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Article

Removal of Mercury, Antimony, Cadmium and Lead from Aqueous Solution using 1,3,5-Trithiane as an Adsorbent

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Neste trabalho, utilizou-se 1,3,5-tritiano (TT) na remoção dos íons Hg(II), Sb(III), Cd(II) e Pb(II) em soluções aquosas. A influência das condições de remoção tais como pH, tempo de contato e concentração inicial de TT na capacidade de ligação dos íons foi testada. As capacidades de adsorção máxima para os íons Hg(II), Sb(III), Cd(II) e Pb(II) foram 35,5 ± 0,6, 16,9 ± 0,4, 12,1 ± 0,1 e 9,5 ± 0,1 mg g^{-1} em pH 5,0, respectivamente. A seletividade do tritiano para os íons foi determinada como tendo a seguinte ordem decrescente: Hg(II) > Sb(III) > Cd(II) > Pb(II). Os modelos de isotermas de adsorção foram aplicados aos dados experimentais, e o de Langmuir apresentou-se como sendo o melhor ajuste para a adsorção dos íons Hg(II) em TT. Os íons dos metais tóxicos podem ser efetivamente dessorvidos por lixiviação ácida e o tritiano regenerado por pelo menos cinco vezes sem qualquer perda na capacidade de adsorção.

In this work, 1,3,5-trithiane (TT) was used for removal of Hg(II), Sb(III), Cd(II) and Pb(II) ions from aqueous solutions. The influence of the uptake conditions such as pH, contact time and initial TT feed concentration on the ion binding capacity of TT was tested. Maximum adsorption capacities for Hg(II), Sb(III), Cd(II) and Pb(II) were 35.5 ± 0.6, 16.9 ± 0.4, 12.1 ± 0.1 and 9.5 ± 0.1 mg g^{-1} at pH 5.0, respectively. Selectivity of TT for the ions was determined as having the following decreasing order: Hg(II) > Sb(III) > Cd(II) > Pb(II). Adsorption isotherm models were applied to the experimental data, and the Langmuir model presented as the best fit for the adsorption of Hg(II) ions on TT. Adsorbed toxic metal ions can be effectively desorbed by acid leaching and the regenerated TT can be reused at least five times without any significant loss in adsorption capacity.

Keywords: adsorption, 1,3,5-trithiane, metal-preconcentration, Langmuir model

Introduction

As a result of industrialization and urbanization, the presence of metal ions in water streams has been increased in the past five decades. The metals are released into the environment by coal combustion, sewage wastewaters, automobile emissions, battery industry, mining activities, tanneries, alloy industries and the utilization of fossile fuels. The metal ions are prioritized among all pollutants due to their toxicity and mobility in natural water ecosystem.[1-4]

Solvent extraction, ion exchange, chemical precipitation, membrane filtration (reverse osmosis, nanofiltration, etc.), coagulation, photoreduction and adsorption are commonly used methods for removal of metal ions.[5-8] However, most of these techniques have some disadvantages such as complicated treatment process, high cost and energy use. Although the main disadvantage is the high price of the adsorbents, the adsorption is the most preferred technique due to its high efficiency, easy handling and availability of different adsorbents. Some adsorbents such as active carbon,[9,10] alumina,[11] ferric oxides,[12] fly ash,[13,14] lignite,[15] phosphate rock[16] and kaolinite-based clays[17] are preferably used in wastewater treatment due to their large specific surface areas and high metal adsorption capacities.[18,19]

The adsorbent containing one or more electron donor atoms such as N, S, O and P can form coordinate bonds with most of the toxic metals.[20,21] Superior reactivity of the sulfur compounds toward some metal ions is the key principle for using thiol anchor groups.[22] Other sulfur containing polymer-supported ligands such as xanthate,[23] thiourea,[24] pyridine-based thiols and dithiozone[25] are also used for toxic metal removal.

