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ENHANCED Zn(II) AND Pb(II) REMOVAL FROM WASTEWATER USING THIOLATED CHITOSAN BEADS (ETB)

(Peningkatan Jerapan Zn(II) dan Pb(II) daripada Sisa Air dengan Manik Kitosan Tertiol)

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Abstract

Chitosan beads (E) was first prepared by phase inversion of chitosan acetate solutions. Thiolated chitosan beads (ETB) was synthesised by soaking E in a mixture of ethanol and carbon disulfide for 7 days and then rinsed thoroughly with water and ethanol. Sulfur content of ETB is 7.88 %. The thiolation process has increased the Brunauer-Emmett-Teller (BET) surface area of E beads from 39.5 m^2/g to 46.3 m^2/g. ETB is categorised as macroporous material (pore aperture: 182 nm) with multiple and uniform porous layers. A new shoulder at 1594 cm^{-1} was found in Fourier Transform infrared spectroscopy (FTIR) spectra of ETB, is assigned to thiourea moiety and was confirmed by X-ray photoelectron spectroscopy (XPS) spectra. The Pb(II) sorption capacity by ETB was higher than E beads at all sorbent dosage (except 5.0 g/L). At sorbent dosage of 5.0 g/L, sorption capacity of Zn(II) by ETB was enhanced by 3.2 times as compared to E beads. Sorption data fitted well to linearised Freundlich isotherm model and Ho's pseudo second order kinetic model. The higher K_F value of ETB than E indicated greater sorption capacity. The increase in Zn(II) and Pb(II) sorption capacities were attributed to enhanced chemisorption with thiol group in ETB beads.

Keywords: chitosan, heavy metal, thiourea, crosslink, chemisorption

Abstrak

Manik kitosan (E) terlebih dahulu disediakan dengan proses pembalikan fasa larutan kitosan dalam asid asetik. Manik kitosan tertiol (ETB) telah disintesis dengan merendam E ke dalam campuran etanol dan karbon disulfida selama 7 hari dan kemudian dibilas bersih dengan air dan etanol. Kandungan sulfur ETB adalah 7.88 %. Proses tiolasi telah meningkatkan luas permukaan Brunauer-Emmett-Teller (BET) basi manik E dari 39.5 m^2/g hingga ke 46.3 m^2/g. ETB dikategorikan sebagai bahan makropor (liang bukaan: 182 nm) dengan beberapa lapisan berliang yang seragam. Kehadiran kumpulan tiourea di dalam ETB ditunjukkan oleh satu bahu baru pada 1594 cm^{-1} di dalam spektrum Fourier Transform inframerah (FTIR), dan juga telah disahkan dengan analisis spektrum X-ray fotoelektron (XPS). Jerapan Pb(II) oleh manik ETB adalah lebih tinggi daripada manik E pada setiap dos bahan penjerap (kecuali pada 5.0 g/L). Pada dos 5.0 g/L, penjerapan Zn(II) oleh ETB telah dipertingkatkan sebanyak 3.2 kali berbanding dengan manik E. Data penjerapan dilengkapi dengan baik untuk model linear isoterma Freundlich dan model linear kinetik tertib pseudo dua Ho. Nilai K_F bagi ETB adalah lebih tinggi berbanding E, ini menunjukkan kapasiti jerapan ETB yang lebih besar berbanding E. Peningkatan kapasiti jerapan Zn(II) dan Pb (II) dikaitkan dengan peningkatan jerapan kimia dengan kumpulan tiol dalam manik ETB.

