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REMOVAL OF COMPLEXED MERCURY FROM AQUEOUS SOLUTIONS USING DITHIOCARBAMATE GRAFTED ON SILICA GEL

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ABSTRACT

Sorption of mercury from aqueous solution by dithiocarbamate grafted on silica gel was investigated. The influence of pH, Hg^{2+} concentration, time, temperature, and presence of various anions and complexing agents on the sorption of mercury was studied. The sorption data obtained as a function of mercury concentration was fitted into a Langmuir adsorption model, which showed a sorption capacity of ~61 mg/g. Kinetic data indicated a very rapid sorption in the early stages of equilibration. The endothermic enthalpy change accompanied by the sorption of mercury from 0.1 M HCl media was found to decrease from 44.7 to 24.4 kJ/mol when the initial concentration of mercury was increased from 7.5×10^{-4} to 1.5×10^{-3} M.

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INTRODUCTION

The hazardous effects of heavy elements in the environment on human beings have limited their use considerably in various industries. However, with ever-increasing population and rapid industrial growth, the contamination of environment is inevitable due to the discharge of these metals from various industries (1). Serious outbreaks of mercury poisoning in Japan, Iraq, and Northern America have resulted in numerous deaths (2,3). Statutory bodies (WHO) have fixed the maximum allowable limit of mercury, in potable water at 1 μg/L and the maximum permissible tolerance level of intake by human beings at 43 μg/d of which not more than 29 μg/d should be methyl mercury (2,4). Thus, the increased awareness of toxicity of mercury and the stringent environmental safety regulations demand the removal of this heavy metal from the various discharges to avoid contamination of the geosphere and the biological ecosystem.

Organic extractants grafted on silica gel matrix, are well known for their applications in separation technology (5) and in recent years for the treatment of radioactive waste (6). Sulfur containing soft-base ligands, such as self-assembled mercaptans (7), and 2-mercaptoimidazole bonded on silica gel (8), were reported to form a strong complex with mercury and have been explored for the removal of mercury. Recently, we have studied the extraction properties of dithiocarbamate (dtc) grafted on silica gel for the removal of ^{60}Co from aqueous solutions (9). Coucouvanis (10) reported a stability constant of 1.2×10^{38} for $Hg(Et_2dtc)_2$ complex. Mahmoud (11) studied the extraction of mercury by dtc immobilized on silica gel as a function of pH and time.

In this paper, we report the results of the studies on the extraction properties of mercury from aqueous solutions by dtc grafted on silica gel (Si–dtc), as a function of pH, mercury concentration, time, and temperature.

EXPERIMENTAL

Materials

Silica gel (LR grade), of 60–120 mesh size, was obtained from S.D. Fine Chemicals, Mumbai, India. This was dried at 393K under vacuum for 24 hr before silyation. γ-Aminopropyltriethoxysilane was procured from Lancaster, UK. Analar grade carbon disulfide, isopropanol, toluene, methanol, and acetone were used. Mercury was obtained as $^{203}Hg(NO_3)_2$ in dilute nitric acid from Board of Radiation and Isotope Technology, Mumbai, India.

Preparation of Dithiocarbamate Anchored Silica Gel

Gafting of dtc on dried silica gel is reported elsewhere (9). The sequences of reactions are shown in Sch. 1. In the first step, a mixture containing silica gel (20 g), toluene (108 mL), and γ-aminopropyltriethoxysilane (12.5 mL) was refluxed for 6 hr. The mixture was filtered and washed, in sequence, with toluene, isopropanol, acetone, methanol, and acetone and was finally air-dried at room temperature to give product 1. This white colored product was then mixed with 100 mL of 0.1 *M* sodium hydroxide, 20 mL of isopropanol, and 16 mL of carbon disulfide and agitated for 4 hr. The mixture was filtered, washed with isopropanol, and air-dried at room temperature. The degree of functionalization of the yellowish-orange colored final product was determined by sulfur analysis.

