for Pb(II) adsorption. In addition, the adsorption isotherm analyses for Cd(II) were deduced that Langmuir model (R^2=0.996) was well fitted than Freundlich model (R^2=0.965), demonstrating that the adsorption ofPb(II) and Cd(II) on Dz@CANSs adsorbent can be occurred through a monolayer process (**Fig. 4**).

The linear relationship between C_e/q and C_e ($C_e/q=0.001C+0.102$ and $C_e/q=0.004C+0.088$ for lead and cadmium ions, respectively) shows the applicability of the Langmuir model for the desired ions adsorption on Dz@CANSs. The experiments have been resulted in 0.009 and 0.045 for K and 1000 and 250 for q_m of lead and cadmium ions, respectively. It should be noted that C_e (mg L^{-1}) is the equilibrium concentration of the metal ions in the solution, q (mg metal ions per g adsorbent) is the equilibrium adsorption amount of metal ions, q_m is the maximum adsorption amount of metal ions per weight of adsorbent (mg g^{-1}) and K is the Langmuir adsorption equilibrium constant in liter per milligrams of adsorbent (L mg^{-1}).

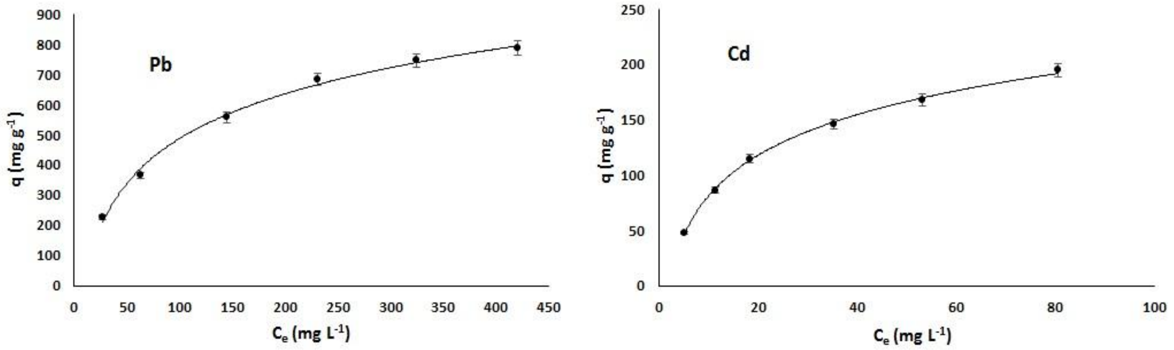

Figure 4: The plots of isotherms for Pb and Cd ions adsorbed by Dz@CANSs at 25 °C and pH 6.0.

3.4. Effect of electrolytes

Based on knowledge, ionic strength has considerable effect on the adsorption properties of an adsorbent. Natural salts present in aquatic environment, which are representative of electrolytes in the water samples, in the vicinity of heavy metal ions may interfere their adsorption process by adsorbent. To study the effect of electrolyte (adjusted by 0.001-0.1 mol L^{-1} KNO_3) on lead and cadmium adsorption, 50 mL of water samples (Pb^{2+} 50 mg L^{-1}, Cd^{2+} 10 mg L^{-1}) at 25 ºC and pH 6.0 were chosen. It was observed that removal efficiency of lead and cadmium was more than 95 % below the 0.001 mol $L^{-1}KNO_3$. According to obtained results, electrolyte effect on cadmium seems to be more influent than lead. The interaction between Cd^{2+} and dithizone is more sensitive than Pb^{2+}. As regards the reducing ionic radius increases charge density, the tendency of Cd^{2+}, that its ionic radius is smaller than Pb^{2+}, to form complex with dithizone was more than Pb^{2+}. Potassium ions in the test solution, as hard Lewis acid, cannot compete with lead and cadmium ions, as soft acids, to occupy active negative sites of dithizone (sulfur groups, as soft Lewis bases) on CANSs, but it is suggested that increasing electrolyte concentration causes covering negative sites of adsorbent by the electrolyte cations (K^+), leading to a decrement in the adsorption of the metal ions.

3.5. Reusability

Reusability of an adsorbent may be a criterion for applicability of a method to remove the noxious compounds. This ability was tested on the Dz@CANSs in controlled conditions (Pb^{2+} 50 and Cd^{2+} 10 mg L^{-1}, 50 mL, pH 6.0, contact time 10 min. and stirring speed 200 rpm). 20 mL of HNO_3 1 mol L^{-1} was used in order to completely elute lead and cadmium ions on adsorbent. The results showed that Dz@CANSs can be reused for four times without a considerable loss in their adsorption efficiency (>95 %).