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In this work, the use of 1,3,5-trithiane (TT) containing S electron donor atom for removal of the toxic metals such as Hg(II), Sb(III), Cd(II) and Pb(II) is presented. TT $(CH_2S)_3$ is the cyclic trimer of the otherwise unstable species thioformaldehyde, showing insolubility in water, low molecular weight, flexible structure and the presence of three donating sulfur atoms. It consists of a six-membered ring with alternating methylene and thioether groups. Cyclic thioethers are important ligands for the complexation of toxic metal ions. Extraction by means of complexation to thioethers may have important medicinal perspectives for treating toxic metal poisoning.[26] It is also used in the determination of Ce(III) and preparation of poly(methyl methacrylate) polymer with low polydispersity.[27,28]

The adsorption kinetics and the adsorption capacity of the metals along with the effect of pH on the adsorption were investigated in this study. Reusability under competitive and non-competitive conditions was also examined. Langmuir and Freundlich adsorption isotherms were determined and the mechanism for the formation of metal-TT was discussed. The preconcentration factor, limits of detection (LOD) and of quantification (LOQ) and relative uncertainty values were calculated. The adsorption isotherm models determined were used to validate the experimental data.

Experimental

Materials

1,3,5-Trithiane was obtained from Sigma-Aldrich and used as adsorbent. All water used in the experiments was purified using Milli Q-Water purification system (Millipore). 1000 mg L^{-1} Hg(II), Sb(III), Cd(II) and Pb(II) standard solutions and all other chemicals were of reagent-grade and purchased from Merck. All metal analyses were measured by using Analytik Jena AG ZEEnit 700 AAS atomic absorption spectrometer. An acetate buffer solution was prepared from acetic acid and sodium acetate. Nitric acid was used as a desorption agent in the desorption study. For the evaluation of the measurement precision and accuracy, SPS-WW1 Batch 110 wastewater reference material was used. Working standard solutions were prepared fresh from these stock solutions on a daily basis. The resulting purified water (deionized water) has a specific conductivity of 18.2 mΩ cm.

Single-component toxic metal adsorption studies

The adsorption properties of TT for metal ions Hg(II), Sb(III), Cd(II) and Pb(II) were investigated in the batch experiments. To find optimum pH for maximum adsorption, 0.1 g TT samples were immersed in 50 mg L^{-1} ionic solutions at room temperature for 24 h. The pH of the initial solutions was adjusted with HCl and NaOH to cover range of 2.0 to 6.0.

The effects of initial toxic metal ion concentration and of the adsorption capacity were also examined. 0.1 g TT samples were contacted with different concentration of metal ion solutions (1-1000 mg L^{-1}) in acetate buffer at pH 5.0. The sample solutions were stirred magnetically at 200 rpm at room temperature. The solutions were then centrifuged, and filtered through a Millipore filter of pore size of 0.45 μm. The toxic metal concentrations were determined by atomic absorption spectroscopy. Each value reported in this work is an average of at least three separate measurements. Metal ion concentrations adsorbed *per* unit mass of TT (mg metal ion g^{-1} dry TT) were calculated by using the following expression:

$$\text{The amount of metal ion adsorbed (mg g}^{-1}\text{)} = \frac{(C_0 - C)\,V}{100\text{ m}} \quad (1)$$

where C_o and C are the concentrations of the metal ions in the aqueous phase before and after the adsorption, respectively, (mg L^{-1}), V is the volume of the aqueous phase (mL) and m is the amount of dry TT used (g).

Adsorption kinetics

The adsorbent dosage was 0.25 mg and the initial toxic metal concentrations (C_0) were 500 mg L^{-1} for Hg(II), and 600 mg L^{-1} for Sb(III), Cd(II) and Pb(II). To determine the effect of contact time, TTs were immersed into 10 mL of the solution containing a metal ion concentration at pH 5.0 for several time periods up to 8 h. Samples were taken out from the adsorption medium periodically and metal ion concentrations were measured by AAS, after samples were filtered through a Millipore filter.

