



Biosorption of Pb(II) ions by modified quebracho tannin resin

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ABSTRACT

In this study, the effect of temperature, pH and initial metal concentration on Pb(II) biosorption on modified quebracho tannin resin (QTR) was investigated. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to investigate QTR structure and morphology. Besides, the specific BET surface area and zeta-potential of the QTR were analysed. Thermodynamic functions, the change of free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of Pb adsorption on modified tannin resin were calculated as $-5.43 \text{ kJ mol}^{-1}$ (at $296 \pm 2 \text{ K}$), $31.84 \text{ kJ mol}^{-1}$ and $0.127 \text{ J mmol}^{-1} \text{ K}^{-1}$, respectively, indicating the spontaneous, endothermic and the increased randomness nature of Pb^{2+} adsorption. The kinetic data was tested using pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion model. The results suggested that the pseudo-second-order model ($R^2 > 0.999$) was the best choice among all the kinetic models to describe the adsorption behavior of Pb(II) onto QTR. Langmuir, Freundlich and Tempkin adsorption models were used to represent the equilibrium data. The best interpretation for the experimental data was given by the Langmuir isotherm and the maximum adsorption capacity (86.207 mg g^{-1}) of Pb(II) was obtained at pH 5 and 296 K.

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1. Introduction

Heavy metal ions such as Pb, Cd, Hg, Cr, Ni, Zn and Cu are non-biodegradable, can be toxic and carcinogenic even at very low concentrations, and, hence, usually pose a serious threat to the environmental and public health [1]. Due to industrial activity and technological development, releases of Pb(II) metal ions to the environment are on the rise. They pose a significant threat to the environment and public health because of toxicity, incremental accumulation in the food chain and persistence in the ecosystem [2,3]. Lead is extremely toxic, which makes it a hazardous environmental pollutant [4]. This pollutant is introduced into natural waters by a variety of industrial wastewaters including those from battery, paper and pulp, mining, electroplating, lead smelting and metallurgical finishing, dyeing, storage-battery and automotive industries. It directly enters the water bodies through the effluent discharges and causes a marked increase in concentrations [5,6]. When accumulated at high levels, lead can generate serious health problems. Lead poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnant women [7,8].

Among the techniques employed for the treatment of heavy metals are chemical precipitation, adsorption, electrolytic methods, ion-exchange, solvent extraction, chemical oxidation or reduction,

filtration, membrane systems and reverse osmosis [9,10]. However, these methods require high capital investment as well as creating sludge disposal problem [11]. Most of the recent studies to remove heavy metals from aqueous solutions focus on the production of much more effective low-cost adsorbents through naturally occurring materials [12]. Many researchers suggest a cost effective process, such as biosorption, for removing heavy metals from wastewaters [13]. Biosorption, a biological method of environmental control can be an alternative to conventional waste-treatment facilities [10]. The concept of biosorption refers to the passive sorption and/or complexation of metal ions by biomass [14]. Mohanty et al. argue that a wide range of non-living biomass like bark, lignin, peanut hulls as well as living biomass like fungi, bacteria, yeast, moss, aquatic plants and algae has been used as biosorbents [15]. To remove some heavy metals there are other studies in which various waste biomaterial sources in different parts of the world are used as adsorbent. For instance; tea waste adsorbent (for Cu and Pb) [6], pectin compounds (for Pb) [2], lichen (*Cladonia furcata*) biomass (for Pb and Ni) [16], diethylenetriamine functionalized polymeric adsorbent (for Cu and Pb) [1], crab and arca shell biomass (for Cu and Pb) [17], olive stone waste (for Cu, Pb, Cd and Ni) [18], tamarind wood activated carbon (for Pb) [7], treated sawdust (*Acacia arabica*) (for Cr(VI), Cu and Pb) [19], anaerobic granular biomass (for Cu, Pb, Cd and Ni) [13], formaldehyde polymerized banana stem (for Pb) [5], *Cassia grandis* seed gum-graft-poly(methylmethacrylate) (for Pb) [8]. Several studies have been proposed in the literature about the use of modified tannin resins, in relation with heavy metal biosorption from water (Table 1). In the last decade, researches

