

Recycling of styrofoam waste: synthesis, characterization and application of novel phenyl thiosemicarbazone surface

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An attempt has been made to recycle Styrofoam waste to a novel functional polymer, Phenyl thiosemicarbazone surface (PTS). Polystyrene (PS) obtained from Styrofoam waste was acetylated and then condensed to PTS by reacting it with 4-Phenyl-3-thiosemicarbazide ligand and characterized by FT-IR spectroscopy and elemental analysis. Synthesized PTS was applied successfully for the treatment of lead contaminated water by batch extraction method. Sorption variables were optimized (pH 8, adsorbent dose 53mg, initial Pb(II) ion concentration 10mg l⁻¹ and agitation time 90min) by factorial design approach. Lead uptake by PTS was found much sensitive to the pH of Pb(II) ion solution. The maximum removal (99.61%) of Pb(II) ions was achieved at optimum conditions. The Langmuir and D-R isotherm study suggested the monolayer, favorable (RL=0.0001-0.01) and chemisorption (E=20.41±0.12kJmol⁻¹) nature of the adsorption process. The sorption capacity of PTS was found to be 45.25±0.69mgg⁻¹. The FT-IR spectroscopy study showed the involvement of nitrogen and sulphur of thiosemicarbazone moiety of PTS for the uptake of Pb(II) ions by five membered chelate formation.

Keywords: Recycling, Styrofoam, Functional polymer, Pb(II) ion removal, Phenyl thiosemicarbazone surface, Factorial Design Approach.

INTRODUCTION

Styrofoam is a trade name of expanded polystyrene (EPS) composed of about 5% polystyrene (PS) and 95% air. Styrofoam is generally used as an insulator and packaging material for household electrical appliances¹. Styrofoam waste (white pollutant) with the characteristics of stable chemical properties, large volume, aging resistance, corrosion resistance, non-degradable nature is recognized as a worldwide environmental threat and waste management problem^{2,3}. It is generally disposed in landfill which becomes environmental risk because of its large volume and chemical inertness⁴. Several attempts have been made to recycle Styrofoam waste by different recycling methods but unfortunately all methods have drawbacks of cost and quality in addition to the environmental threat as well⁵. Therefore, great attention has been paid to chemical recycling of Styrofoam waste to different useful materials, especially by sulfonation⁶⁻¹⁴. In the present study, we focused on a novel route for polar functionalization of PS to the novel Phenyl thiosemicarbazone Surface (PTS) by acetylation of PS (obtained from Styrofoam waste) then condensed with 4-Phenyl-3-thiosemicarbazide ligand. PTS is applied for the treatment of lead contaminated water. Lead uptake is optimized by Response Surface Methodology (RSM).

MATERIALS AND METHODS

Adsorbent: synthesis of phenyl thiosemicarbazone surface (PTS)

Figure 1 shows the reaction scheme for the conversion of PS into PTS. EPS (A) was collected from Sindh University, Jamshoro, Pakistan. 3.0g of pre-cleaned waste material, EPS was dissolved into 100ml of carbon tetrachloride then filtered off to remove insoluble impurities. The filtrate was transferred into a 500ml round bottom

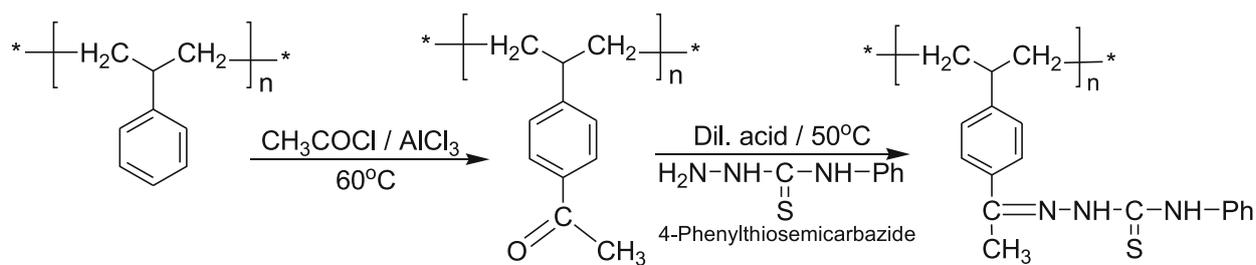
flask containing 3.4g of anhydrous aluminum chloride and 1.9ml of acetyl chloride was added drop wise with a continuous magnetic stirring. The reaction mixture was refluxed at 60°C for 50min. The reaction mixture was kept at room temperature to work up with 0.05N HCl. The product was filtered off and then washed with 1.0N sodium bicarbonate solution to remove the excess of acid. Finally, acetyl-PS (B) was washed thoroughly with de-ionized water and air-dried. 3.0g of acetyl-PS (B) was placed into the 250ml round bottomed flask containing 50ml of ethanol and 8–10ml of acetic acid. The reaction mixture was heated at 50°C for 30min and 100ml of 4-phenyl-3-thiosemicarbazide solution (4% w/v in methanol) was added drop wise with a continuous magnetic stirring and refluxed for 40min at 50°C. The final thiosemicarbazone product (C) was filtered, washed and air-dried.

Sorbate: Pb(II) ion solution

A stock solution of Pb(II) ion was prepared (1000mg l⁻¹) by dissolving an appropriate amount of Pb(NO₃)₂ (Merck) in de-ionized water. The stock solution was diluted with de-ionized water to obtain the working solutions (5–50mg l⁻¹). The initial pH of the solutions was maintained at 2.0, 5.5 and 9.0 with 1.0N HCl, acetate buffer, and 0.5N NaOH, respectively. CH₃COOH, CH₃COONa, NaOH and HCl were taken from Merck (Darmstadt, Germany).