Kata kunci: kitosan, logam berat, tiourea, taut silang, jerapan kimia

Introduction

Chitosan has been used in wastewater treatment as coagulant and adsorbent for organic and inorganic pollutants [1]. The metal removal ability of chitosan is due to extensive network of C_2 amine groups (-NH_2) and C_6 hydroxyl groups (-OH) which works either by chemisorption or physisorption [2]. However, most toxic or precious trace metals with different chemical properties may have relatively weak interactions with unmodified chitosan. According to the Pearson Hard Soft Acid Base concept (HSAB), amine and hydroxyl groups which are hard Lewis bases may not form strong interaction with soft Lewis acids such as Pb(II). In order to enhance sorption selectivity for heavy metals, sulfur containing 'soft' functional groups such as dithiocarbamate (-HN-CS_2-) [3], xanthate (-O-CS_2-) [4] and thiourea (-HN-CS-NH-) [5] were chemically introduced to chitosan structure. By using thiolated porous chitosan beads, treatment of wastewater in a continuous flow reactor can be enhanced. Potential formation of disulfide or thioamide crosslinks improve stability of chitosan beads, thus minimising pore clogging and maintaining flow of wastewater during treatment. In this study, thiolated chitosan beads were synthesised and characterised to investigate their potential use as Zn(II) and Pb(II) sorbent for wastewater treatment.

Materials and Methods

Preparation and characterisation of ETB

Chitosan beads made by phase inversion of chitosan acetate solutions were neutralised and soaked in a mixture of ethanol and carbon disulfide for 7 days. All beads were rinsed thoroughly with ethanol and stored in distilled water. The pH_{ZPC} was determined by immersing and shaking 0.01 g of (Thiolated chitosan beads) ETB in 10mL of 0.01 M $NaNO_3$ with initial pH of 2 - 9 for 48 hours at 25 °C. The final solution pH was measured with a pH meter. The difference of final and initial pH (ΔpH) was calculate and plotted against initial pH (pH_o). The (pH_{ZPC}) was the intersection of x-axis [6]. Determination of cationic exchange capacity (CEC) began by dispersing 0.1g of ETB in 40mL of 0.02 M sodium acetate solution. The content was shaken for 83 hours, centrifuged and then decanted at room temperature. This step was again repeated twice with two aliquots of 40mL of isopropyl alcohol to eliminated excess $NaNO_3$. Finally, the Na(I) ions adsorbed on ETB were desorbed with two aliquots of 50 mL of 0.02 mM ammonium acetate to make 100mL using a volumetric flask. The Na(I) concentration was determined using inductively coupled plasma optical emission spectrometry (ICP-OES). The CEC value is represented by sodium ion concentration [7]. The sulfur content was determined using *LECO* sulfur elemental analyser and energy-dispersive X-ray spectroscopy (EDX). The surface and core morphology was studied using X-ray microtomography (CT) and scanning electron microscopy (SEM) while the Brunauer-Emmett-Teller (BET) surface area was determined using Micrometrics Gemini surface analyser. The FTIR spectra were obtained using Perkin Elmer Spectrum400.

Metal Sorption Study

The sorption pH and sorbent dosage of ETB was optimised prior to kinetics and isotherm studies. ETB at various sorbent dosages (0.2, 0.5, 1.0, 2.0 and 5.0g/L) were added to 30 mL of 1.0 mM Zn(II) and Pb(II) nitrate solution and were shaken using the end/end shaker for 5000 minutes. The optimum sorption pH was determined between pH 3 and 7 at constant ETB dosage of 2.0 g/L. Time based sorption experiment was conducted at ETB dosage of 2.0 g/L, using 1.0 mM of Zn(II) and Pb(II) nitrate solution at pH 5.4 and 4.4 respectively. The sorption isotherms experiments were conducted at a fixed ETB dosage (2.0 g/L) from 0.02 to 1.0 mM of initial metal concentration. The equilibrium concentration of Zn(II) and Pb(II) were analysed using ICP-OES. Metal sorption data were analysed using Microsoft Office Excel 2007.

Kinetics and Isotherm Analysis

Metal sorption kinetics was analysed using linearised pseudo first order model and linearised pseudo second order model. The pseudo-first-order kinetic equation or the Lagergren equation is given as Equation 1 [8].

$$\frac{dq}{dt} = k_1\left(q_e - q\right) \tag{Eq. 1}$$

The linearised form of the pseudo first-order rate equation is shown in Equation 2.

$$\log\left(q_e - q\right) = \log q_e - \frac{k_1 t}{2.303} \qquad \text{(Eq. 2)}$$

where q_e (mg/g) and q (mg/L) is the amount of the metal ions adsorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the equation (min^{-1}). The pseudo second order of Lagergren rate equation can be expressed as Equation 3 [9].

$$\frac{dq}{dt} = k_2\left(q_e - q\right)^2 \qquad \text{(Eq. 3)}$$

The integrated linear form of Equation 3 can be represented as Equation 4.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \qquad \text{(Eq. 4)}$$

where, k_2 (g/mg min) is the rate constant of the second-order equation, q_t (mg/g) is the amount of sorption time t (min) and q_e is the amount of sorption equilibrium (mg/g).