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Table 1
Tannin biosorbents

Tannin biosorbents	Removed metals	Maximum adsorption, pH, T	Reference
Tannin sorbent (<i>Eucalyptus saligna</i>)	Cr(VI)	47.87 mg g ⁻¹ , pH 2	
Tannin sorbent (<i>Lysiloma latisiliqua</i>)	Cr(VI)	197.58 mg g ⁻¹ , pH 2	[20]
Condensed Mimosa tannin	Cr(VI)	287 mg g ⁻¹ , pH 2	[21]
Condensed Wattle tannin	Pb(II)	114.9 mg g ⁻¹ , pH 4.2	[22]
Condensed Wattle tannin	Au(III)	8000 mg g ⁻¹	[23]
Persimmon peel gel	Au(III)	NA	[24]
Bayberry tannin immobilized collagen fiber membrane	Pt(IV)	(Lang) 45.8 mg g ⁻¹ , pH 3	[25]
Bayberry tannin immobilized collagen fiber membrane	Pd(II)	(Lang) 33.4 mg g ⁻¹ , pH 4	[25]
Bayberry tannin immobilized on collagen fiber	Bi(III)	0.348 mmol g ⁻¹ , 303 K	[26]
Bayberry tannin immobilized collagen fiber membrane	UO ₂ ²⁺	56.8 mg U g ⁻¹	[27]
Black wattle tannin immobilized collagen fiber membrane	UO ₂ ²⁺	53.0 mg U g ⁻¹	[27]
Immobilized persimmon tannin	U	pH 6, <i>t</i> > 30 °C	[28]
Myrica rubra tannin immobilized onto collagen fibres	Th(IV)	73.67 mg g ⁻¹	[29]
Larch tannin immobilized onto collagen fibres	Th(IV)	18.19 mg g ⁻¹	[29]
<i>Lysiloma latisiliqua</i> tannin sorbent	Ce, Cu(II), U(VI), Eu, Fe(III), Th, Nd	E.g. Cu removal: 54.2% mg, pH 7	[30]
Pinus pinaster bark	Cd(II) and Hg(II)	pH ≥ 6	[31]
<i>Eucalyptus saligna</i> Sm sorbent	Hg	1.2 mmol g ⁻¹ , pH 7	[32]
<i>Lysiloma latisiliqua</i> sorbent (LTS)	Hg	8.5 mmol g ⁻¹ , pH 7	[32]
Persimmon Tannin gel	V (from VOCl ₂ solution) V (from NH ₄ VO ₃ solution)	0.832 mmol g ⁻¹ , pH 5–6 0.955 mmol g ⁻¹ , pH 3.75	[33]
Wattle tannin gel (TANNIX [®])	Am	1.7 mg Am g ⁻¹	[34]

NA, not available.

have synthesized adsorbent from commercial tannins using various methods. Then, they used them to remove various metals from wastewaters.

Tannins are high molecular weight polyphenols that can be found in different parts of plants and trees such as seeds, fruits, roots and barks. As tannins contain an abundant amount of adjacent hydroxyl groups in their molecules, they form chelates with metals. They are water soluble and must be immobilized when using them as sorbents [20]. Tannins are divided into two classes of polymers, the hydrolysable tannins and the condensed tannins [35]. Condensed tannins also known as polyflavonoids or proanthocyanidins comprise a group of polyhydroxyflavon-3-ol oligomers and polymers linked by carbon-carbon bonds between flavanol subunits [36]. Quebracho is a condensed tannin that has a polymeric structure containing the flavanoid units. Quebracho is mainly based on combinations of resorcinol, catechol and pyrogallol building blocks (Fig. 1) [37].

The objective of this research was to investigate the sorption capacity of modified quebracho tannin (QT) for the removal of Pb(II) ions from aqueous solution and to optimise the different experimental conditions, such as temperature, pH of solution, initial ion concentration and contact time.

2. Materials and methods

2.1. Preparation of modified quebracho tannin resin (QTR)

Raw tannin material was provided from Tuzla Org. Leather Ind. Zone, Turkey. The low-cost modified tannin resin was prepared

from commercial Quebracho tannin by chemical activation with formaldehyde for the adsorption of Pb(II) from aqueous solution. 20 g of tannin powder was gelled through polymerization with 40 mL of formaldehyde (37 wt%) as a cross-linking agent at room temperature and then it was stirred in alkaline solution which was prepared by adding 10 mL of 0.25 mol dm⁻³ NaOH. After gelation at 353 K for 8 h, the tannin resin obtained was crushed and sieved to produce 38–53 μm particles. They were washed successively with distilled water and HNO₃ (0.1 mol dm⁻³) solution to remove unreacted substances, and finally rinsed with distilled water again and dried at 378 K.

2.2. Physical and chemical characterization of the adsorbent

Characterization of the tannin resin was performed by scanning electron microscopy (SEM), infrared spectroscopy (IR) and by determination of the BET surface area and zeta potential.