Batch sorption experiments

All sorption experiments were performed in a thermostated shaker at controlled temperature of 30°C with the shaking speed 100rpm for a period of 10-180min, using the 250ml conical flasks containing 10ml Pb(II) ion solutions (5–50mg l⁻¹) of different pH 2–9 and the weighted amount (10–100mg) of PTS. The residual concentration of Pb(II) ion was determined with the Perkin Elmer Atomic Absorption Spectrophotometer. The percent removal of Pb(II) ions was calculated by eq. 1.



A. Styrofoam (polystyrene)

B. Acetylated Styrofoam (polystyrene)

C. PTS

Figure 1. Scheme for the synthesis of Phenyl thiosemicarbazone Surface (PTS) from EPS waste

$$\% \text{Removal} = \frac{C_i - C_e}{C_i} \cdot 100 \quad (1)$$

Where C_i and C_e are the initial and equilibrium concentrations (mg l^{-1}) of Pb(II) ion solutions, respectively.

Experimental Design

RSM is an experimental technique designed to find the optimum response of independent variables. Central Composite Design (CCD) was selected to study the effect of adsorbent dose (A, mg), pH of Pb(II) ion solution (B), initial Pb(II) ion concentration (C, mg l^{-1}) and agitation time (D, min) on percent removal of Pb(II) ions. Each variable was studied at three different levels (low, medium and high, coded as -1, 0 and +, respectively) as shown in Table 1. The design consisted of eighteen runs, each run was performed twice to find the mean value for CCD analysis. The design of experiments was statistically analyzed by Stat Graphics plus for Windows 5.1 (Stat Point Technologies Inc. 2009)¹⁵.

Table 1. Variable ranges used in experimental design for removal of Pb(II) ions by PTS

Independent variable	Coded levels		
	-1	0	+1
Amount (mg), A (x_1)	10	55	100
Concentration (mg l^{-1}), B (x_2)	5	27.5	50
pH, C (x_3)	2	5.5	9
Time (min), D (x_4)	10	95	180

Table 2. Experimental design and results for %removal of Pb(II) ions by PTS

Trail	Coded values				% Removal (Experimental)	% Removal (Predicted)
	A	B	C	D		
1	-1	-1	+1	-1	88.86	89.07
2	-1	-1	-1	-1	19.87	19.50
3	0	+1	0	0	98.43	98.77
4	+1	+1	-1	-1	06.87	06.50
5	+1	+1	+1	-1	96.12	96.32
6	0	0	0	-1	96.79	97.12
7	-1	+1	+1	+1	89.68	89.88
8	+1	0	0	0	96.04	96.38
9	0	0	+1	0	90.78	89.98
10	+1	-1	+1	+1	77.30	77.50
11	0	0	-1	0	25.54	27.02
12	+1	-1	-1	+1	56.92	56.55
13	-1	+1	-1	+1	18.78	18.40
14	0	-1	0	0	90.34	90.68
15	-1	0	0	0	95.98	96.32
16	0	0	0	+1	93.39	93.73
17	0	0	0	0	97.87	96.09
18	0	0	0	0	96.34	96.09

RESULTS AND DISCUSSION

Characterization

In order to confirm the formation of acetyl-PS and PTS, Infrared spectra of starting material PS, acetyl-PS and PTS were recorded using Thermo Nicolet FT-IR spectrometer containing diamond accessory.

Fig. 2(a-b) shows the FT-IR spectra of plain PS (a) and acetyl-PS (b). By comparing the FT-IR spectra (a-b), the appearance of additional peaks in spectrum-b at 1707.6cm^{-1} , 1356.19cm^{-1} and 1217.25cm^{-1} for C=O stretching, C-H bending and C-O stretching, respectively, supported the formation acetyl-PS. Fig. 3 (a-b) shows the FT-IR spectra of acetyl-PS (a) and PTS (b). By comparing the FT-IR spectra (a-b), the disappearance of peak at 1707.6cm^{-1} for C=O stretching and an appearance of corresponding peaks for stretching of N-H, C=N, C=S and C-N at 3301.25cm^{-1} , 1634.05cm^{-1} , 1282.63cm^{-1} and 1061.97cm^{-1} , respectively, supported a successful formation of PTS by condensation of acetyl-PS with 4-phenyl-3-thiosemicarbazide ligand.

Both acetyl-PS and PTS were also analyzed by elemental analysis. Acetyl-PS resulted as C, 82.43; H, 7.57.64; O, 10.01% and the theoretically calculated values for $\text{C}_{11}\text{H}_{12}\text{O}$ are C, 82.46; H, 7.55; O, 9.99%. The elemental analysis data confirmed the successful formation of acetyl-PS.