The Langmuir isotherms assume that adsorption takes place at specific homogeneous sites within the adsorbents. The Langmuir isotherm equation is represented as Equation 5 [10].

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \qquad \text{(Eq. 5)}$$

Linearised form of Langmuir equation is shown as Equation 6.

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{\max}}\right)\frac{1}{C_e} + \frac{1}{q_{\max}} \qquad \text{(Eq. 6)}$$

where, q_e is the equilibrium concentration of metal cations on the sorbent (mg/g); C_e is the equilibrium concentration of trace metal in the solution (mg/L), $q_{\max}$ is the maximum monolayer sorption capacity of the adsorbent (mg/g) and K_L is the Langmuir sorption constant (L/mg) which reflects the affinity of metal adsorbate to sorbent. The $q_{\max}$ values were calculated from the intercept of the $1/q_e$ versus $1/C_e$ plot. The K_L value was obtained from subsequent substitution of $q_{\max}$ to the slope ($1/K_L q_{\max}$).

The degree of suitability of ETB for trace metals will be estimated with separation factor constant (R_L) calculated using Equation 7.

$$R_L = \frac{1}{1 + K_L C_o} \qquad \text{(Eq. 7)}$$

where K_L is the Langmuir sorption constant and C_o is the initial concentration (mg/L) of trace metals. The Freundlich isotherm is an empirical equation employed to describe heterogeneous absorption system. The Freundlich equation is given as Equation 8 [11].

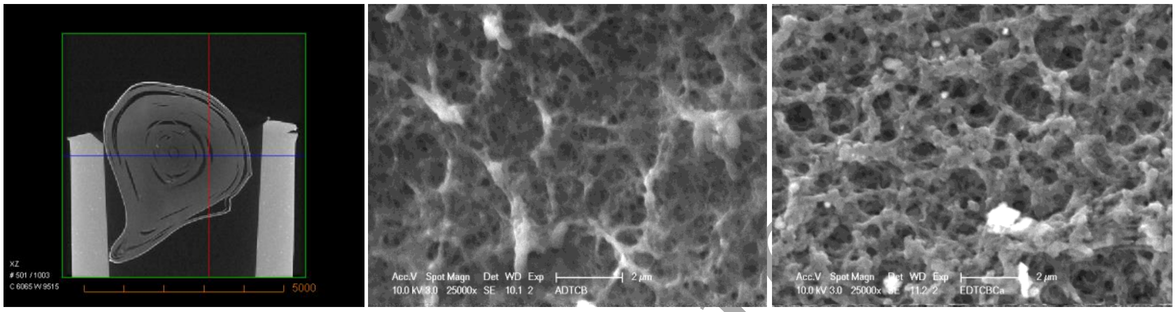
$$q_e = K_F C_e^{1/n} \qquad \text{(Eq. 8)}$$

The logarithmic form of the equation is given as Equation 9.

$$\ln q_e = \frac{1}{n}(\ln C_e) + \ln K_F \qquad \text{(Eq. 9)}$$

where, q_e is the sorption capacity of metal per unit weight of adsorbents (mg/g), C_e is the equilibrium concentration of metal ions in solution (mg/L), K_F is the Freundlich constants denoting sorption capacity (mg/g) and n is the empirical constant, indicating of sorption intensity (L/mg). The n parameter could be calculated from the reciprocal of slope of ln q_e versus ln C_e plot. The K_F value can be obtained from the intercept ln K_F.