2.2.1. Scanning electron microscopy

The SEM enables the direct observation of the changes in the surface structures of the resin. Morphological analysis of the QT and QTR was performed by SEM using a Jeol JSM-6060LV. As shown in Figs. 2 and 3, many small pores and particles with diameter <5 μm are seen on the surface of Raw QT and QTR. Studying the SEM images, it is possible to see that the loose nature of tannin condenses as it forms into a resin. In Fig. 4 the pores of QTR are completely covered with Pb ions.

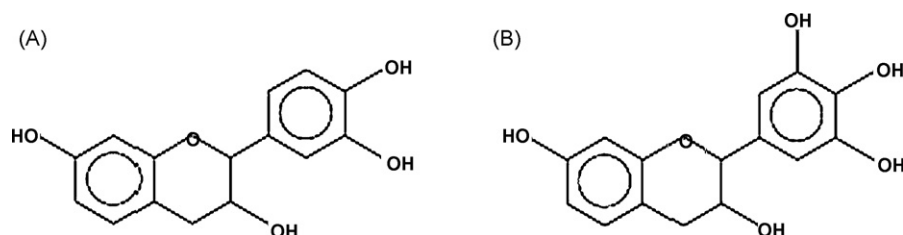


Fig. 1. Quebracho tannin (monoflavonoids and their oligomers).

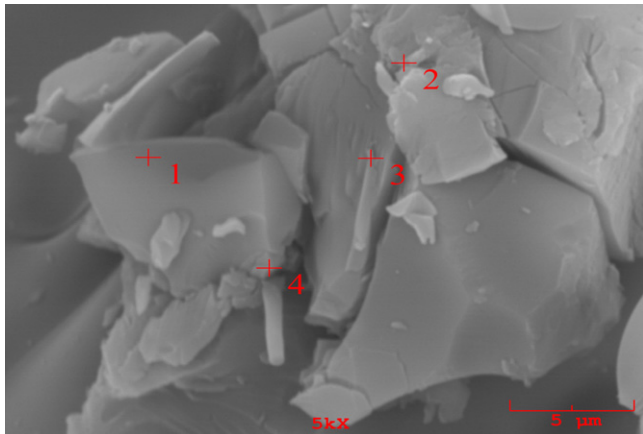


Fig. 2. SEM images of raw QT.

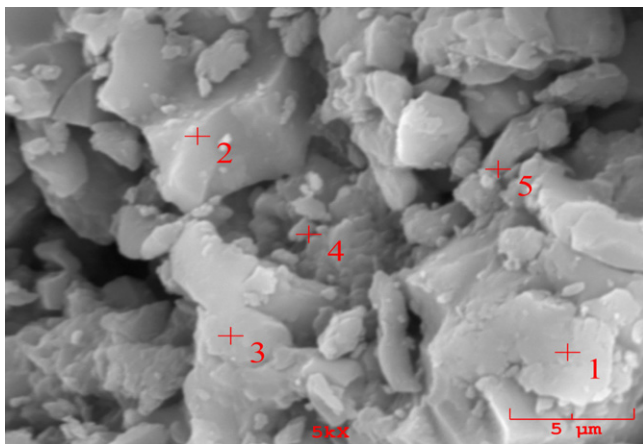


Fig. 3. SEM images of QTR (38–53 μm particles).

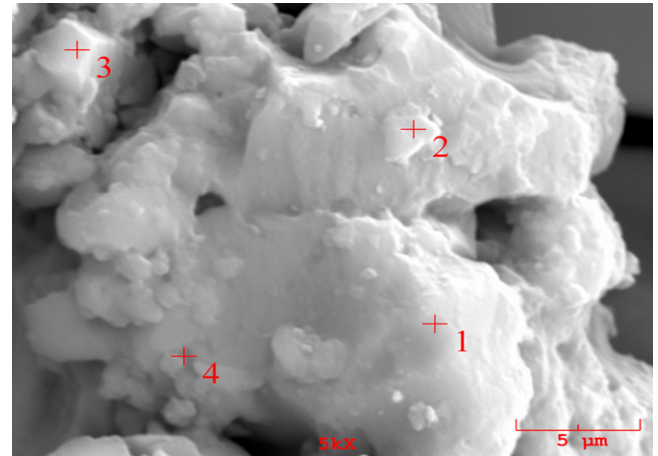


Fig. 4. SEM images of Pb adsorbed QTR at 366 ± 2 K (38–53 μm particles, $C_0 = 75 \text{ mg L}^{-1}$).

