

# Removal of mercury species with dithiocarbamate-anchored polymer/organosmectite composites

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## Abstract

Mercury is one of the most toxic heavy metals found in solid and liquid waste disposed by chloro-alkali, paint, paper/pulp, battery, pharmaceutical, oil refinery and mining companies. Any form of mercury introduced to nature through any means is converted into a more toxic form such as methylmercury chloride (as produced by aquatic organisms) which usually accumulates in the tissue of fish and birds.

The primary aim of this study was to investigate performance of dithiocarbamate-anchored polymer/organosmectite composites as sorbents for removal of mercury from aqueous solution. The modified smectite nanocomposites then were reacted with carbondisulfide to incorporate dithiocarbamate functional groups into the nanolayer of the organoclay. These dithiocarbamate-anchored composites were used for the removal of mercury species [Hg(II), CH<sub>3</sub>Hg(I) and C<sub>6</sub>H<sub>5</sub>Hg(I)]. Mercury adsorption was found to be dependent on the solution pH, mercury concentration and the type of mercury species to be adsorbed. The maximum adsorption capacities were equal to 157.3 mg g<sup>-1</sup> (782.5 μmol g<sup>-1</sup>) for Hg(II); 214.6 mg g<sup>-1</sup> (993.9 μmol g<sup>-1</sup>) for CH<sub>3</sub>Hg(I); 90.3 mg g<sup>-1</sup> (325 μmol g<sup>-1</sup>) for C<sub>6</sub>H<sub>5</sub>Hg(I). The competitive adsorption capacities (i.e. adsorption capacities based on solutions containing all three mercuric ions) are 7.7 mg g<sup>-1</sup> (38.3 μmol g<sup>-1</sup>), 9.2 mg g<sup>-1</sup> (42.6 μmol g<sup>-1</sup>) and 12.7 mg g<sup>-1</sup> (45.7 μmol g<sup>-1</sup>) for Hg(II), CH<sub>3</sub>Hg(I) and C<sub>6</sub>H<sub>5</sub>Hg(I), respectively, at 10 ppm initial concentration. The adsorption capacities on molar basis were in order of C<sub>6</sub>H<sub>5</sub>Hg(I) > CH<sub>3</sub>Hg(I) > Hg(II).

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**Keywords:** Mercury; Adsorption; Removal; Organoclay; Smectite

## 1. Introduction

Mercury is one of the most toxic heavy metals found in wastewater deposited by chloro-alkali production, oil refinery, paint production, pharmaceutical, paper/pulp, battery production and mining companies as well as in garbage/municipal wastes [1–3]. Any form of mercury introduced from a variety of sources into the nature is converted to a more toxic form methylmercury chloride, which is predominantly encountered in the tissue of aquatic organisms such as fish and birds [4]. Methylmercury chloride is one of the causes of serious metal poisoning cases as in the Minamata disease [5].

Therefore, the removal of mercury in water and wastewater is crucial. Several methods involving chemical precipitation, conventional coagulation, line softening, reverse osmosis, ion-exchange and adsorption on activated carbon are currently available techniques for the removal of heavy metals in water and wastewater. Due to the cost of activated carbon, low-cost adsorbents (i.e., clay minerals, chitosan, saw-dust, etc.) typically are preferred for use in spite of some disadvantages in their applications, such as low binding affinity, low selectivity and low susceptibility to chemicals, heat and radiation. Nevertheless, clay minerals are desirable for their adsorptive properties [6–16]. Improving the removal efficiency and the adsorption capacity of naturally occurring clay adsorbents has been subject to intensive research, including research focused on modification of the clay surface into a more potent adsorbent form [17–19].

For instance, polymer/clay composites have been synthesized by in situ polymerization of monomers on a series of modified clays [20] and by intercalation from solution [21]. Organ-

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oclays were first employed by the Toyota Research Institute [22–24] to fabricate Nylon/organomontmorillonite composites with improved mechanical, thermal and rheological properties, thereby expanding the applications of Nylon products. Numerous research articles on different polymer/organoclay composites such as clay/polystyrene [25,26], epoxy resin [27] and polypropylene [28,29] also have been reported in literature.