Multi-component toxic metal adsorption

Adsorption of the toxic metal ions from synthetic wastewaters and reference material (SPS-WW1 Batch 110) was carried out in a batch system. To determine possible interferences on the toxic-metal uptake originating from foreign ions, two different synthetic wastewater solutions (called as A-representing some cation effect, and B-representing some cation, anion and organic effect, from this point on) were prepared using NaAc-AcOH buffer solution (pH 5.0). The concentration of metal ions in the synthetic wastewater solution A was as follows: 0.1 mmol L^{-1} for each of Ni(II), Zn(II), Fe(II), Co(II), Sn(II) and Ag(I), and 500 mg L^{-1} Hg(II), 600 mg L^{-1} Sb(III), 600 mg L^{-1} Cd(II) and 600 mg L^{-1} Pb(II). In order to adjust salinity, 700 mg L^{-1} NaCl was added to the composition of A.[29] The concentration of metal ions in synthetic wastewater solution B is as follows: 0.5 mg L^{-1} $MnCl_2{\cdot}4H_2O$, 83.6 mg L^{-1} $MgCl_2{\cdot}6H_2O$, 20.6 mg L^{-1} $(NH_4)_2SO_4$, 83 mg L^{-1} NH_4Cl, 66.6 mg L^{-1} $(NH_4)_2CO_3$, 133.7 mg L^{-1} Na_2CO_3, 49.9 mg L^{-1} $CaCO_3$, 3.1 mg L^{-1} $FeCl_3{\cdot}6H_2O$, 74.7 mg L^{-1} KH_2PO_4, 21.4 mg L^{-1} urea, 277 mg L^{-1} glucose and 500 mg L^{-1} Hg(II), 600 mg L^{-1} Sb(III), 600 mg L^{-1} Cd(II) and 600 mg L^{-1} Pb(II).[30] SPS-WW1 Batch 110 reference wastewater solution (called SPS from this point on) was also used to check for the additional effect of foreign ions on the adsorption. The concentration of metal ions in SPS is 2000 µg L^{-1} Al, 100 µg L^{-1} As, 20 µg L^{-1} Cd, 60 µg L^{-1} Co, 200 µg L^{-1} Cr, 400 µg L^{-1} Cu, 1000 µg L^{-1} Fe, 400 µg L^{-1} Mn, 1000 µg L^{-1} Ni, 1000 µg L^{-1} P, 100 µg L^{-1} Pb, 100 µg L^{-1} V, 600 µg L^{-1} Zn and 500 mg L^{-1} Hg(II), 600 mg L^{-1} Sb(III), 600 mg L^{-1} Cd(II) and 600 mg L^{-1} Pb(II). 0.25 g of TT sample was transferred into 25 mL of each wastewater solution A, B and SPS, then, they were stirred and incubated at room temperature (pH 5.0). After adsorption, the concentration of the metal ions in the remaining solution was determined by AAS as described above.

Adsorption isotherms of metals

The adsorption isotherms of toxic metals on TT were studied using batch tests at room temperature and a pH value of 5.0. The adsorbent dosage was 0.25 mg and the initial toxic metal concentrations ranged from 1 to 1000 mg L^{-1}.

Metal adsorption-desorption studies

The toxic metals adsorbed on TT can be eluted repeatedly by treating with 0.1 mol L^{-1} HNO_3 to obtain metal-free TT. Thus, flask containing toxic metal-loaded TT sample (0.25 g) and 25 mL of 0.1 mol L^{-1} HNO_3 were put into a constant temperature bath oscillating at 200 rpm, at room temperature for 1 h. The solutions were then centrifuged and filtered through a Millipore filter (pore size 0.45 µm). The toxic metal concentrations were measured by AAS. The desorption ratio was calculated by the following equation:

$$\text{Desorption ratio} = \frac{\text{Amount of metal ions desorbed in the elution medium}}{\text{Amount of metal ions adsorbed onto TT}} \times 100 \quad (2)$$

Used TT was then neutralized with dilute NaOH, washed with deionized water and subjected again to adsorption processes to determine its reusability. This adsorption-desorption cycle was repeated five times by using the same TT.

Preconcentration factor

Hg(II), Sb(II), Cd(II) and Pb(II) ion solutions were used for the preconcentration of the metal ions on TT. In order to investigate the adsorption efficiency of TT, enriched Hg(II), Sb(III), Cd(II) and Pb(II) ion solutions were prepared with various concentrations (1-0.1 mg L^{-1}) and volumes (50-500 mL), and 0.1 g TTs was immersed in the solutions and stirred at room temperature for 24 h at 200 rpm. Then, TTs were separated from the adsorption medium and transferred into a flask containing 5 mL of 0.1 mol L^{-1} HNO_3 solution and stirred at 200 rpm at room temperature for 24 h. After, the concentrations of the desorption solutions were measured by AAS, the preconcentration factor was calculated by the ratio of the highest sample volume and the desorption agent volume (5 mL). Each value reported is an average of at least three separate measurements.

