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 with 4-phenyl 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) 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 95% polystyrene (PS) and 5% air. Styrofoam is generally used as an insulator and packaging material for household electrical appliances. 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. It is generally disposed in landfill which becomes environmental risk because of its large volume and chemical inertness. 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 well. Therefore, great attention has been paid to chemical recycling of styrofoam waste to different useful materials, especially by sulfonation. In the present study, we focused on a novel root 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 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 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) 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). 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 thermostat 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) 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.
Where $C_i$ and $C_e$ are the initial and equilibrium concentrations (mg/l) 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) 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).

**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 C$_{11}$H$_{12}$O are C, 82.46; H, 7.55; O, 9.99%. The elemental analysis data confirmed the successful formation of acetyl-PS.

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

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

<table>
<thead>
<tr>
<th>Independent variable</th>
<th>Coded levels</th>
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<tr>
<td>Amount (mg), A ($x_1$)</td>
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</tr>
<tr>
<td>Concentration (mg/l), B ($x_2$)</td>
<td>5 27.5 50</td>
</tr>
<tr>
<td>pH, C ($x_3$)</td>
<td>2 5.5 9</td>
</tr>
<tr>
<td>Time (min), D ($x_4$)</td>
<td>10 95 180</td>
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</table>

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

<table>
<thead>
<tr>
<th>Trail</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>% Removal (Experimental)</th>
<th>% Removal (Predicted)</th>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>96.34</td>
<td>96.09</td>
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</tbody>
</table>
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_{3}S 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 results\(^{16}\). 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 advantages\(^{15}\). 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 rejected\(^{17}\), 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 adequacy\(^{18}\).

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 infinitesimal 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 (5–50mg 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%), Pb(OH)\(^{2+}\)(~45%),
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-
maximum at pH 8 throughout the whole agitation time (10–180 min).

Fig. 5d shows the combined effect of the adsorbent dose (10–100 mg) and the agitation time (10–180 min) keeping the optimum pH (8) and the initial Pb(II) ions concentration (10 mg ml⁻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 10–50 mg due to desorption and increases at adsorbent dose ranging 50–100 mg 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 10–80 min, becomes almost constant at the agitation time 80–90 min and increases at the agitation time 90–180 min. The optimum removal (~99.61%) of Pb(II) ions is achieved at the optimum adsorbent dosage (53 mg) and the initial Pb(II) ions concentration (10 mg ml⁻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 53 mg, agitation time 90 min and pH 8. The Langmuir and Dubinin-Radushkevich (D-R) models were evaluated using eq. 2 and 3, respectively.

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

\[
\ln C_{ads} = \ln K_{D-R} - \beta e^2 \quad (3)
\]

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 (mg g⁻¹), Q and b are the Langmuir constants related to the monolayer sorption capacity (mg g⁻¹) and affinity of the binding sites (l g⁻¹), respectively. Where \(\beta\) 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 \(e\) is Polanyi potential and is equal to RT \(\ln (1+1/C_e)\),
where $T$ is temperature and $R$ is general gas constant (Jmol$^{-1}$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 place. The Langmuir sorption capacity of PTS was calculated 45.25±0.69mgg$^{-1}$.

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.

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

(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 $0<R_L<1$: favorable. 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$C_{ads}$ and $c^2$ 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 ($\beta$) was 20.41±0.12kJmol$^{-1}$. The magnitude of $E$ indicates the nature of the sorption process, $E>8$-16kJmol$^{-1}$ (chemisorption) and $E<8$kJmol$^{-1}$ (physisorption). On the basis of this observation it can be anticipated that the sorption of Pb(II) ions on PTS predominantly followed chemisorption.

**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 10mgl$^{-1}$, 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...
Figure 7. FT-IR Spectra for PTS plain (a) and Pb(II) ion loaded (b)

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.

LITERATURE CITED