The wide peaks in the range of $3000\text{--}3600 \text{ cm}^{-1}$ show that phenolic --OH groups are intensively present within the nature of raw tannin. In QTR spectrum, this wide band has undergone some changes and broadened extensively. This suggests the existence of intense hydrogen bonds. Between 3000 and 3200 cm^{-1} aromatic C--H peaks have increased in QTR spectrum in contrast with the one for raw QT. On the contrary, between 2900 and 3000 cm^{-1} aliphatic C--H groups in QTR spectrum have decreased. The peaks, between 1600 and 1650 cm^{-1} indicate the aromatic C=C bonds. The peak around 1190 cm^{-1} is due to the presence of ether (C--O--C) groups.

2.2.3. BET surface area (m^2/g)

Surface area is related to the adsorption capacity of an adsorbent. The multipoint BET surface area analysis of QTR powder was performed with Quantachrome Autosorb Automated Gas Sorption System (Vers. 1.27). The analysis is carried out through an adsorption of N_2 gas (gas effluent temperature = 75°C versus bath temperature = 77.35°C). The measured BET specific surface area for QTR was $0.820 \text{ m}^2 \text{ g}^{-1}$.

2.2.4. Zeta potential

QTR zeta potential was measured with a Zeta Potential and Mobility Measurement System (MALVERN Nano ZS90). Fig. 6 shows that QTR isoelectric point occurs at pH 2.17, indicating that above this pH the surface will be negative charged due to the ionization

2.2.2. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to determine the vibration frequency changes in the functional groups in the resin. The spectra of resin were measured by an FTIR spectrometer within the range of $400\text{--}4000 \text{ cm}^{-1}$ wave number. The dry beads (about 0.1 g) was thoroughly mixed with KBr and pressed into a pellet and the FTIR spectrum of raw QT and QTR was then recorded (Fig. 5).

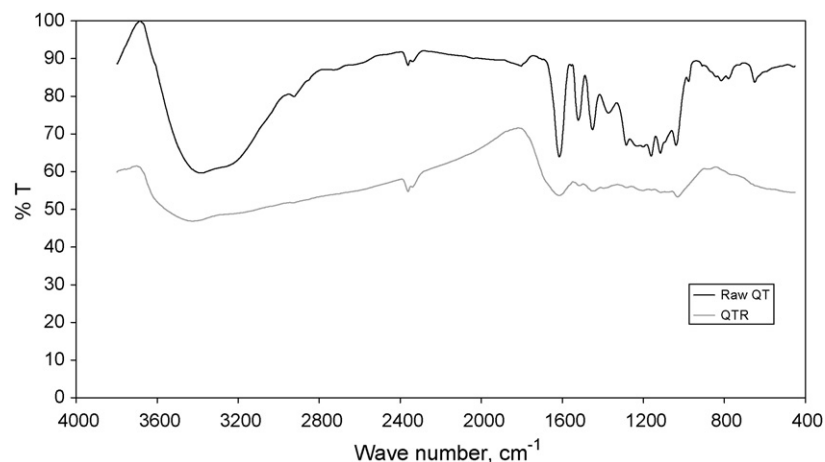


Fig. 5. FTIR spectra of the raw QT and QTR.

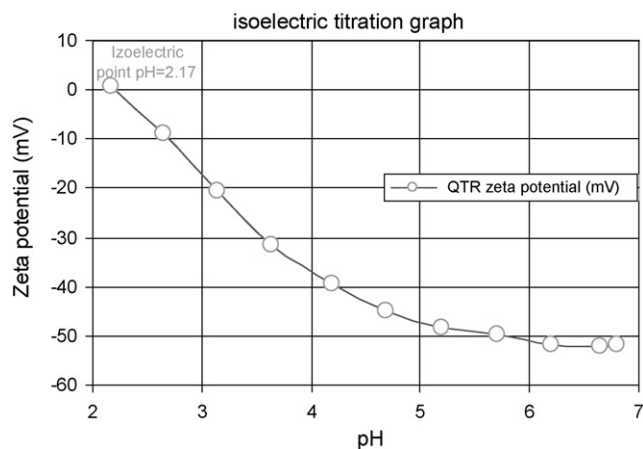


Fig. 6. Isoelectric titration graph of QTR.

of phenolic ($-\text{OH}$) groups. As the sorption process must be in electrostatic attraction basis, it is expected that Pb adsorption increases with pH 5–7.