Results and Discussion

Effect of pH

The toxic metal adsorption on both non-specific and specific adsorbents is pH dependent. In the absence of complexing agents, the hydrolysis and precipitation of the metal ion are affected by the concentration and form of soluble metal species. In addition to using a specific ligand, selective adsorption could be achieved by adjusting the pH of the medium. In this study, the effect of pH on metal uptake capacity of TT was examined at different pH values ranging from 2.0 to 6.0 for Hg(II), Sb(III), Cd(II) and Pb(II) ions.

As seen in Figure 1, the metal ion adsorption capacity between pH 4.5-5.0 increased extremely and then decreased very dramatically at pH higher than 5.0. This may be attributed to the presence of free lone pair of electron on sulfur atom (or deprotonation of –SH group) suitable for coordination with the metal ion to give the corresponding resin-metal complex. At low pH, the surface of the adsorbent is surrounded by H^+ ions, which prevent the metal ions from approaching the adsorptive sites of the adsorbent. However, with the increasing pH value, the competitive adsorption of H^+ ions decreases and the TT surface becomes more negatively charged. Thus, the positively charged metal ions can be readily adsorbed onto the negatively charged sites of the adsorbent.[31,32] The maximum adsorption values of the metal ions are obtained at pH 5.0 for Hg(II), Sb(III), Cd(II) and Pb(II). This is assumed to be optimal since these metals precipitate as metal hydroxides at pH values of 5.5 to 10.0. The pK values are 25.4 for $Hg(OH)_2$, 49.1 for $Sb(OH)_3$, 13.6 for $Cd(OH)_2$ and 16.1 for $Pb(OH)_2$.[33]

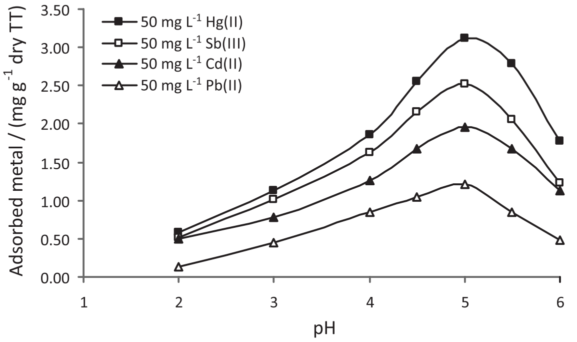

Figure 1. Effect of pH on the metal uptake capacity of TT. Conditions: 50 mg L^{-1} Hg(II), 50 mg L^{-1} Sb(III), 50 mg L^{-1} Cd(II) and 50 mg L^{-1} Pb(II).

The adsorption capacities of TT at the optimum pH are 3.12 mg g^{-1} for 50 mg L^{-1} Hg(II), 2.52 mg g^{-1} for 50 mg L^{-1} Sb(III), 1.95 mg g^{-1} for 50 mg L^{-1} Cd(II) and 1.21 mg g^{-1} for Pb(II) ion solution. The increasing order of affinity of the metal ions at initial concentration of 50 mg L^{-1} is found as Hg(II) > Sb(III) > Cd(II) > Pb(II).

Initial metal ion concentration effect

The dependence of adsorption capacity of TT on the initial concentrations of metal ions was determined by equilibrating the fixed amount of TT with the metal ion solutions by gradually increasing their concentration. Adsorption capability of TT for Hg(II), Sb(III), Cd(II) and Pb(II) ions using solution concentrations varying from 1 to 1000 mg L^{-1} is given in Figure 2. All measurements were performed at optimum pH 5.0. The metal uptake increases rapidly with the increasing initial metal ion concentration (Figure 2). After reaching a maximum at 500 mg L^{-1} for Hg(II), 600 mg L^{-1} for Sb(III), 600 mg L^{-1} for Cd(II) and 600 mg L^{-1} for Pb(II), the metal uptake levels off. From these plateau values, the maximum load capacities are estimated as 35.5 ± 0.6, 16.9 ± 0.4, 12.1 ± 0.1 and 9.5 ± 0.1 mg g^{-1} dry TT for Hg(II), Sb(III), Cd(II) and Pb(II) ion, respectively, indicating that the removal of such metals from wastewater by using TT may find potential applications in industry.