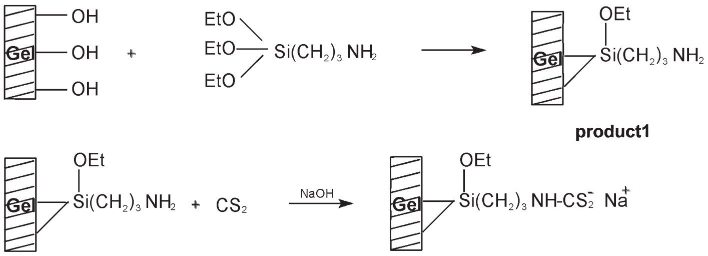
Mercury(II) Extraction Studies

Effect of pH

Sorption isotherm of mercury(II) ion as a function of pH was studied by equilibrating 0.05 g of the sorbent with 10 mL of the solution containing $5 \times 10^{-5}\,M$ Hg^{2+} added in the form of mercury(II) chloride, spiked with ^{203}Hg tracer at 298K for 6 hr. Acetic acid/sodium acetate buffer was used for experiments in the pH range 3–7, while 0.1 *M* HCl was used for experiments at pH 1. Radioassay of mercury was performed by measuring the γ-activity of the sample with a well-type NaI(Tl) scintillation counter. Distribution coefficient (K_d in mL/g) for mercury was derived using the Eq. (1)

$$K_d = \left(\frac{A_i - A_f}{A_f}\right)\left(\frac{V}{m}\right) \tag{1}$$

where A_i and A_f (cpm/mL) are the initial activity and activity at equilibrium,



Scheme 1. Reaction scheme to anchor dtc on silica gel.

respectively, *m* the weight (g) of the sorbent, and *V* the volume (mL) of aqueous solution used for equilibration.

Kinetic Studies

Sorption of mercury(II) ion as a function of time was studied by batch equilibration of 0.05 g of the sorbent with 10 mL of solution containing 0.1 *M* HCl and 5×10^{-5} *M* Hg^{2+} added in the form of mercury(II) chloride spiked with ^{203}Hg at 298K. The equilibration was stopped at pre-fixed time intervals. The solution phase activity was measured after centrifugation of the equilibration tube. From the initial activity and the activity measured at various intervals of time the percentage of mercury sorbed was calculated. The initial concentration of Hg(II) in the above experiment varied from 5×10^{-5} to 5×10^{-4} *M*. Similar experiments were also performed at pH 7, with acetic acid and sodium acetate.

Effect of Mercury Concentration

Sorption isotherm as a function of mercury concentration was obtained at 298K by equilibrating 0.05 g of the sorbent with 10 mL of the solution containing 0.1 *M* HCl spiked with ^{203}Hg tracer. The concentration of Hg^{2+} in this solution varied from 5×10^{-4} to 1.5×10^{-3} *M* by adding $HgCl_2$. After 2 hr of equilibration the mixture was centrifuged and the activity of the supernatant was measured as described above. Similar experiments were also performed at pH 7.

Effect of Temperature

Batch experiments were conducted at various temperatures ranging from 298 to 313K by equilibrating 0.05 g of Si–dtc with 10 mL of the solution containing 0.1 *M* HCl and 7.5×10^{-4} *M* Hg^{2+} added in the form of mercury(II) chloride spiked with ^{203}Hg tracer, for 2 hr. The distribution coefficient was measured as described above. The experiments were repeated for different initial concentrations of Hg(II) from 7.5×10^{-4} to 1.5×10^{-3} *M*.

Effect of Various Additives

The effect of various complexing agents on the sorption of mercury was studied by equilibrating 0.05 g of the sorbent with 10 mL of the solution containing 5×10^{-5} *M* Hg^{2+} added in the form of mercury(II) chloride spiked with ^{203}Hg tracer and 1.0 *M* interfering complexing agent. The pH of the stock solution was pre-adjusted to pH 7 by sodium acetate and acetic acid buffer. For studying the effect of ascorbic acid on the sorption of mercury by Si–dtc, the solution pH was maintained at 3.

RESULTS AND DISCUSSION

Characterization of Si–dtc by IR and ^{29}Si MAS-NMR have been described elsewhere (9). The sulfur analysis of the sorbent indicated the presence of 3.7×10^{-4} mol/g of dtc groups available for the formation of complex with the Hg(II) ion. Figure 1 shows the percentage of mercury sorbed by product (1) and Si–dtc as a function of pH. It is seen that the percentage of mercury sorbed for a particular pH is always higher for Si–dtc over product (1). This is due to the higher affinity of Si–dtc, a soft-base ligand donor, for Hg(II) over the product (1) wherein the nitrogen acts as donor.