2.3. Batch equilibrium studies

A series of batch experiments were conducted to study the Pb adsorption mechanism on the tannin resin, the adsorption isotherms and kinetics. All chemicals used in this work, were of analytical reagent grade and were used without further purification. The lead standard solutions employed in adsorption were produced by diluting a stock solution [$\text{Pb}(\text{NO}_3)_2$ in H_2O] of 1000 mg L^{-1} of the given element supplied by Merck & Co. Inc. (Darmstadt, Germany). The erlenmeyer flasks (1 L) were placed on a magnetic stirrer bath (H+P magnetic stirrer, Germany) and subjected to moderate agitation (350 rpm) for 180 min, which shows that the time period is rather adequate. Pb metal ions were analysed by an Atomic Absorption Spectrometry Instrument (Shimadzu AA6701F) in accordance with the standard methods for the examination of water and wastewater [38]. The adsorbed metal concentrations were obtained from the difference between initial and final metal concentration in water solution.

The amount of Pb ion adsorption onto QTR can be calculated by

$$q_e = \frac{C_i - C_e}{m} V$$

where q_e is the lead ion adsorbed onto the QTR (mg g^{-1}), C_i the initial metal ion concentration (mg L^{-1}), C_e the final metal ion concentration in the solution (mg L^{-1}), V is the volume of the solution (L) and m is the amount of QTR adsorbent (g) used.

The pH of solution was measured with a Hanna P211 micro-processor pH-meter using a combined glass electrode. The pH of the solution was adjusted to desired values with 0.1N HNO_3 and 0.1N NaOH . Adsorption studies were carried out at different temperatures (296, 306, 326, 346 and 366 K) in order to obtain thermodynamic parameters. Adsorption isotherms were studied by mixing a known amount of QTR (1 g) with various initial Pb(II) solution concentrations ranging from 10 to 150 mg L^{-1} at $296 \pm 2 \text{ K}$ and pH 5.0. In order to investigate the mechanism of adsorption, intraparticle diffusion, Elovich, the first-order and second-order kinetic models were used to test dynamical experimental data.

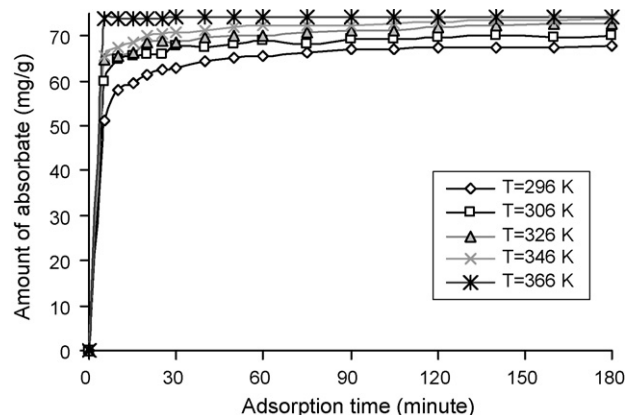


Fig. 7. Temperature influence on the Pb^{2+} uptake by QTR ($C_0 = 75 \text{ mg L}^{-1}$, particle size = $38\text{--}53 \text{ }\mu\text{m}$, pH 5 and adsorbent dose: 1 g L^{-1}).

3. Results and discussion

3.1. Sorption studies

The influence of agitation rate on the binding of lead by QTR was studied using 130, 250, 350, 450 and 800 rpm (revolutions per minute) stirring speeds. It was found that agitation rate has no influence on the values of lead uptake by QTR. The effect of contact time on Pb sorption on QTR was studied. Although Pb saturation is reached in the first 10 min, the time of contact in all batch experiments was fixed in 180 min.

3.1.1. Effect of temperature on the lead adsorption by QTR

Sorption studies were performed at five different temperatures (296, 306, 326, 346 and 366 (± 2) K). Results are shown in Fig. 7. The adsorption capacity of Pb increased with increasing T indicating that the endothermic nature of the sorption process.

3.1.2. Effect of initial pH on the lead adsorption by QTR

Fig. 8 shows the effect of pH on the Pb adsorption by QTR. Adsorption of Pb in QTR increased as pH increased due to the fact that dissociation of active groups on the QTR surface also increased with pH. The maximum lead uptake by QTR was at pH 5. Hence, initial pH was fixed at pH 5 in all sorption experiments.