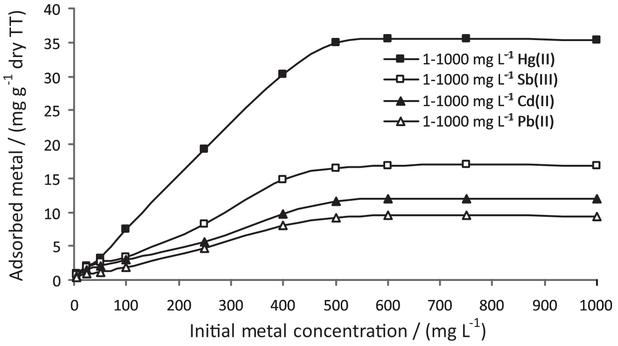

Figure 2. Effect of the initial metal ion concentration on the metal uptake capacity of TT Conditions: 1-1000 mg L^{-1} Hg(II), 1-1000 mg L^{-1} Sb(III), 1-1000 mg L^{-1} Cd(II) and 1-1000 mg L^{-1} Pb(II).

Adsorption isotherms

Adsorption isotherms are important for the description of molecules or ions of adsorbate interaction with adsorbent surface sites and also, are critical in optimizing the use of adsorbent. When an adsorbent is in contact with the surrounding solution with a certain composition, both the adsorbent and the surrounding fluid reach equilibrium after a sufficiently long time. The correlation of equilibrium data is necessary for the practical design and operation of adsorption systems.[34] Langmuir and Freundlich adsorption models were fitted to the data obtained from the adsorption isotherm. The Langmuir equation was originally developed to describe individual chemical adsorbents, and is applicable to physical adsorption (monolayer) within a low concentration range. The Freundlich equation is an empirical approach for adsorbents with very uneven adsorbing surfaces. The Freundlich model is applicable for adsorption of a single solute system within a fixed range of concentration.[35] The equations of the above two types of sorption isotherms are expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n}(\ln C_e) \tag{3}$$

$$q_e = \frac{Q_m k_L C_e}{1 + k_L C_e} \tag{4}$$

where q_e is equilibrium uptake capacity of TT, C_e is the concentration of metal ions in the supernatant after sorption, n and K_F are empirical constants, Q_m and k_L are Langmuir constants related to the capacity and energy of the adsorption, respectively. In order to investigate the effect of the initial metal ion concentration on the adsorption capacity of TT, the experiments were carried out from 1 to 1000 mg L^{-1} concentrations at room temperature for 24 h. The adsorptions of metal ions from aqueous solution by TT are presented in Figures 3 and 4, and the constants of adsorption isotherms are summarized in Table 1. The Langmuir equation fits well for metal ion adsorption on TT (Table 1).

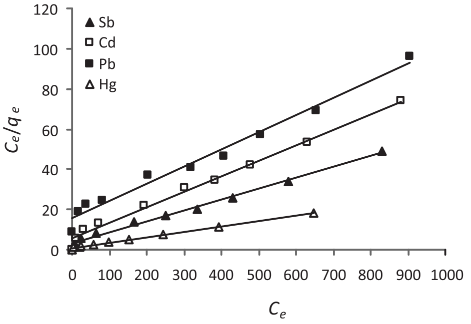

Figure 3. Langmuir isotherm plots for the adsorption of Hg(II), Sb(III), Cd(II) and Pb(II) ions on TT.

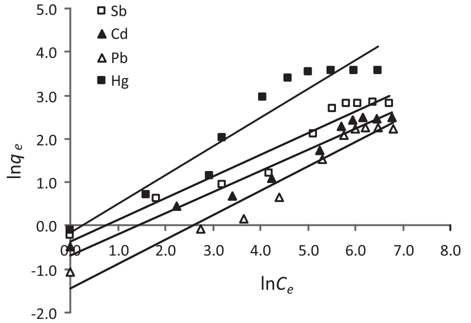

Figure 4. Freundlich isotherm plots for the adsorption of Hg(II), Sb(III), Cd(II) and Pb(II) ions on TT.