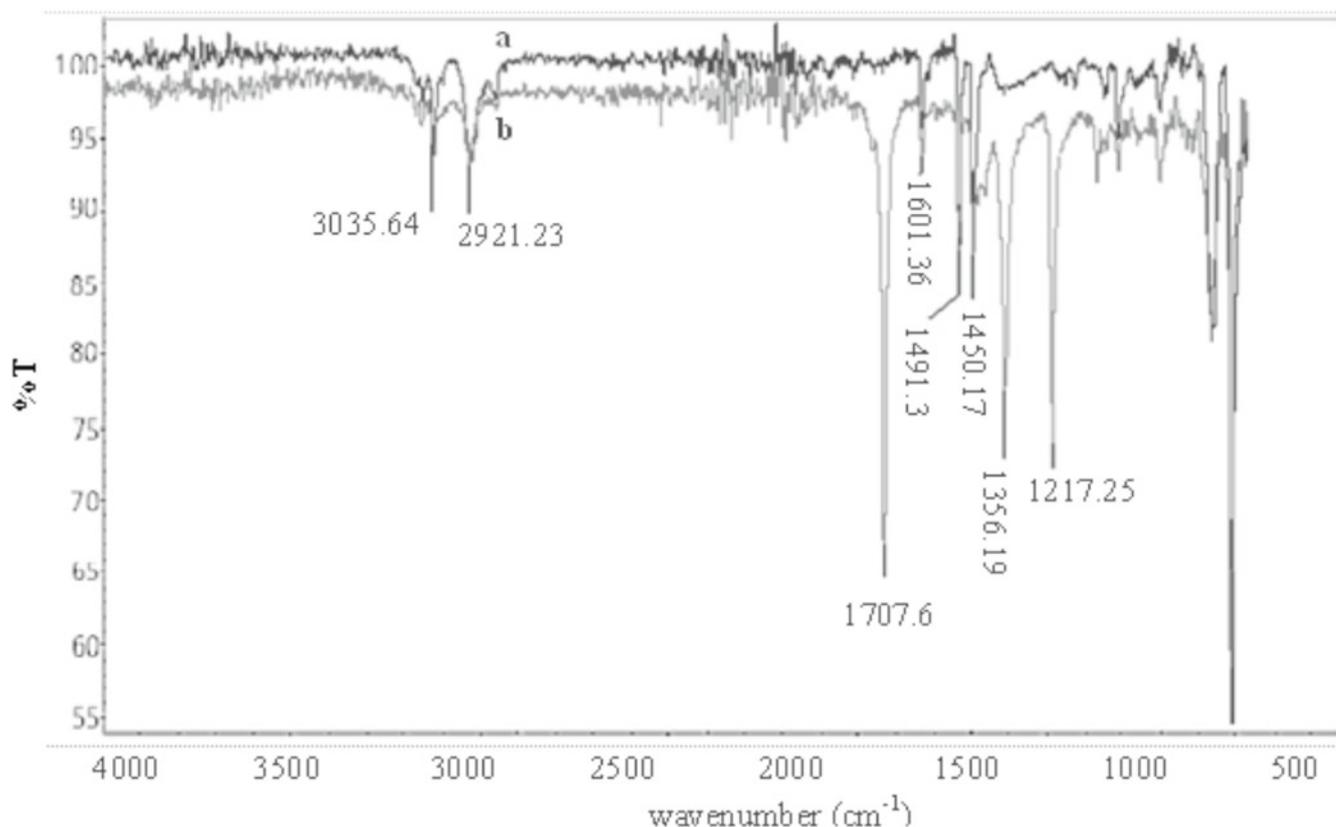


Figure 2. FT-IR Spectra of PS (a) and acetyl-PS (b)

The elemental analysis of PTS resulted as C, 69.88; H, 6.20; N, 13.57; S, 10.37% and the theoretically calculated values for $C_{18}H_{19}N_3S$ are C, 69.87; H, 6.19; N, 13.58; S, 10.36%, confirmed the successful formation of PTS.

Sorption optimization by RSM

The conventional batch sorption method requires a large number of experiments to find the optimum response. The major disadvantage of the conventional method is that it uses a variation of only one parameter at a time keeping the other parameters constant and thus, the cumulative effect of all the affecting parameters at a time cannot be studied which could lead to unreliable results¹⁶. However, in RSM, the interactions of two or more variables can be studied simultaneously with more reliable results and less process variability. Shorter treatment time and minimum costs are additional advantages¹⁵. The maximum removal of Pb(II) ions was predicted at optimum variables (adsorbent dose 53mg, pH 7.5, initial Pb(II) ion concentration 10mg l^{-1} and agitation time 90min) by PTS using CCD model. Experimentally, the removal of Pb(II) ions was achieved at predicted optimum variables. The correlation coefficient (0.99) between predicted and experimental values showed a close agreement as shown in Table 2.

Statistical analysis

The accuracy and fitting of the model were evaluated by analysis of variance (ANOVA) as shown in Table 3. The ANOVA results showed that the lack of fit is not significant as $P < 0.05$ ($0.0053 < 0.05$) and the null hypothesis could not be rejected¹⁷, as the approximating model would give poor or misleading results if it was an inadequate fit. The residual and three dimensional

(3D) surface plots were examined to approximate the model adequacy¹⁸.

Interpretation of residual graphs

The residual is the difference between the observed and the predicted values from the regression to obtain the normal distribution. Fig. 4 plots the residuals versus the predicted values, the residuals are scattered randomly about zero showing that the errors have a constant variance. It is important to identify the outliers because they can significantly influence the model and the potentially misleading results. The plot showed that all points were found in the range of +1.5 to -1.5, confirmed the fitting of the model and do not violate the regression assumptions.