The primary aim of this study is to present the results of a laboratory study focused on efforts to remove mercury species (Hg(II), CH<sub>3</sub>Hg(I) and C<sub>6</sub>H<sub>5</sub>Hg(I)) in aqueous solutions via modified smectite nanocomposites. Initially, the modification of the natural smectite mineral was performed by treating it with quartamine styrene and chloromethylstyrene and then modified smectite nanocomposites were reacted with carbon disulfide, in order to incorporate dithiocarbamate functional groups into the nanolayer of the organoclay. The adsorption of the mercury species was investigated as a function of equilibrium time, pH, adsorption capacity and selectivity.

## 2. Experimental

### 2.1. Materials

Azobisisobutyronitrile (AIBN) was purchased from Fluka. All other chemicals were of reagent grade and purchased from Merck (Darmstadt, Germany).

The smectite [6] used throughout the experiments was obtained from Northern Anatolia, Turkey. The smectite was rigorously crushed and sieved to obtain fine particles that are less than 200 μm in size.

### 2.2. Instrumentation

Inductively coupled plasma atomic emission spectrometry (ICP-OES-Perkin-Elmer 4300 DV Model) was used to determine Hg(II), CH<sub>3</sub>Hg(I) and C<sub>6</sub>H<sub>5</sub>Hg(I). Hg(II), CH<sub>3</sub>Hg(I) and C<sub>6</sub>H<sub>5</sub>Hg(I) species at 253.652 nm. Dithiocarbamate-anchored composites were characterized by FTIR (Perkin-Elmer 2000 Model). Competitive adsorption measurements were carried out by a Solid Phase Extraction-Reverse Phase HPLC (HP-series 1100-Agilent) system. pH measurements were implemented by a Jenway 3100 pH-meter.

### 2.3. Preparation of dithiocarbamate-anchored polymer/organosmectite composites

The organoclay was prepared in a similar way as described by Tabtiang et al. [30]. The smectite (20 g) was dispersed in deionized water (500 mL) at 80 °C in a reaction vessel. A solution of quartamine [dimethyl(dihydrogenated tallow) ammonium chloride] (0.05 mol) and concentrated HCl (5 mL) in deionized water (100 mL) were added to the mixture, which was then stirred for 3 h. The suspension was filtered off, and the solid residue was rinsed with hot distilled water to thoroughly remove residual chloride ions. The crude product was first dried in a vented oven at 55 °C for several days, and then dried under vacuum for 24 h, yielding the quartamine modified smectite (QS).

Polymer/quartamin modified smectite (PQS) was prepared as follows: Azobisisobutyronitrile (AIBN) (0.1 g) was added to a reaction flask containing 12 ml of extracted styrene and QS dispersed in 50 mL of distilled hexane. The reaction vessel was suspended for 9 h in a thermostated water bath at 65 °C, which was then added 3 mL of chloromethylstyrene, 0.050 g of AIBN and 20 mL of hexane, and stirred for 24 h. The polymerized QS was cleaned by and the dithiocarbamate functional group was incorporated on the subsurface of the organoclay in two steps [31]. Firstly, 10 g of the nanocomposite was suspended in a mixture of 50 mL of water and 1.5 mL of benzylamine and the mixture was magnetically stirred at 600 rpm at 20 °C for 24 h. Then, the amine groups of benzylamine were transformed into dithiocarbamate groups by reacting with carbon disulfide. The mixture containing benzylamine immobilized nanocomposites was then added to a mixture of 50 mL of water and 4.0 mL of 1,4-dioxane, whose pH was rapidly brought to 11 by addition of a sufficient amount of a 1.0 M KOH solution. 4.0 mL of carbon disulfide was added to the media, which was then stirred at 20 °C for 24 h, to convert the amino group of benzylamine to a dithiocarbamate group. The final product was recovered from the reaction mixture as powder by evaporation of the solvent, followed by a drying procedure under vacuum at 55 °C. Incorporation of dithiocarbamate (DTC) groups into nanolayer to form DTC-PQS (Fig. 1) was characterized by FTIR. We postulate that mercury species form complex structures with the thiol end groups of dithiocarbamates as schematically shown in Fig. 1.