Adsorption kinetic studies

The equilibration time is an important parameter for economical wastewater treatment plant applications. For the feasible removal, recovery and pre-concentration of the metal ions from different sources, the adsorption time should be short enough for the time consuming in the experiments in the laboratories and for the industrial applications. Therefore, adsorption kinetics of the toxic metal ions onto TT were examined at 500 mg L^{-1} for Hg(II) and 600 mg L^{-1} for Sb(III), Cd(II), Pb(II) metal ion solutions with the time at pH 5.0 and the results are given in Figure 5. It can be seen that, the adsorption of Sb(III), Cd(II) and Pb(II) sharply increased as a function of time up to 60 min at initial 600 mg L^{-1} and kept slow increase thereafter. The rate of adsorption of Hg(II) on TT was more rapid than the others. The maximum binding of Hg (II) ion occured about 35.5 mg g^{-1} within 45 min and reached equilibrium after 60 min. These results suggest that adsorption time onto TT is really short and feasible for the metal ion adsorption processes.

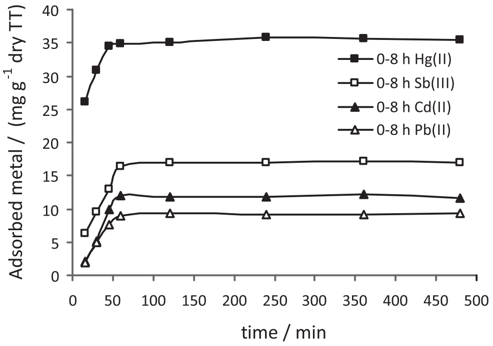

Figure 5. Effect of contact time on the toxic metal adsorption on TT. Conditions: 0-8 h Hg(II), 0-8 h Sb(III), 0-8 h Cd(II) and 0-8 h Pb(II).

Multi-component toxic metal chelation

It is hoped that in the presence of different metal ions, one metal ion could be selectively adsorbed by a chelating agent. Adsorption capacity of a ligand toward the different metal ions, effect of pH of the feed metal solutions and adsorption equilibrium time are important factors over the selectivity properties of ligands in competitive adsorption.[36,37] To investigate such items, chelating of toxic metals from synthetic and reference wastewater were carried out in a batch system. The averages of three measurements are provided in Table 2 for each metal. The results show that the binding capacities of all ions were decreased under the competitive conditions. The competitive adsorption of metal ions was found to be Hg(II) > Sb(III) > Cd(II) > Pb(II) for TT as adsorbent.

Desorption and repeated use

The adsorption and desorption processes were repeated to examine the potential toxic metal uptake of TT for practical applications. The desorption behavior of TT was studied with acidic solutions, and the results are summarized

Table 1. Equations of adsorption isotherms of TT

Adsorbed metal ion	Freundlich		Langmuir			
	Model	R^2	Model	R^2	Q_m	k_L
Hg(II)	$\ln q_e = 0.660 \ln C_e - 0.161$	0.917	$C_e/q_e = 0.027 C_e + 0.777$	0.997	37.03	0.035
Sb(III)	$\ln q_e = 0.501 \ln C_e - 0.379$	0.948	$C_e/q_e = 0.054\ C_e + 2.970$	0.991	18.52	0.018
Cd(II)	$\ln q_e = 0.484 \ln C_e - 0.673$	0.964	$C_e/q_e = 0.077\ C_e + 5.373$	0.990	12.99	0.014
Pb(II)	$\ln q_e = 0.560 \ln C_e - 1.433$	0.945	$C_e/q_e = 0.085\ C_e + 15.32$	0.981	11.76	0.006

Q_m and k_L: Langmuir constants related to the capacity and energy of the adsorption, respectively. R^2: correlation coefficient.