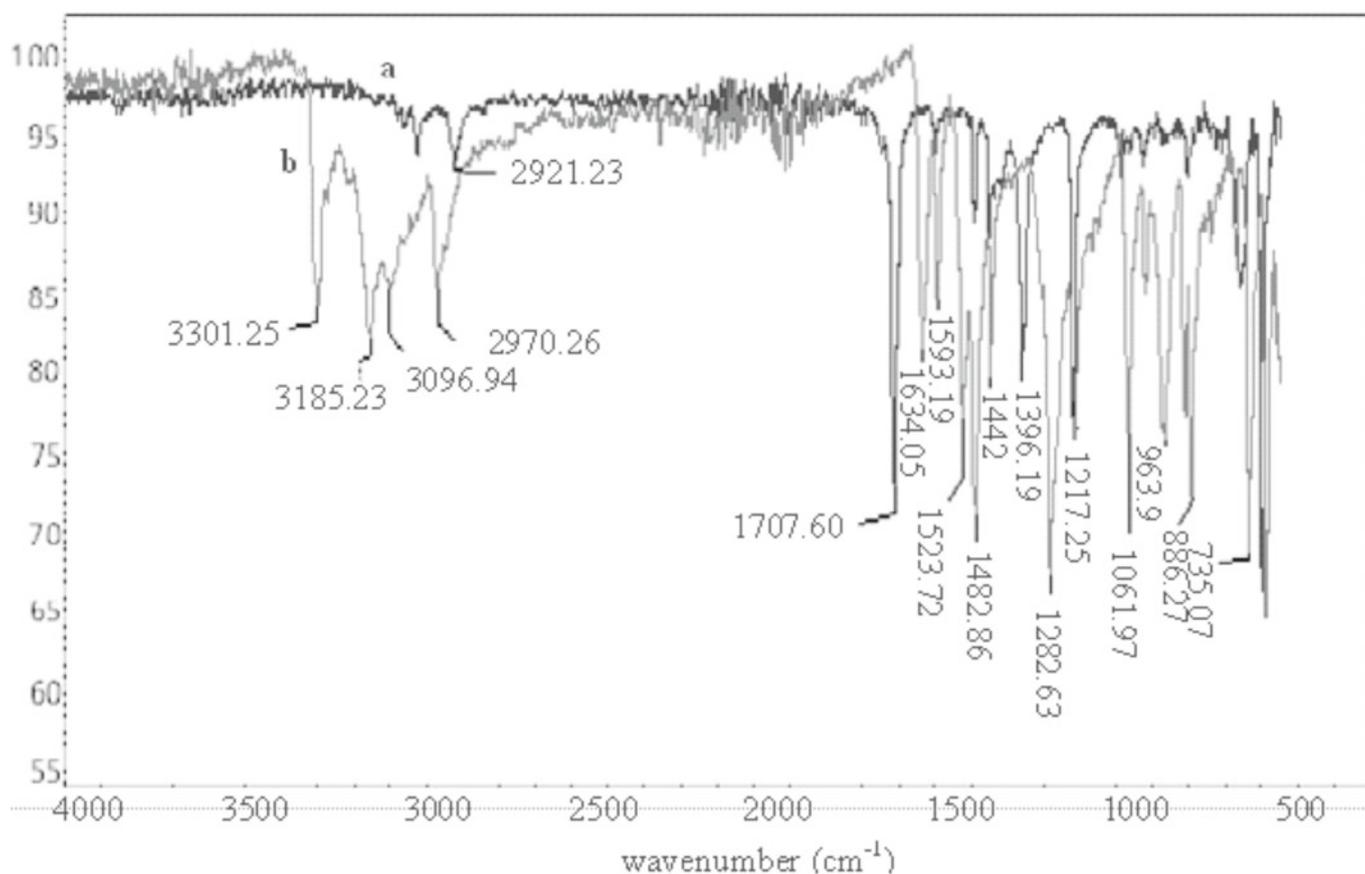
Interpretation of 3D response surface plots

The 3D response surface plots are the graphical representations of regression equation. The main goal of response surface is an efficient hunt for the optimum values of the variable when response is maximized. Each graph represents an infinite number of the combinations of two test variables with the other two maintained at their respective optimum value.

Fig. 5a explores a combined effect of pH (2–9) and initial Pb(II) ion concentration ($5\text{--}50\text{mg l}^{-1}$) on the percent removal of Pb(II) ions keeping an optimum adsorbent dose (53mg) and agitating time (90 min). Pb(II) ions uptake slightly decreases with an increase of initial Pb(II) ion concentration, while regularly increases with an increase of pH and becomes maximum at pH 8. While exploring the effect of pH on the sorption of Pb(II) ions onto PTS, it is essential to know the speciation of lead ions at different pH, the main species of lead is Pb^{2+} (>80%) at pH 7 and Pb^{2+} (~50%), $\text{Pb}(\text{OH})^+$ (~45%),

Table 3. ANOVA and estimated regression coefficients for Pb(II) ions removal by PTS

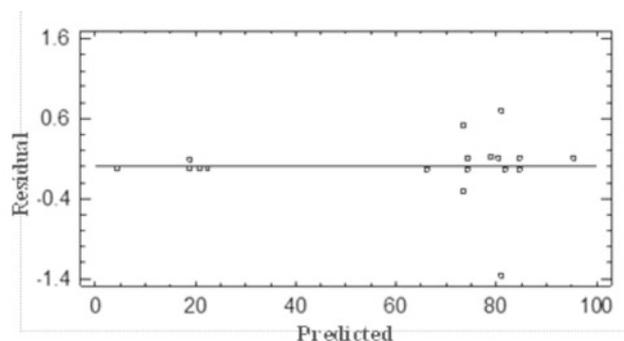
Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value	Regression coef.
Constant						-57.550
A:amount	0.0013	1	0.0013	0.00	0.9832	0.0716
B:con	32.7241	1	32.7241	13.18	0.0360	0.136365
C:pH	9907.02	1	9907.02	3991.66	0.0001	43.6578
D:time	5.743	1	5.743	2.31	0.2256	0.0732
AA	0.1661	1	0.1662	0.07	0.8126	0.0001
AB	49.5338	1	49.5338	19.96	0.0209	-0.0055
AC	114.489	1	114.489	46.13	0.0065	-0.0240
AD	101.991	1	101.991	41.09	0.0077	0.0021
BB	4.7573	1	4.7574	1.92	0.2602	-0.0027
BC	626.155	1	626.155	252.29	0.0005	0.1123
BD	9.8212	1	9.8212	3.96	0.1408	-0.0013
CC	3567.5	1	3567.5	1437.39	0.0001	-3.0692
CD	560.388	1	560.388	225.79	0.0006	-0.0281
DD	1.12282	1	1.1228	0.45	0.5494	-0.0001
Lack-of-fit	6.2753	2	3.13767	2.68	0.00531	
Total error	7.4448	3	2.4189			
Pure error	1.17045	1	1.1705			
Total (corr.)	18170.7	17				