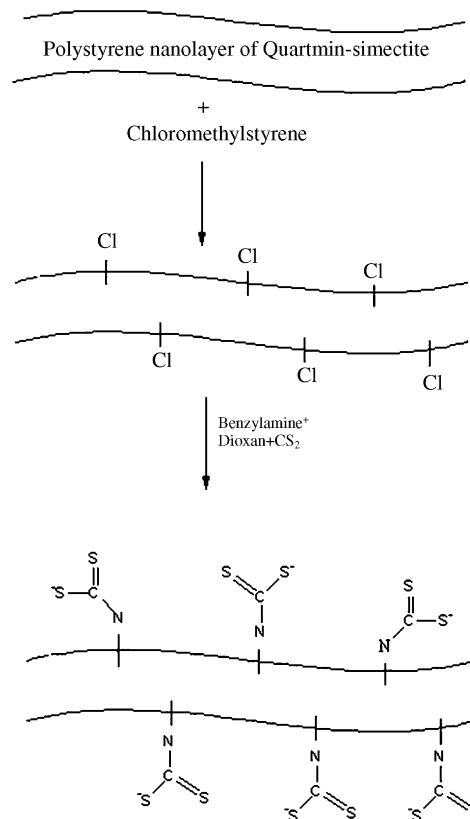


Fig. 1. Structure of dithiocarbamate modification into PS/QS nanolayer.

#### 2.4. Adsorption of alkyl mercury species and inorganic mercury

The dithiocarbamate-anchored polymer/organosmectite composites were tested in batch systems for their ability to adsorb alkyl and inorganic mercuries in aqueous solutions. Mercury solutions (25 mL) containing different amounts of mercury species (in the range of 10–1000 ppm) were incubated with 25 mg of nanocomposites at varying pH (pH 2.0–8.0, adjusted by either 0.1 N NaOH or 0.1 N HNO<sub>3</sub>) at room temperature of 25 °C for different time periods in adsorption flasks and magnetically stirred at 600 rpm. The atomic emissions of the mercury species left in the solution after treatment with nanocomposites were measured by ICP-AES, which were then quantified by Eq. (1) to determine the amount of mercury ions adsorbed per unit mass of the nanocomposites:

$$Q = \frac{[(C_0 - C_A)V]}{m} \quad (1)$$

$C_0$  and  $C_A$  are the initial and the final equilibrium concentrations (mg/mL) of the mercury ions in the aqueous phase,  $V$  is the volume of the aqueous phase (mL), and  $m$  is the mass weight (g) of the nanocomposite used.

Competitive adsorption studies were also carried out using a solution containing a mixture of the mercury species. Twenty-five millilitres of a solution was prepared by mixing equal amounts of the stock solutions (10 mg/L) for each mercury species at pH 6.0, and was treated with 25 mg of nanocomposites in a reaction flask, which was then magnetically stirred at 600 rpm at room temperature. After adsorption equilibrium was reached, the final concentrations of the alkyl and inorganic mercury species in the supernatant were measured by SPE-RP (Solid Phase Extraction-Reverse Phase) HPLC [32].

### 3. Results and discussion

#### 3.1. Characterization of dithiocarbamate-anchored polymer/organosmectite composites

The synthesis of dithiocarbamate-anchored composites was characterized by comparing its FTIR spectrum with that of PQS. According to a FTIR spectrum, the N–H stretching band is detected at 3400 cm<sup>-1</sup>, and the peaks detected at 2920 cm<sup>-1</sup>, 2840 cm<sup>-1</sup> and 800 cm<sup>-1</sup> correspond to the C–H, the C–H of CH<sub>2</sub> and the C–Cl stretching frequencies, respectively. The FTIR spectrum gave peaks at 3300 cm<sup>-1</sup>, 1500 cm<sup>-1</sup>, 1560 cm<sup>-1</sup>, 1180 cm<sup>-1</sup> and 800 cm<sup>-1</sup> for the N–H, the C=C, the C–N, the C=S and the C–Cl, respectively, and at 2920 and 2840 cm<sup>-1</sup> for the C–H stretching frequencies, suggesting that the organoclay was converted to polymer/organo nanocomposite.