3.6. Effect of sample volume on the removal efficiency

To achieve a tolerable volume of lead and cadmium sample solution per adsorbent amount used for removal, different sample volumes ranging from 25 to 500 mL were studied (pH 6.0, contact time 10 min., stirring speed

200 rpm, 25 °C). Solution volumes were increased while the total weight of Pb^{2+} and Cd^{2+} in solution remained fixed at 1.25 and 0.25 mg, respectively. The obtained results (data are not given) showed that the complete removal of Pb^{2+} and Cd^{2+} were applicable up to 300 and 200 mL of solutions, respectively.

3.7. Loading capacity

The maximum adsorption capacity of Dz@CANSs was investigated while 5 mg of adsorbent was added to a 50 mL solution (Pb^{2+} 500 mg L^{-1}, Cd^{2+} 100 mg L^{-1}). The solutions were stirred for 24 hours at 200 rpm. Then, Pb^{2+} and Cd^{2+} amounts were determined before and after adsoprtion process by FAAS. Appropriate dilution of solutions was performed to fix the concentration of analyte in the linear range of calibration curve. The loading capacities for lead and cadmium ions were obtained to be 787 and 195 mg g^{-1}, respectively.

3.8. Real samples

The proposed solid phase extraction (SPE) method was used for the removal of lead and cadmium ions in the water sample solutions. To specify the usability and accuracy of the method, several 50 mL Pb^{2+} (spiked 5 and 10 mg L^{-1}) and Cd^{2+} (spiked 2 and 5 mg L^{-1}) contaminated solutions were prepared using different water samples with different matrices. Then, the adsorption process was carried out under controlled condition (pH 6.0, contact time 10 min., stirring speed 200 rpm, 25 °C). As required, the removal percent of analytes was evaluated using FAAS and GFAAS techniques before and after adsorption process. As shown in **Table 1**, in the samples with less complicated matrices like Karoon river sample, removal efficiencies were at acceptable level. Furthermore, in more chemically complicated samples (Persian Gulf and Caspian Sea samples) the removal percent declined due to inadequate selectivity of the adsorbent. As discussed above, electrolyte concentration has more vigorous effect on the adsorption of cadmium versus lead ions. It can be explained that the elimination of cadmium at complicated matrices encountered problems due to great electrolyte effect on its adsorption process.

Table 1: Removal efficiencies of spiked real samples (50 mL, pH 6.0, 25 °C, contact time 10 min., 200 rpm)

	Pb^{2+}		**Cd^{2+}**	
Sample	**Added (mg L^{-1})**	**Removal (%)**	**Added (mg L^{-1})**	**Removal (%)**
Karoon river	5	>99.8	2	93.1
	10	>99.8	5	84.8
Caspian Sea	5	91.8	2	24.3
	10	74.6	5	17.4
Persian Gulf	5	77.3	2	29.7
	10	75.4	5	22.0

Table 2 demonstrates the comparison between some parameters of the reported methods and adsorbents in the literature and the proposed method. Present study shows high potential for removal of Pb(II) and Cd(II) from water samples with almost complicated matrices.

Table 2: Comparison table of present study with respect to previously represented studies

	Loading capacity (mg g^{-1})		**Adsorbent amount (mg)**	**Time (min.)**	**Ref.**
Type of adsorbent	**Pb(II)**	**Cd(II)**			
Succinylated corn starch	11.1	12.3	100	10	[30]
Cellulose chitin beads	176.0	69.7	100	300	[31]
Succinylated sugarcane bagasse	83.3	43.6	100	10	[32]
Succinylated cellulose	205.9	86.0	100	10	[28]
sugarcane bagasse modified by TETA	86.2	69.4	50	20	[33]
sugarcane bagasse modified by EDTAD	333.0	149.0	50	20	[34]
Modified pine bark	13.0	13.8	250	60	[35]
Polymer Pactcac	21.5	6.9	8	10	[36]
Dz@CANSs	787	195	15	0.1	This work

Conclusions

A simple, cost-effective and rapid SPE method for removal of Pb(II) and Cd(II) from aqueous solution has been successfully tested with dithizone-modified cellulose acetate nanosponges. The adsorption behavior can be described by the Langmuir isotherm. A short time (0.1 min.) was sufficient to perform the adsorption process

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