**Figure 3.** FT-IR Spectra of acetyl-PS (a) and PTS (b)

$\text{Pb}_3(\text{OH})_4^{2+}$ (~3%), and $\text{Pb}(\text{OH})_2$ (~1%) at pH 8¹⁹. Thiosemicarbazone moiety of PTS become active to capture the Pb(II) ions species at pH 8.

Fig. 5b shows the combined the effect of pH (2–9) and the adsorbent dose (10–100mg), keeping the optimum initial Pb(II) ion concentration (10mgml⁻¹) and the agitation time (90min). The percent removal of Pb(II) ions increases with the increase of pH and becomes maximum at pH 8 at all adsorbent dose (10–100mg).

Fig. 5c shows the combined effect of pH (2–9) and the agitation time(10–180min), the percent removal of Pb(II) ions increases with the increase of pH and beco-

**Figure 4.** Residual versus predicted plot for % removal of Pb(II) ions by PTS

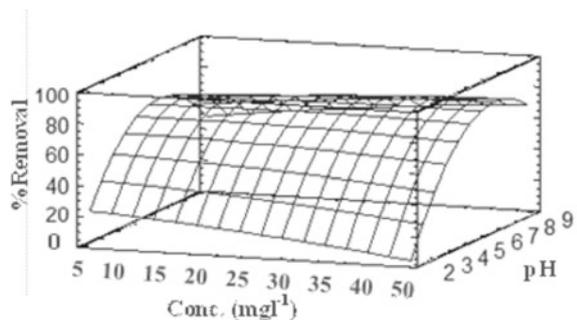


Figure 5a. Plot for combined effect of pH and concentration on % removal of Pb(II) ions by PTS

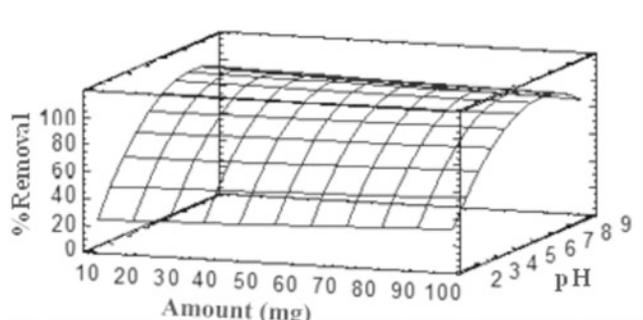


Figure 5b. Plot for combined effect of adsorbent amount and pH on % removal of Pb(II) ions by PTS

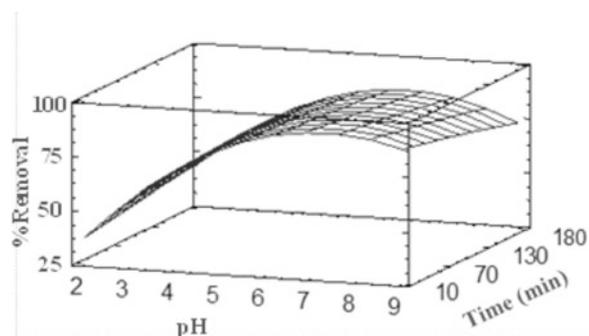


Figure 5c. Plot for combined effect of pH and agitation time on % removal of Pb(II) ions by PTS

mes maximum at pH 8 throughout the whole agitation time (10–180min).

Fig. 5d shows the combined effect of the adsorbent dose (10–100mg) and the agitation time (10–180min) keeping the optimum pH (8) and the initial Pb(II) ions concentration (10mgml⁻¹). The agitation time has a different effect with a different adsorbent dose, with the increase of agitation time, percent removal of Pb(II) ions decreases at the adsorbent dose ranging 10–50mg due to desorption and increases at adsorbent dose ranging 50–100mg because the number of molecules containing active moieties increases. Similarly the adsorbent dose has a different effect at different agitation time, with the increase of adsorbent dose, percent removal of Pb(II) ions decreases at the agitation time 10–80min, becomes almost constant at the agitation time 80–90min and increases at the agitation time 90–180min. The optimum removal (99.61%) of Pb(II) ions is achieved at the adsorbent dose 53mg and the agitation time 90min.