Table 2. Adsorption amount of toxic metals under competitive conditions

Toxic metal	Non-competitive condition / (mg g^{-1})	Competitive with wastewater A / (mg g^{-1})	Competitive with wastewater B / (mg g^{-1})	Competitive with SPS-WW1 Batch 110 reference wastewater / (mg g^{-1})
Hg(II)	35.5 ± 0.6	34.8 ± 0.6	31.6 ± 0.6	32.9 ± 0.6
Sb(III)	16.9 ± 0.4	15.7 ± 0.4	12.4 ± 0.3	13.1 ± 0.3
Cd(II)	12.1 ± 0.1	11.7 ± 0.1	9.8 ± 0.1	10.4 ± 0.1
Pb(II)	9.5 ± 0.1	8.4 ± 0.1	6.5 ± 0.09	7.2 ± 0.09

in Table 3. In this experiment, TT was completely saturated with the metal ions at the optimum pH, initial metal ion concentration and contact time. Then, the adsorbed metal ions were desorbed by using 0.1 mol L^{-1} HNO_3. In order to obtain the reusability of TT, the adsorption-desorption cycles were repeated at least 5 times by using the same TT for determination of adsorption capacity. Table 3 represents the regeneration procedure by treatment with 0.1 mol L^{-1} HNO_3 solution, and the desorption efficiency was generally high and TT could be used five times due to the slight loss of their adsorption capacities.

The enrichment factor was studied by a recommended procedure using an increasing volume of metal ion solution. Contact time of 60 min and pH value of 5.0 for all metals were used in this part. The total amount of loaded metal ions were kept constant at 10 mg L^{-1} concentration level for Hg(II), Sb(III), Cd(II) and Pb(II). The preconcentration factors were calculated from experimental results. As can be seen in Table 4, the results demonstrated that the recoveries were quantitative ($\geq$ 93) up to 250 mL initial volume for Hg(II) and Cd(II), except Sb(III) and Pb(II). The recoveries changed between 90.1 and 94.2% for Sb(III), 89.7 and 94.7% for Pb(II) at different spike levels. The recoveries decreased with the increase of the initial sample volume. Preconcentration factors of TT were found as 50 for Hg(II) and Cd(II). It was found to be 20 for Sb(III) and Pb(II).

Limits of detection, quantification and relative uncertainty

Standard solutions of toxic metals were prepared at seven different concentration levels for Hg(II), Sb(III), Pb(II) (0.50, 1.00, 1.50, 2.00, 2.50, 3.00 and 5.00 mg L^{-1}) and for Cd(II) (0.05, 0.10, 0.20, 0.40, 0.60, 0.80 and 1.0 mg L^{-1}). LOD and LOQ values were calculated using the standard deviation values of the replicate measurements of the lowest concentration in the linear calibration plot (n = 13). The relative standard deviations (RSD) and relative uncertainty values for the toxic metals were also calculated using uncertainty factors such as volumetric flask, pipets and standard solutions. LOD was calculated by the following equation:

$$\mathrm{LOD} = \frac{3S_d}{m} \tag{5}$$

where, S_d is standard deviation of solutions and m is the slope. LOD, LOQ and relative uncertainty values were summarized in Table 5.

Comparison with other methods

A comparison of the proposed systems with other systems is given in Table 6. Some parameters obtained were comparable to those presented by other methods described in the literature. As seen from the data in Table 6, the

Table 3. The results of adsorption and desorption capacities of TT

Cycle	Hg(II)		Sb(III)		Cd(II)		Pb(II)	
	Adsorption / (mg g^{-1})	Desorption / %	Adsorption / (mg g^{-1})	Desorption / %	Adsorption / (mg g^{-1})	Desorption / %	Adsorption / (mg g^{-1})	Desorption / %
1	35.5	97.2	16.9	94.5	12.1	93.7	9.5	94.7
2	35.1	96.8	15.4	93.1	11.8	93.1	8.8	94.2
3	34.8	96.2	14.7	92.4	11.4	92.5	8.3	93.6
4	34.4	95.7	14.1	91.2	10.9	92.2	7.8	93.1
5	33.9	95.1	13.2	90.5	10.3	91.7	7.4	92.6

Table 4. The recovery results and enrichment factors (ER) of the toxic metals with TT