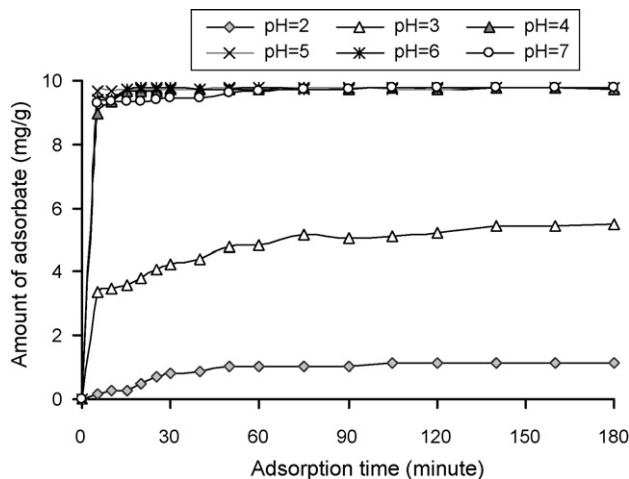


Fig. 8. pH influence on the Pb^{2+} uptake by QTR ($C_0 = 10 \text{ mg L}^{-1}$, particle size = $38\text{--}53 \text{ }\mu\text{m}$, $T = 296 \pm 2 \text{ K}$ and adsorbent dose: 1 g L^{-1}).

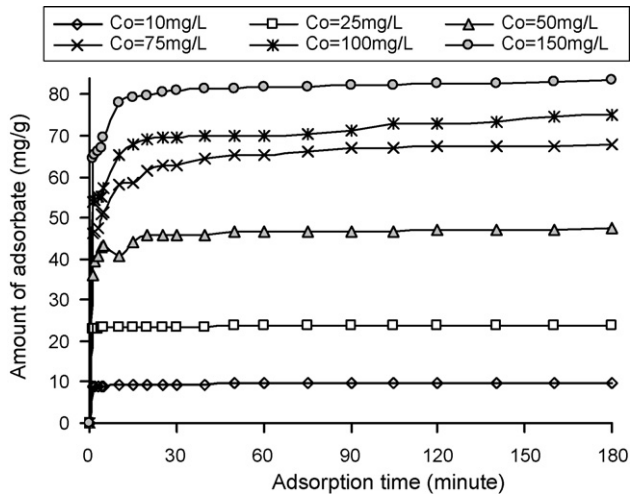


Fig. 9. Initial Pb^{2+} concentration influence on the Pb^{2+} uptake by QTR (pH 5.0, particle size = 38–53 μm , $T = 296 \pm 2$ K and adsorbent dose: 1 $g L^{-1}$).

3.1.3. Effect of initial Pb^{2+} concentration

The effect of lead concentration in the solution for six different concentrations of Pb (10, 25, 50, 75, 100 and 150 $mg L^{-1}$) on the adsorption is shown in Fig. 9. It can be seen from Fig. 9 that the percentage of Pb adsorption decreases when Pb initial concentration increases. Fig. 9 shows that the adsorption of Pb(II) increases with time from 0 to 10 min and then becomes almost constant up to the end of experiment. It can be concluded that the rate of lead binding to QTR is higher at initial stages, then gradually decreases and becomes almost constant after 10 min.

3.2. Application of adsorption isotherm models for lead adsorption by quebracho tannin resin

Adsorption isotherms are basic requirements for designing any sorption system. The distribution of metal ions between the liquid phase and the adsorbent is a measure of the position of equilibrium in the adsorption process and can generally be expressed by one or more of a series of isotherm models. Out of these isotherm equations, three have been applied for this study, the Langmuir, Freundlich and Tempkin isotherms, which are, respectively, reported in the following.

3.2.1. The Langmuir isotherm model

The Langmuir model [39] is described by the equation:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (1)$$

which may be written in linearized form as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (2)$$

where q_e is the equilibrium amount adsorbed ($mg g^{-1}$), C_e the equilibrium concentration of the adsorbate ($mg L^{-1}$). The empirical constants K_L and a_L for Langmuir model are related to the maximum capacity ($L g^{-1}$) and bonding strength ($L mg^{-1}$), respectively. The theoretical monolayer capacity is Q_0 and is numerically equal to K_L/a_L .

3.2.2. The Freundlich isotherm model

The Freundlich [40] model can be described by the following equation:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Table 2

Langmuir, Freundlich and Tempkin isotherm constants for the adsorption of lead(II) onto QTR (at 296 \pm 2 K, pH 5)

	Pb^{2+}
Langmuir isotherm	
a_L (L/mg)	0.372
K_L (L/g)	32.051
Q_0 ($mg g^{-1}$)	86.207
R^2	0.999
Freundlich isotherm	
K_F (L/g)	34.308
n	3.213
R^2	0.828
Tempkin isotherm	
B	14.743
A (L/g)	6.719
R^2	0.939

where q_e is the amount of metal ion adsorbed per unit weight and C_e is the equilibrium concentration of Pb^{2+} . K_F ($mg g^{-1}$) and n ($g L^{-1}$) are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. Eq. (3) can be linearized to the form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The slope of line expressed by Eq. (4) gives the value $1/n$ and intercept of the line gives the value $\log K_F$.