Fig. 5e reflects the combined effect of the initial Pb(II) ion concentration (5–50mg/l⁻¹) and adsorbent dosages (10–100mg) on percent removal of lead(II) ions keeping

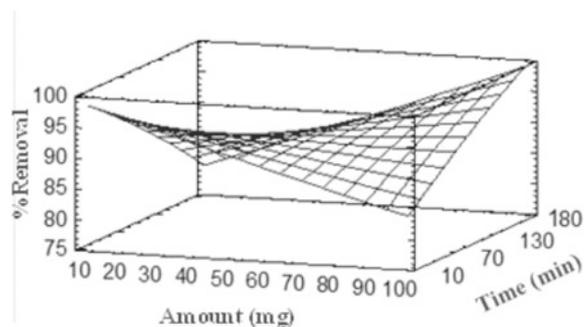


Figure 5d. Plot for combined effect of adsorbent amount and agitation time on % removal of Pb(II) ions by PTS

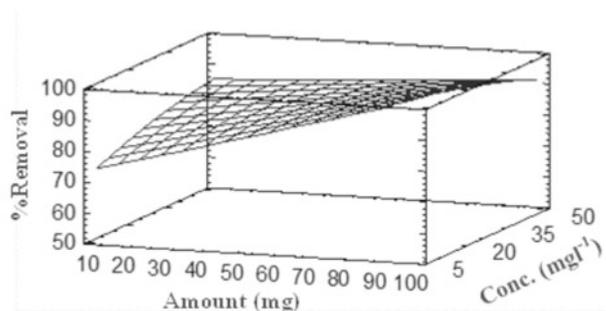


Figure 5e. Combined effect adsorbent amount concentration on % removal of Pb(II) ions by PTS

the optimum pH (8) and the agitating time (90min). Pb(II) ions sorption increases with the increase of initial Pb(II) ions concentration at the whole adsorbent dose (10–100mg). The extent of sorption decreases with the increase of adsorbent dose because the number of molecules containing active moieties increases with the increase of adsorbent dose, these increased molecules utilize to uptake the increased Pb(II) ions. With the increase of adsorbent dose ~10–60mg, sorption increases intensively, while sorption on the adsorbent ranging ~60–100mg slightly increases with increasing the initial Pb(II) ion concentration. The maximum removal ~99.61% of Pb(II) ions is achieved at the optimum adsorbent dosage (53mg) and the initial Pb(II) ions concentration (10mg/l⁻¹).

Isotherms

Several isotherm models have been used for the description of sorption equilibrium. The isotherm study was carried out by varying the initial metal ion concentration at 30°C, adsorbent dose 53mg, agitation time 90min and pH 8. The Langmuir and Dubinin-Radushkevich (D-R) models were evaluated using eq. 2 and 3, respectively.

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (2)$$

$$\ln C_{ads} = \ln K_{D-R} - \beta \epsilon^2 \quad (3)$$

Where C_e is the equilibrium concentration of Pb(II) ion (mg/l⁻¹) and C_{ads} is the amount of Pb(II) ions adsorbed onto PTS (mgg⁻¹), Q and b are the Langmuir constants related to the monolayer sorption capacity (mgg⁻¹) and affinity of the binding sites (lg⁻¹), respectively. Where β is related to the mean free energy of sorption per mole of the sorbent when it is transferred from infinite distance in the solution to the surface of the solid and ϵ is Polanyi potential and is equal to $RT \ln(1 + C_e/C_e)$,

where T is temperature and R is general gas constant ($\text{Jmol}^{-1}\text{K}^{-1}$).

The Langmuir isotherm is based on the assumption that all the sorbent sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. The saturation value is reached when no further adsorption can take place²⁰. The isotherm constants Q and b were calculated from the slope and the intercept of plot between C_e/C_{ads} and C_e . The isotherm showed good fit to the experimental data with good correlation coefficient (0.992). The Langmuir sorption capacity of PTS was calculated $45.25 \pm 0.69 \text{mgg}^{-1}$.

The separation factor R_L is an essential characteristic of the Langmuir isotherm which describes the type of isotherm and can be mathematically represented by eq. 4.

$$R_L = \frac{1}{1 + (bC_i)} \quad (4)$$

Where b is the Langmuir constant and C_i is the initial concentration of Pb(II) ion. According to the value of R_L , the isotherm shape can be interpreted as $R_L=0$; irreversible, $R_L>1$; unfavorable, $R_L=1$; linear and $0 < R_L < 1$; favorable²¹. The R_L values calculated for the sorption of Pb(II) ions onto PTS were in the range of 0.0001-0.01, indicated the favorable nature of sorption.

The D-R isotherm assumes no homogeneous surface of the sorbent material, a good linear relationship between $\ln C_{\text{ads}}$ and e^2 with correlation coefficient 0.98. The applicability of isotherms showed, possibility of heterogeneous energetic distribution of active sites on the surface of the PTS. The estimated values of mean sorption energy (E), calculated from slope of the plot (β) was $20.41 \pm 0.12 \text{kJmol}^{-1}$. The magnitude of E indicates the nature of the sorption process, $E > 8-16 \text{kJmol}^{-1}$ (chemisorption) and $E < 8 \text{kJmol}^{-1}$ (physisorption)¹⁷. On the basis of this observation it can be anticipated that the sorption of Pb(II) ions on PTS predominantly followed chemisorption.

Table 4. Model validation for Pb(II) ions removal by PTS

Amount of adsorbent A (mg)	pH B	Initial Concentrations C (mg^{-1})	Time D (min)	% Removal	
				Predicted	Experimental
53	8	10	90	100	99.61

Possible sorption mechanism

Thiosemicarbazone moiety has a strong ability to form a five-membered chelate with metal ions²². Nitrogen and sulphur of thiosemicarbazone moiety of PTS participated for the uptake of Pb(II) ion by forming a five-membered chelate as shown in Fig. 6.

The FT-IR spectral study confirmed the proposed mechanism. Fig. 7(a-b) shows the FT-IR spectra for PTS plain (a) and Pb(II) ions loaded (b). By comparing the spectra (a-b), the characteristic peak of disappearance at 3301.25cm^{-1} (for N-H stretching), shifting of peak; 1634.05cm^{-1} to 1979.0cm^{-1} (for C=N stretching) and significant decrease in intensity of peak; 1282.63cm^{-1} (for C=S stretching) in spectrum-b confirmed the involvement of Nitrogen and Sulphur of thiosemicarbazone moiety of PTS for uptake of Pb(II) ion by chelate formation.