#### 3.2. Heavy metal adsorption

##### 3.2.1. Adsorption rate

The adsorption data in Fig. 2 reflect the rates of adsorption shown by dithiocarbamate-anchored polymer/organosmectite

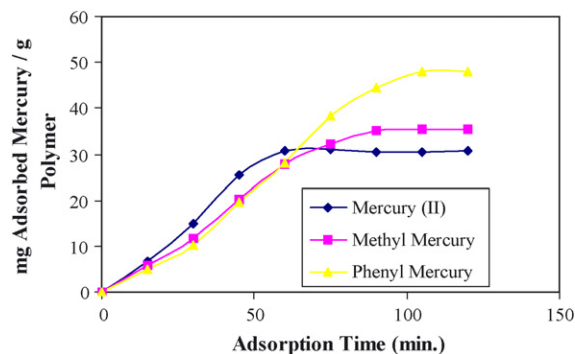


Fig. 2. Adsorption rates shown by dithiocarbamate-anchored polymer/organosmectite composites for the mercury species. Experimental conditions: initial concentration of metal ions = 50 mg/L; pH 6; temperature = 25 °C.

composites for various mercury species in aqueous solution. The adsorption ordinate values in the plot, calculated by Eq. (1), indicate that the adsorptions of Hg(II), CH<sub>3</sub>Hg(I), and C<sub>6</sub>H<sub>5</sub>Hg(I) gradually reach equilibria and saturate in 60 min, 75 min, and 105 min, respectively.

Several studies of mercury adsorption onto various sorbents have shown a wide range of adsorption rates [33–35]. For example, Sağlam et al. [33] have investigated the biosorption of some mercury species by *Phanerochaete Chrysosporium Mycelium* and reported an average equilibrium adsorption time of 6 h. Murty and Ryan have conducted some adsorption studies with mercury, copper, cadmium, lead and uranium species using cellulose-dithiocarbamate resins and reported that, although slow adsorption rates were obtained, a 30 min equilibration time could still be reproducibly reached [35]. Salih et al. [34] have carried out another set of adsorption studies with mercury species using dithizone-anchored microbeads and reported a 60 min equilibration time for the adsorption. However, it is quite difficult to comparatively evaluate the adsorption rates in literature, due to different experimental parameters, including the stirring rates (or flow) in aqueous phase, the structural properties (i.e., porosity, surface area, etc.) of the sorbent used, the amount of the sorbent, the ionic properties (e.g., ionic radius) of the heavy metal species, the initial concentrations of the heavy metal species, chelate formation rates, and the presence of other heavy metal species were applied.

##### 3.2.2. The effect of the initial concentrations of alkyl and inorganic mercury species on adsorption

The adsorption capacities of dithiocarbamate-anchored polymer/organosmectite composites for mercury species present in separate aqueous solutions versus the initial concentrations of the mercury species are plotted in Fig. 3. As seen in Fig. 3, adsorption significantly increases as the initial mercury concentration increases. The maximum adsorption capacities of dithiocarbamate-anchored polymer/organosmectite composites were found to be 157.3 mg g<sup>-1</sup> (782.5 μmol g<sup>-1</sup>), 214.6 mg g<sup>-1</sup> (993.9 μmol g<sup>-1</sup>) and 90.3 mg g<sup>-1</sup> (325 μmol g<sup>-1</sup>) for Hg(II), CH<sub>3</sub>Hg(I) and C<sub>6</sub>H<sub>5</sub>Hg(I), respectively. These findings indicate that the affinity of the nanocomposite for CH<sub>3</sub>Hg(I) is stronger than it is for the Hg(II) and C<sub>6</sub>H<sub>5</sub>Hg(I) mer-