3.2.3. The Tempkin isotherm model

Tempkin and Pyzhev [41] considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Tempkin isotherm has been used in the following form:

$$q_e = \frac{RT}{b} (\ln A C_e) \quad (5)$$

Eq. (5) can be expressed in its linear form as

$$q_e = B \ln A + B \ln C_e \quad (6)$$

where

$$B = \frac{RT}{b}$$

The adsorption data can be analyzed according to Eq. (6). A plot of q_e versus $\ln C_e$ enables the determination of the constants A and B . The constant B is related to the heat of adsorption.

The outcome values of parameters a_L , K_L , Q_0 , K_F , n , B , A and R^2 for all the experiments for removal of Pb(II) are presented in Table 2. Results from Table 2 show that the maximum monolayer adsorption capacity (Q_0) is 86.207 $mg g^{-1}$. The Langmuir equation is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites. The results suggested that the Langmuir model was the best choice ($R^2 = 0.9991$) among the other isotherm models to describe the adsorption behavior of Pb(II) onto QTR.

3.3. Kinetics study of lead adsorption by quebracho tannin resin

Intra-particle diffusion model, Lagergren pseudo-first-order, pseudo-second-order and Elovich models were used to test the experimental data and thus explain the adsorption kinetic process.

The intraparticle diffusion model [42] can be described as

$$q_t = k_{int} t^{1/2} \quad (7)$$

Table 3
Kinetic parameters for the sorption of Pb²⁺ on QTR

Pb ²⁺ C ₀ (mg L ⁻¹)	q _e (mg g ⁻¹)	Intraparticle diffusion model		Pseudo-first-order kinetic model		Pseudo-second-order kinetic model		Elovich equation		
		k _{int} (mg/g dak ^{1/2})	R ²	k ₁ (1 min ⁻¹)	R ²	k ₂ (g/mg dak)	R ²	α (mg/g dak)	β (g min ⁻¹)	R ²
10	9.634	0.0553	0.714	0.0273	0.879	0.3249	1.0000	6.129E+23	6.3613	0.896
25	23.789	0.0554	0.898	0.0093	0.792	0.1729	1.0000	7.046E+67	6.9013	0.954
50	47.718	0.6466	0.668	0.0165	0.786	0.0225	0.9999	1.733E+09	0.5350	0.867
75	67.712	1.7029	0.786	0.0281	0.939	0.0083	0.9999	6.213E+04	0.2097	0.958
100	74.956	1.5965	0.768	0.0200	0.860	0.0068	0.9994	6.016E+05	0.2248	0.926
150	83.517	1.3925	0.666	0.0224	0.828	0.0130	1.0000	3.147E+07	0.2455	0.884

where k_{int} is the intraparticle diffusion rate constant and q_t is the amount dye adsorbed (mg g⁻¹) at time (t). Values of k_{int} (mg g⁻¹ h^{1/2}) were calculated from the slope of the linear plots of q_t versus $t^{1/2}$. In a liquid–solid system, the fractional uptake of the solute on particle varies according to a function of diffusivity within the particle and the particle radius.

Lagergren first-order equation [43] is the most popular kinetics equation and only for the rapid initial phase. The pseudo-first-order equation is given by

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

where q_t is the amount of adsorption time t (min) (mg g⁻¹); k_1 the rate constant of the equation (1/min); q_e is the amount of adsorption equilibrium (mg g⁻¹). The adsorption rate constant, k_1 , can be determined experimentally by plotting of $\ln(q_e - q_t)$ against t . This model was successfully applied to describe the kinetics of many adsorption systems.

The second-order model is more likely to predict the kinetic behavior of adsorption with chemical sorption being the rate-controlling step. This equation is in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where k_2 is the rate constant of the second-order equation (g/(mg min)); q_t the amount of adsorption time t (min) (mg g⁻¹); q_e is the amount of adsorption equilibrium (mg g⁻¹). The equilibrium adsorption capacity q_e and the pseudo-second-order rate constant k_2 can be experimentally determined. The slope and intercept of the linear plot t/q_t versus t yielded the values of q_e and k_2 .