MODEL VALIDATION

The optimum sorption conditions determined from CCD Model were validated by comparing the predicted and experimental removal of Pb(II) ions at optimum conditions. The CCD model predicted the maximum removal (100%) of Pb(II) ions within the agitation time of 90min at pH 8, while the adsorbent dose and the concentration were 53mg and 10mg^{-1} , respectively. Experimentally 99.61% removal was achieved at the same conditions. Good agreement between the predicted and the experimental values showed the good prediction ability of the model.

EFFECT OF CONCOMITANT IONS

As the real matrices possess a number of different concomitants, the effect of some common electrolytes

Table 5. Removal of Pb(II) ions from real samples of contaminated drinking water

Sample	Initial Conc. (mg^{-1})	Final conc. (mg^{-1}) after addition $10 \mu\text{g}$ of Pb(II) ions	% Recovery	RSD (%)
S1	2.58	12.58	87.98	1.1
S2	2.74	12.74	79.99	2.7
S3	1.1	11.1	95.71	1.9
S4	2.39	12.39	84.65	3.1

*S1: Hand pump water (Choudhary Mohammad Sadiq Chak 147, Taluka Sadiqabad, Distt: Rahimyar Khan).

*S2: Hand pump water (Basic Health Unit Manthar, Taluka Sadiqabad, Distt: Rahimyar Khan).

*S3: Tap water (Institute of Advance Research studies in Chemical Sciences, University of Sindh, Jamshoro, Pakistan)

*S4: Hand Pump (Madarssa Dar-ul-uloom Manthar Taluka Sadiqabad Distt: Rahimyar Khan).