Toxic metal	Spike / (mg L^{-1})	Initial volume / mL	Enrichment factor	Found / (mg L^{-1})	Recovery / %[a,b]
Hg(II)	1.0	50	10	(9.71 ± 0.17)	97.1
	0.5	100	20	(9.70 ± 0.17)	97.0
	0.2	250	50	(9.68 ± 0.17)	96.8
	0.1	500	100	(9.24 ± 0.16)	92.4
Sb(III)	1.0	50	10	(9.42 ± 0.21)	94.2
	0.5	100	20	(9.11 ± 0.21)	93.7
	0.2	250	50	(9.07 ± 0.20)	90.7
	0.1	500	100	(9.01 ± 0.20)	90.1
Cd(II)	1.0	50	10	(9.38 ± 0.11)	93.8
	0.5	100	20	(9.34 ± 0.10)	93.4
	0.2	250	50	(9.32 ± 0.10)	93.2
	0.1	500	100	(8.91 ± 0.10)	89.1
Pb(II)	1.0	50	10	(9.47 ± 0.13)	94.7
	0.5	100	20	(9.14 ± 0.13)	93.4
	0.2	250	50	(9.06 ± 0.12)	90.6
	0.1	500	100	(8.97 ± 0.12)	89.7

[a]Final volume: 5.0 mL. [b]n = 3.

Table 5. Analytical characteristic of the method

Element	Concentration range / (mg L^{-1})	Regression equation	R^2	LOD / (mg L^{-1})	LOQ / (mg L^{-1})	RSD / %	Relative uncertainty / %
Hg(II)	0.50-5.00	$y = 0.0115x + 0.0021$	0.9986	0.10	0.33	2.7	1.75
Sb(III)	0.50-5.00	$y = 0.0276x + 0.0011$	0.9966	0.15	0.45	3.2	2.26
Cd(II)	0.05-1.00	$y = 0.0084x + 0.0005$	0.9994	0.01	0.03	2.9	1.12
Pb(II)	0.50-5.00	$y = 0.0098x + 0.0009$	0.9991	0.12	0.36	2.8	1.37

R^2: correlation coefficient. LOD and LOQ: limits of detection and of quantification, respectively. RSD: relative standard deviation.

Table 6. Comparative data from some recent studies for adsorption of toxic metals by using TT system

System	Studied metal	pH	Adsorption capacity / (mg g^{-1})	PF	LOD / (mg L^{-1})	Reference
1	Cr(III), Cd(II), Hg(II), Pb(II)	5.0	5.9-2.2	500	–	38
2	Hg(II)	8.0	38.4	–	–	39
3	Hg(II)	4.0	54.7	–	–	40
4	Cr(III), Hg(II), Pb(II)	4.0	38.8-55.5	–	–	41
5	Hg(II), Sb(III), Cd(II), Pb(II)	5.0	35.5-9.5	50 (Hg, Cd), 20 (Sb, Pb)	0.10-0.12	this work

PF: preconcentration factor.

proposed method by using TT system has relatively high adsorption capacities and high pH values in comparison with other methods.

Conclusions

In this study, toxic metal ion binding properties of TT were investigated. Toxic metal ion adsorption capacity and adsorption time onto TT were found to be very suitable for the removal, recovery and preconcentration of the metal ions. The adsorption studies showed that pH, contact time and initial metal ion concentration are the basic parameters affecting the maximum metal uptake capacity of TT. The effects of pH, time and initial metal ion concentration were investigated. The optimum conditions obtained for studied toxic metal ions were: pH value = 5.0, contact time = 45 min for Hg(II) and 60 min for Sb(III), Cd(II), Pb(II), initial concentration = 500 mg L^{-1} for Hg(II) and 600 mg L^{-1} for other toxic metals in the adsorption experiments.

Adsorption-desorption cycle studies showed TT could be used five times due to the slight loss of their adsorption capacities. The desorption ratios were achieved up to 90% for all the toxic metals ions. The results indicate that the Langmuir equation fits well to the experimental data obtained for the sorption of metal ions onto TT. It also shows that the theoretical maximum adsorption capacities are nearly equal to the values which were found empirically. Moreover, the limits of detection, the quantification and relative uncertainty values demonstrate that TT shows a promising application potential for wastewater treatment.

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