The equation defining the Elovich model [44] is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. The linear form of Elovich equation is given by

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (10)$$

where α and β , known as the Elovich coefficients, represent the initial sorption rate (mg g⁻¹ min⁻¹) and the β is related to the extent of surface coverage and activation energy for chemisorption (g mg⁻¹), respectively. The Elovich coefficients could be computed from the plots of q_t versus $\ln t$.

The fitting of the above four models to experimental data was examined by each linear plot of q_t versus $t^{1/2}$, $\ln(q_e - q_t)$ versus t , (t/q_t) versus t , and q_t versus $\ln t$, respectively.

R^2 and several parameters obtained from kinetic models are shown in Table 3. The experimental data fitted well to the pseudo-second-order kinetic model with a high R^2 value (>0.999).

3.4. Thermodynamic studies

The standard free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) thermodynamic parameters have been estimated to evaluate the feasibility of the adsorption process. The

Table 4
Thermodynamic parameters for Pb²⁺ ions adsorption on QTR (C₀ = 75 mg L⁻¹, pH 5, 38–53 μm particles and 350 rpm agitation rate)

	Temperature, T (K)				
	296	306	326	346	366
K _c	9.29	13.88	30.40	57.23	118.90
ΔG° (kJ mol ⁻¹)	-5.43	-6.63	-9.17	-11.54	-14.42
ΔH° (kJ mol ⁻¹)	31.84				
ΔS° (J/mol K)	127.02				

positive value of change in enthalpy (ΔH°) indicates that the adsorption is an endothermic process, while positive value of change in entropy (ΔS°) reflects the increased randomness at the solid/solution interface.

The Gibbs free energy change of the process is related to the K_c by the following equation:

$$\Delta G^\circ = -RT \ln K_c$$

$$K_c = \frac{C_a}{C_e} \quad (11)$$

where K_c is the distribution coefficient for the adsorption, C_a the amount of adsorbate (mg) adsorbed on the adsorbent per liter of the solution at equilibrium and C_e is the equilibrium concentration (mg L⁻¹) of solution.

The thermodynamic parameters such as changes in standard free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were determined by using the following equations:

$$\ln K_c = \frac{\Delta S^\circ - \Delta H^\circ}{R} \frac{1}{T} \quad (12)$$

In order to determine thermodynamic parameters, batch experiments were carried out at different temperatures in the range of 296–366 K for Pb adsorption (Fig. 7).

The values of ΔH° and ΔS° are calculated from the slope and intercept of the plots of $\ln K_c$ versus $1/T$. Results are shown in Table 4. The Gibbs free energy change (ΔG°) negative values increased with temperature, indicating the feasibility and spontaneity of the adsorption process of Pb²⁺ ions on QTR. The positive ΔH° indicated the endothermic nature of the adsorption process and the positive ΔS° an increase in the randomness in the system interface solid/solution during the adsorption process.

4. Conclusions

In this work, chemically modified tannin resin as a sorbent has been proposed to be an efficient and economical alternative in Pb ion removal from water. The findings herein made us conclude that:

- (1) Batch sorption studies of lead ions showed that the QTR can be successfully used to remove Pb²⁺ ions from aqueous solution.
- (2) Langmuir model best describes the lead adsorption process and experimental data are better fitted to Langmuir isotherm

($R^2 > 0.999$). Using the Langmuir model equation, the monolayer adsorption capacity of QTR was found to be 86.207 mg g^{-1} for Pb(II) ions.

- (3) By applying the kinetic models to the experimental data, it was found that the kinetics Pb(II) ions adsorption onto QTR followed by the pseudo-second-order rate equation. Results of kinetic studies demonstrated that the Pb adsorption was rapid and efficient.
- (4) The thermodynamic parameters ΔG° , ΔH° and ΔS° determined, indicated a spontaneous endothermic and an increasing randomness sorption process.
- (5) The specific BET surface area of QTR was found to be $0.820 \text{ m}^2 \text{ g}^{-1}$. In comparing the surface area of QTR and activated carbon, it is seen that the QTR is smaller in size. The surface area of activated carbon ranges between 200 and $1500 \text{ m}^2 \text{ g}^{-1}$. Though the surface area of QTR is not large its adsorption capability to metal ions is high. This shows that functional groups in resin are more efficient than surface area in sorption process.

Given the obtained results, it is apparent that QTR can serve as an appropriate adsorbent in removal process of Pb ions from aqueous solution in terms of its high sorption capacity, naturality and abundance.

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