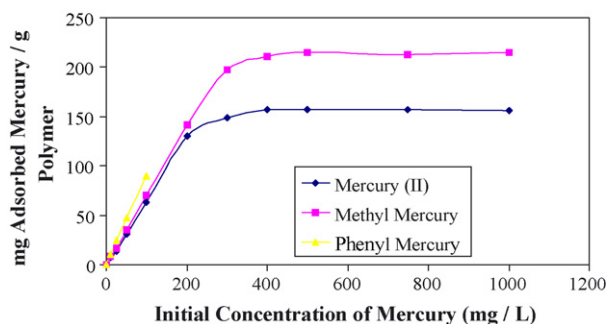


Fig. 3. The adsorption capacity of dithiocarbamate-anchored polymer/organosmectite composites for the mercury species at pH 6.0 and 25 °C.

cury species, resulting in a relative adsorption order of  $\text{CH}_3\text{Hg(I)} > \text{Hg(II)} > \text{C}_6\text{H}_5\text{Hg(I)}$ .

### 3.2.3. The effect of pH on adsorption

Metal ion adsorption both on non-specific and specific sorbents is known to be pH dependent [19,33,36,37]. In the absence of complexing agents, the hydrolysis and precipitation of metal ions are affected by their concentrations and form of soluble metal species. The solubility of metal ions is governed by the concentration of hydroxyl or carbonate present in media. The effect of pH on mercury species adsorption by the dithiocarbamate-anchored polymer/organosmectite composites is graphically presented in Fig. 4.

As seen in Fig. 4, the adsorption capacity of dithiocarbamate-anchored polymer/organosmectite composites increases as pH increases and reaches a saturation value at pH  $\sim 6.0$ . Compared to inorganic mercury, the dithiocarbamate-anchored polymer/organosmectite composites appear to have a greater adsorption capacity for organic mercury species, suggesting that the donor atoms in the dithiocarbamate side group of dithiocarbamate-anchored polymer/organosmectite composites selectively coordinate with organomercury species. Adsorption capacities of raw smectite (S), quartamine smectite (QS) and dithiocarbamate modified PS/QS are given in Table 1 for Hg(II),  $\text{CH}_3\text{Hg(I)}$  and  $\text{C}_6\text{H}_5\text{Hg(I)}$  species. As seen in Table 1, regardless of mercury species, the adsorption capacity of the sorbents increases in the order of  $\text{PS/QS} > \text{QS} > \text{S}$ . Considering that the adsorption mechanism for raw smectite materials (S) is thought

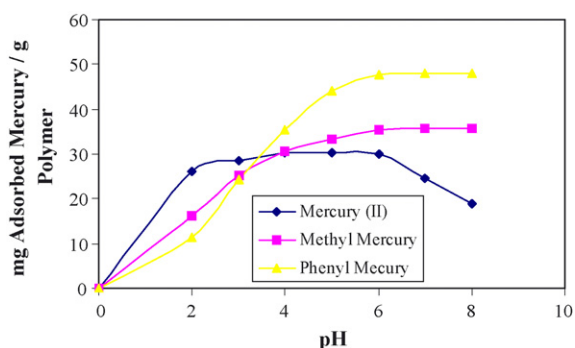


Fig. 4. The Effect of pH on the adsorption of mercury species dithiocarbamate-anchored composites at 25 °C. Initial concentration of the metal ions: 50 ppm.

Table 1

Adsorption capacities of raw smectite (S), quartamine smectite (QS) and dithiocarbamate modified PS/QS

Material	Q (mg/g)		
	Hg(II)	$\text{CH}_3\text{Hg(I)}$	$\text{C}_6\text{H}_5\text{Hg(I)}$
Raw smectite (S)	15.1	12.7	9.5
Quartamine smectite (QS)	13.4	21.6	20.4
Dithiocarbamate modified PS/QS	63.4	69.8	90.3

Amount of adsorption (mg/g).

to be of ion-exchange origin, some other mechanisms such as hydrogen bonding or hydrophobic interactions may be involved, which may also explain the reason for stronger adsorption interactions measured for more sophisticated synthetic smectite materials such as PS/QS.