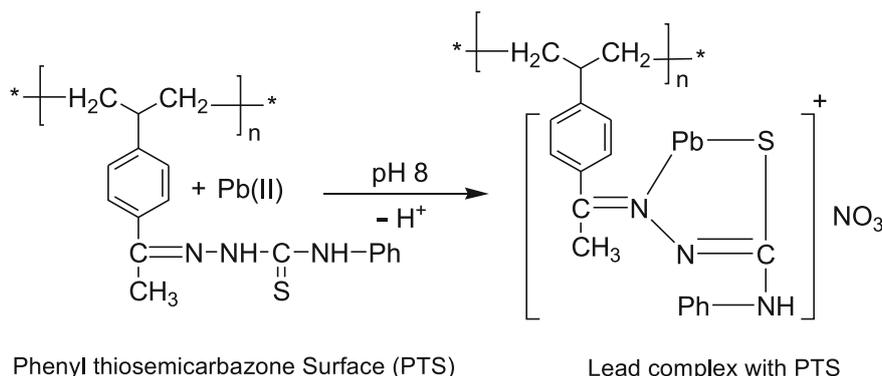


Figure 6. Chelate formation of Phenyl thiosemicarbazone with Pb(II) ion

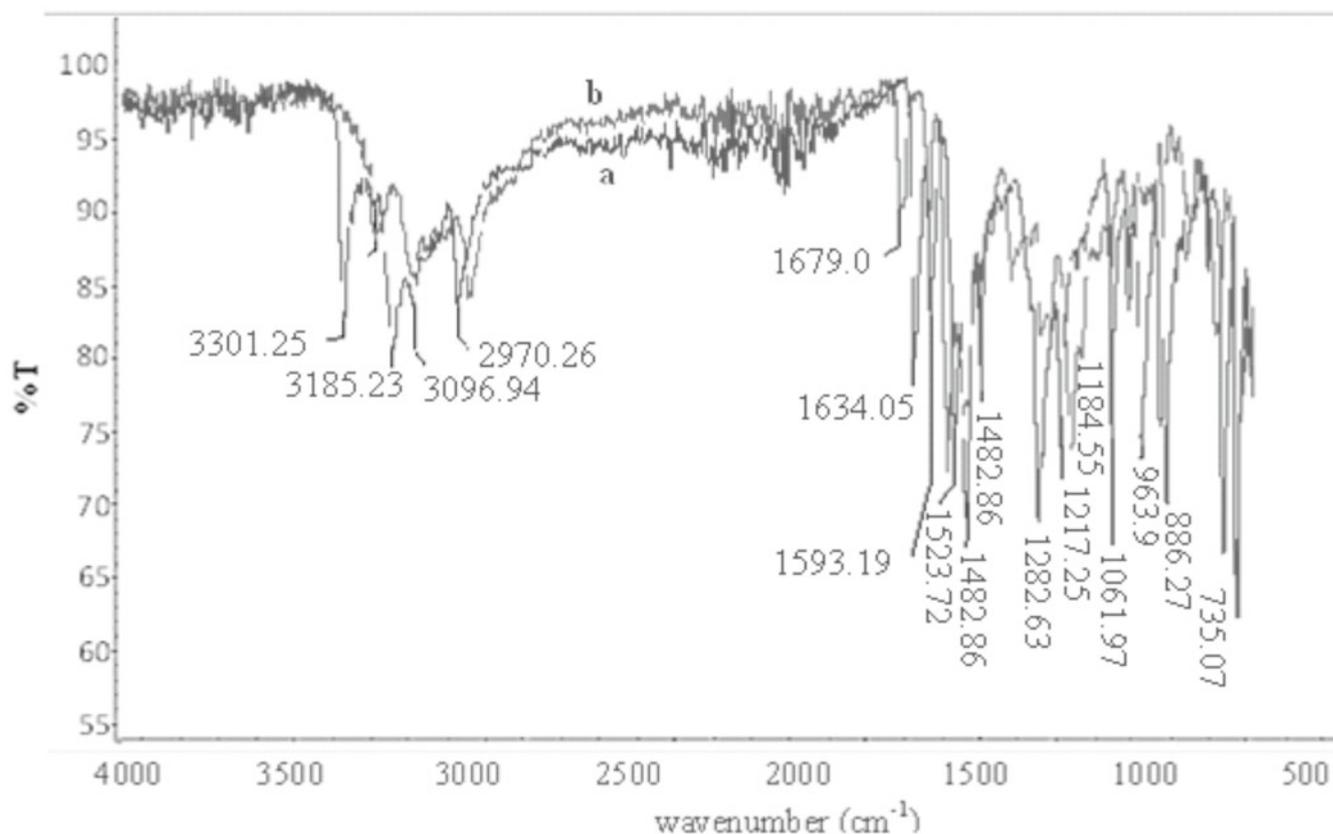


Figure 7. FT-IR Spectra for PTS plain (a) and Pb(II) ion loaded (b)

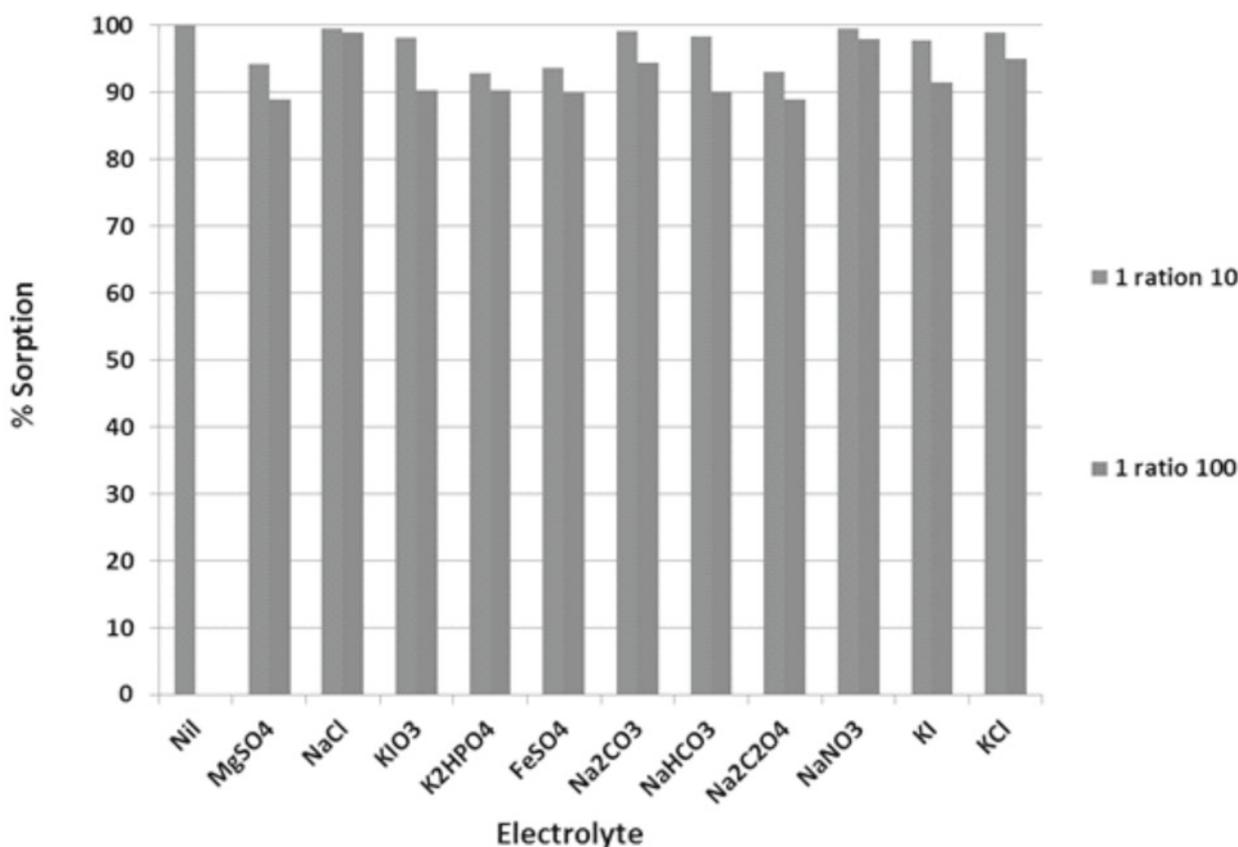


Figure 8. Effect of common concomitant ions onto sorption of Pb(II) ions on PTS

in the ratios of 1:10 and 1:100 were examined on the removal efficiency Pb(II) ions by PTS. No appreciable interfering effect of the studied electrolytes was observed on the removal of Pb(II) ions by PTS as shown in Fig. 8.

APPLICATION OF PTS

The synthesized sorbent (PTS) was successfully applied for the removal of Pb(II) ions from the drinking water samples. The samples were collected from different areas

of Pakistan. Table 5 shows the efficiency of PTS for the removal of Pb(II) ions from the real water systems.

CONCLUSIONS

Styrofoam waste was successfully recycled to novel functional PTS. The conversion was confirmed by the FT-IR spectroscopy and elemental analysis. The functionality of PTS was advantaged for the uptake of Pb(II) ions by chelate formation. The multi-variant Sorption optimization was achieved using the Factorial Design approach. The isotherm study and the FT-IR spectroscopy supported the chemical nature of the interaction between the surface and Pb(II) ions with an involvement of thiosemicarbazone moiety of PTS.

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