Results and Discussion



(i) **(ii)** **(iii)**

Figure 1. CT image **(i),** surface SEM **(ii)** and cross-sectioned SEM **(iii)** micrographs of ETB bead

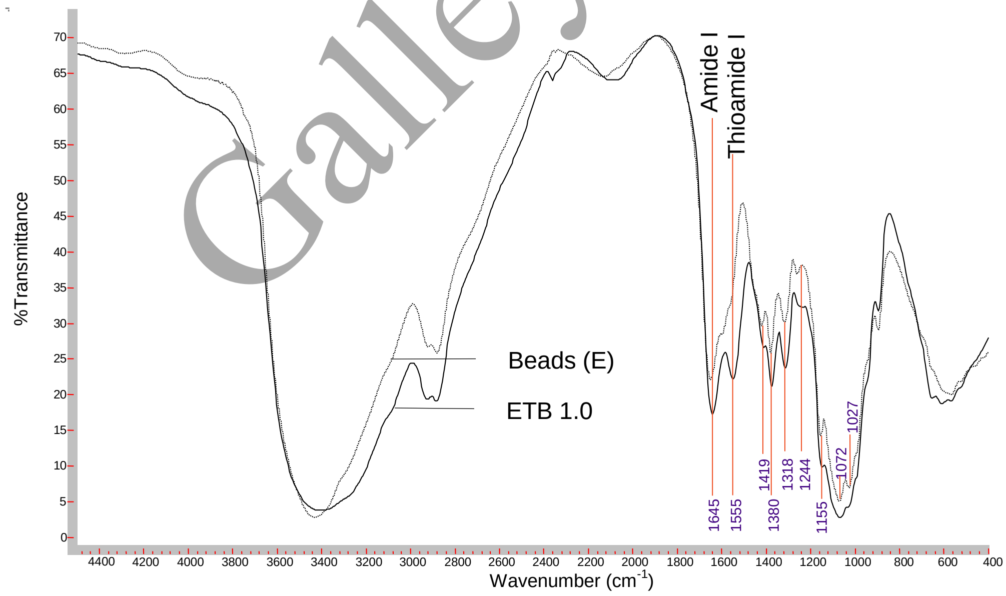
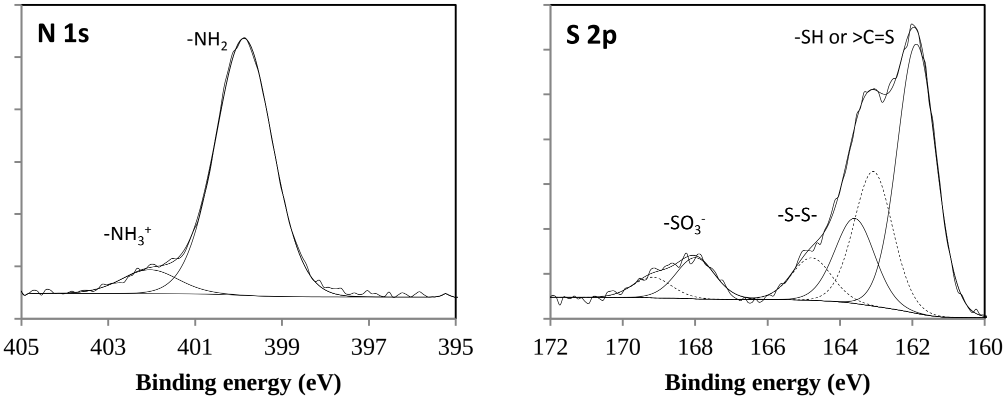


Figure 2. FTIR spectra of chitosan beads (E) (dotted), ETB (solid)

Characterisation of ETB

The thiolation process on beads E has increased the BET surface area from 39.5 to 46.3 m^2/g. The mean pore aperture of ETB was 182 nm, which is categorised as macroporous material. The internal structure of ETB consisted of multiple porous layers with most cavities located near the surface of the bead. The surface and core pore structure of ETB were also similar (Figure 1). The surface charge of ETB is more negative as compared to beads E. The pH of point of zero charge (pH_{ZPC}) of ETB is 6.3, slightly lower than beads E (6.5). The cationic exchange capacity (CEC) of ETB is 20.2 cmol/kg. The sulfur content of ETB determined by *LECO* analyser was 7.88 % which is similar to EDX sulfur (6.8 and 7.0 %). Analysis of FTIR spectra of ETB found a new peak at 1555 cm^{-1}, which is assigned to interaction of C=S stretching with C-N stretching vibrations of thiourea moiety (Figure 2) [5]. The presence of sulfur was confirmed by XPS spectra where a peak was detected at 163 eV (Figure 3).