### 3.2.4. Competitive adsorption

In addition to the affinity experiments mentioned above, competitive adsorption experiments with dithiocarbamate-anchored polymer/organosmectite and a ternary solution including Hg(II),  $\text{CH}_3\text{Hg(I)}$  and  $\text{C}_6\text{H}_5\text{Hg(I)}$  at 10 ppm concentration each were conducted at pH 6 and at 25 °C to determine the affinity order of dithiocarbamate-anchored polymer/organosmectite towards the mercury species. The adsorption capacities Q (mg metal ion/g sorbent) determined in these competitive experiments are presented in Table 2.

The competitive adsorption capacities are  $7.7 \text{ mg g}^{-1}$  ( $38.3 \mu\text{mol g}^{-1}$ ) for Hg(II);  $9.2 \text{ mg g}^{-1}$  ( $42.6 \mu\text{mol g}^{-1}$ ) for  $\text{CH}_3\text{Hg(I)}$ ;  $12.7 \text{ mg g}^{-1}$  ( $45.7 \mu\text{mol g}^{-1}$ ) for  $\text{C}_6\text{H}_5\text{Hg(I)}$  at 10 ppm initial concentration. As seen in Table 2, the affinity order of the dithiocarbamate-anchored polymer/organosmectite composites for the mercury ions under competitive conditions is  $\text{C}_6\text{H}_5\text{Hg(I)} > \text{CH}_3\text{Hg(I)} > \text{Hg(II)}$  on both weight and molar bases. The highest adsorptive capacity for  $\text{C}_6\text{H}_5\text{Hg(I)}$  can be best addressed by favorable hydrophobic interactions between the quartamine and styrene residues of the dithiocarbamate-anchored polymer/organosmectite composites structures, as schematically proposed in Fig. 1, and the aromatic group of  $\text{C}_6\text{H}_5\text{Hg(I)}$ .

## 4. Conclusion

Preparation of a novel sorbent system, namely the dithiocarbamate-anchored polymer/organosmectite composites, and the potential of employing such materials in removal pro-

Table 2

Competitive adsorption of mercury species on the dithiocarbamate-anchored composites

Species	Adsorbed mercury (mg g <sup>-1</sup> )	Adsorbed mercury ( $\mu\text{mol g}^{-1}$ )
Hg(II)	7.7	38.3
$\text{CH}_3\text{Hg(I)}$	9.2	42.6
$\text{C}_6\text{H}_5\text{Hg(I)}$	12.7	45.7

Initial concentration of each mercury species, 10 ppm; pH 6.0, temperature 25 °C.

cess of organic species and the inorganic mercury(II) ion from their aqueous solutions individually or as a mixture were presented and discussed in this paper. The adsorption behavior of the compared organic mercury species differs from the inorganic mercury ion due to the differences in the affinity of these mercury species for the electron donor atoms of the dithiocarbamate group of the dithiocarbamate-anchored polymer/organosmectite composites. Compared to raw smectite (S) and quartamine smectite (QS), dithiocarbamate modified PS/QS was found to have a greater adsorption capacity for Hg(II), CH<sub>3</sub>Hg(I) and C<sub>6</sub>H<sub>5</sub>Hg(I) because of higher affinities shown by dithiocarbamates for mercury species. Finally, the metal affinity order of dithiocarbamate modified PS/QS was found to be C<sub>6</sub>H<sub>5</sub>Hg(I) > CH<sub>3</sub>Hg(I) > Hg(II) on both weight and molar bases under competitive adsorption conditions. This finding is consistent with the hydrophobic structure of the nanolayers in dithiocarbamate modified PS/QS.

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