(i) **(ii)**

Figure 3. Core level (**(i)** N 1s and **(ii)** S 2p) XPS spectra of ETB

Effects of pH and ETB dosage

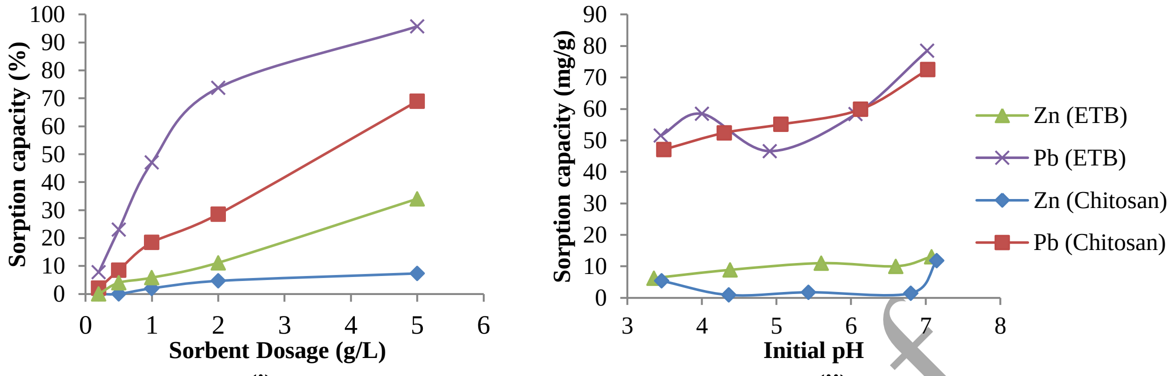
The metal sorption capacities by beads E and ETB at various sorbent dosages were shown in Figure 4 (i). Both Zn(II) and Pb(II) sorption capacities by ETB were clearly greater than beads E. This improvement in metal sorption capacities is more profound at high sorbent dosage (1.0 to 5.0 g/L). As the inflection point were not reached, Zn(II) sorption capacity by ETB and Pb(II) sorption capacity by beads E were unable to be determined. The optimal sorbent dosage for Zn(II) sorption capacity by chitosan beads is 1.0 g/L while Pb(II) sorption capacity by ETB is optimum at 2.0 g/L.

In general, low pH (< 3.5) of initial metal solution caused lower metal sorption capacity by ETB (Figure 4(ii)). Metal sorption capacities by ETB sorbent increased slightly with higher pH value. For example, Zn(II) and Pb(II) sorption capacities by ETB have increased at around pH 7. This may be due to partial precipitation into metal hydroxides. Even though metal sorption capacities by ETB were marginally higher than beads E, the acid stability of ETB were far greater than beads E. Introduction of thiocarbamoyl crosslinks to ETB structure enhanced its resistance to acid attack. As compared to ETB, beads E were completely dissolved at pH < 3.

Effects of contact time

Rapid metal sorption capacity was observed from the beginning until equilibrium. The Zn(II) and Pb(II) sorption equilibrium for ETB were achieved at 500 and 1000th minute respectively, where the equilibrium Zn(II) and Pb(II) sorption capacities were 4.9 and 85 mg/g respectively (Figure 5). The sorption kinetics of ETB is shown in Table 1. The kinetic data for Zn(II) and Pb(II) sorption by ETB fitted well with linearised pseudo second order model with correlation coefficient of 0.997 and 0.999 respectively. The corresponding q_e values for beads E were 6.42 and 38.6

mg/g for Zn(II) and Pb(II), while the q_e for ETB were 4.95 and 87.0 mg/g for Zn(II) and Pb(II) respectively. These q_e values were close to the value determined experimentally.



(i) **(ii)**

Figure 4. Zn(II) and Pb(II) sorption capacity (% and mg/g) by chitosan beads (E) and ETB as a function of **(i)** sorbent dosage (g/L), and **(ii)** initial pH

Table 1. Kinetic parameters for sorption of Zn(II) and Pb(II) by ETB

		Kinetic parameters					
Metal	**Sorbent**	**Pseudo first order**			**Pseudo second order**		
		q_e (mg/g)	**k_1 ($\times 10^{-3}$ min^{-1})**	**R^2**	**q_e (mg/g)**	**k_2 ($\times 10^{-3}$ g/mg min)**	**R^2**
Zn(II)	ETB	1.38	3.46	0.526	4.95	4.58	0.997
Pb(II)	ETB	10.7	0.691	0.598	87.0	1.78	0.999
Zn(II)	E	2.93	0.691	0.195	6.42	4.56	0.989
Pb(II)	E	15.1	0.691	0.598	38.6	0.82	0.996

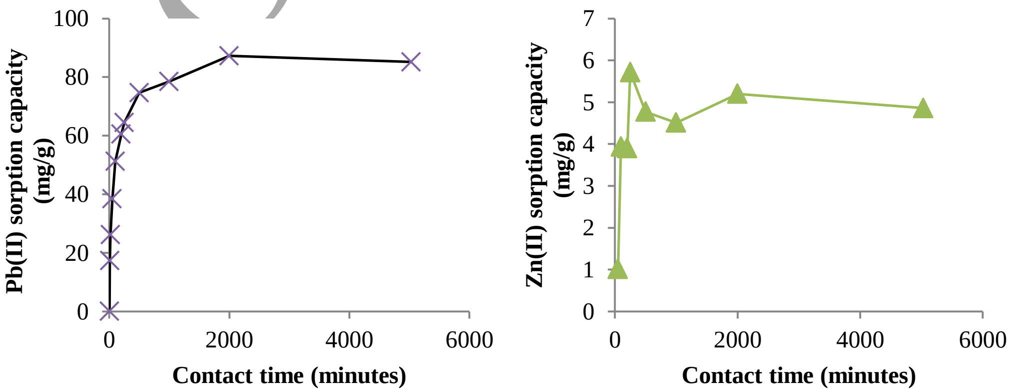
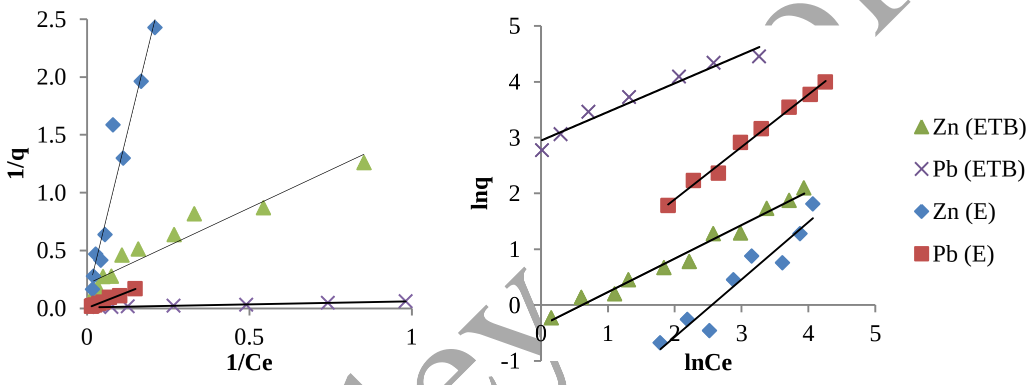


Figure 5. Metal sorption capacity of Zn(II) and Pb(II) (mg/g) by ETB as a function of contact time (minutes) at sorbent dosage 2.0 g/L

Sorption isotherms

The isotherm parameters of ETB were shown in Table 2. In general, Zn(II) and Pb(II) sorption of ETB beads fitted well to both linearised Langmuir and Freundlich model; while beads E fitted well with only Freundlich model (Figure 6). The isotherm parameters of linearised Freundlich model (e.g. n and K_F) describe the sorption intensity and capacity, respectively [12]. The n values for Zn(II) and Pb(II) sorption of beads E were 0.97 and 1.06, respectively. All n values of ETB were greater than 1. This indicates that both Zn(II) and Pb(II) sorption capacities by ETB is more favourable than beads E. Compared to beads E, ETB also has significantly higher K_F values for all metal sorption which again shows greater sorption capacity of ETB than beads E [13].

The q_{max} for Zn(II) sorption by ETB was 4.74 mg/g, lower than Zn(II) sorption capacity of beads E (q_e = 10.9 mg/g). However, the q_{max} for Pb(II) sorption by ETB beads was increased to 110 mg/g. The K_L values for Zn(II) and Pb(II) sorption by ETB were 0.161 and 0.174 respectively. The corresponding R_L value shown in Table 3 was calculated based on the initial metal concentration from 0.02 to 1.0 mM. All R_L values were between 0 and 1, indicating that Zn(II) and Pb(II) sorption with ETB beads were favourable [14].



(i) **(ii)**

Figure 6. Linearised (**i**) Langmuir and (**ii**) Freundlich model plots for Zn(II) and Pb(II) sorption (mg/g) by ETB

Table 2. Isotherm parameters for sorption of Zn(II) and Pb(II) sorption by ETB and E

Metal	**Sorbent**	**Isotherm parameters**					
		Langmuir			**Freundlich**		
		q_{max} **(mg/g)**	K_L **(L/mg)**	R^2	n **(L/mg)**	K_F **(mg/g)**	R^2
Zn(II)	ETB	4.74	0.161	0.93	1.67	0.69	0.98
Pb(II)	ETB	110	0.174	0.99	1.95	19.1	0.96
Zn(II)	E	10.9	0.008	0.88	0.97	0.07	0.91
Pb(II)	E	323	0.003	0.87	1.06	1.01	0.99

Sorption mechanism

The q_{max} Zn(II) ions of ETB were slightly lower than beads E. Zn(II) ions was considered borderline Lewis acid which can bound to either hard Lewis base (hydroxyl or amine groups) or soft Lewis base (thiol or thione groups) [15]. The decrease in q_{max} of Zn(II) sorption by ETB may have been caused by the lower quantity of amine groups after thiocarbamoylation of chitosan. Two amine groups are consumed for every formation of one thione group.

However, Zn(II) sorption capacity of ETB is slightly higher than beads E at pH < 7. Improvement in q_{max} value was observed on Pb(II) sorption. This is probably caused by greater chemisorption between soft Lewis acids of Pb(II) ions with soft Lewis base of thiol group in ETB [16]. The thiourea functional group in ETB forms tautomeric thiol groups [17]. The pH value at equilibrium were decreased by around 0.5, showing that proton was liberated when Zn(II) or Pb(II) were coordinated to thiol groups [18]. Conversely for beads E, equilibrium pH was higher upon metal sorption capacity. This can be explained by immobilisation of solution proton by amine groups [19]. Amine ($-NH_2$) accepts a proton (H^+) to form protonated amine ($-NH_3^+$). This is quite acceptable given that amine is a hard Lewis base and proton is a hard Lewis acid.

Table 3. Isotherm parameters for Zn(II) and Pb(II) sorption by ETB

Initial metal concentration (mM)	R_L	
	Zn(II)	**Pb(II)**
0.02	0.824	0.730
0.04	0.701	0.575
0.06	0.610	0.474
0.08	0.540	0.404
0.10	0.484	0.351
0.15	0.385	0.265
0.20	0.319	0.213
0.30	0.238	0.153
0.40	0.190	0.119
0.60	0.135	0.083
0.80	0.105	0.063
1.00	0.086	0.051

Conclusion

ETB beads with thiourea functionalised crosslinks were introduced with a sulfur content of 7.88 %. Compared to beads E, ETB possessed greater stability in acidic solution as well as enhanced metal sorption capacity. Pb(II) sorption capacity by ETB was improved by 1.8 times at sorbent dosage of 1.0 g/L. Zn(II) sorption capacity was improve by 3.2 times at dosage of 5.0 g/L compared to beads E. Greater metal sorption capacity by ETB is attributed to the chemisorption of functional thiol groups.

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