Figure 2 shows the Langmuir isotherm for the sorption of mercury from 0.1 *M* HCl and pH 7 solution. The Langmuir equation governing the amount of metal ion sorbed and its concentration in solution is given by

$$\frac{C_\mathrm{f}}{C_\mathrm{s}} = \frac{1}{K\mathrm{b}} + \frac{C_\mathrm{f}}{b} \tag{2}$$

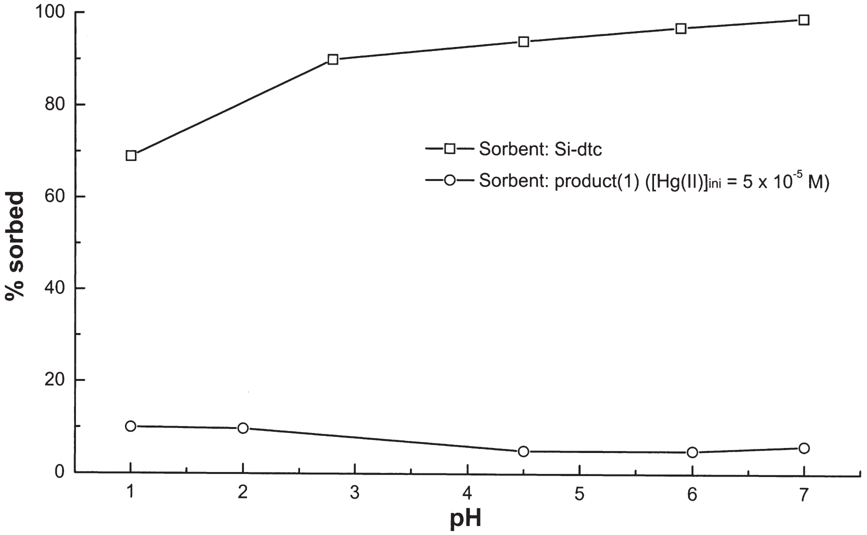


Figure 1. Variation of percentage of sorption of Hg(II) with pH on Si–dtc and product (1).

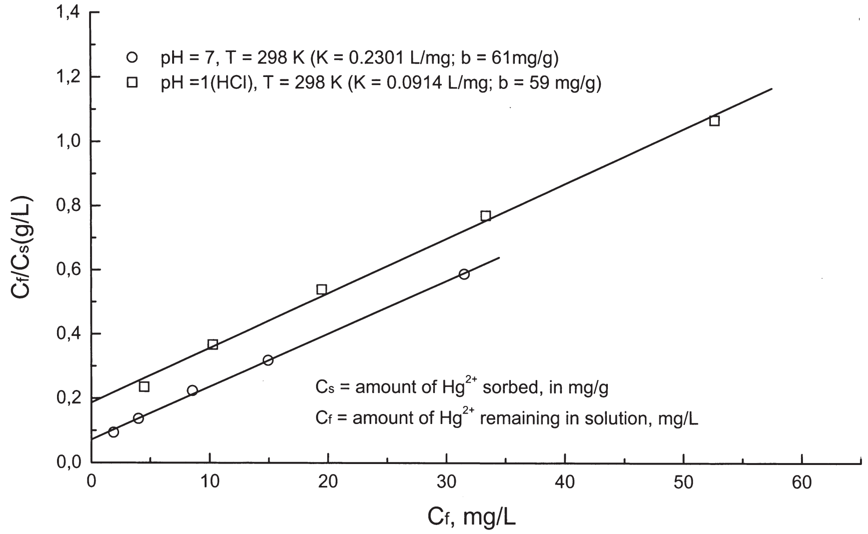


Figure 2. Langmuir adsorption isotherm for the sorption of mercury by Si–dtc as a function of pH.

where C_f is the equilibrium concentration of Hg (mg/L), C_s the amount of Hg sorbed on Si–dtc (mg/g), K the Langmuir adsorption constant (L/mg), and b the maximum amount of Hg that can be sorbed by the sorbent. Fitting of the sorption data by least squares method resulted in 0.2301 L/mg and 61 mg/g, for K and b, respectively, at pH $= 7$. In 0.1 M HCl, the values of K and b were found to be 0.0914 L/mg and 59 mg/g, respectively. The capacity values (b in mg/g) obtained from the Langmuir plot ($\sim 3\times10^{-4}\,\text{mol/g}$) are in close agreement with the degree of functionalization of silica determined by sulfur analysis ($=3.7\times10^{-4}\,\text{mol/g}$) of Si–dtc. This suggests that mercury in the sorbent phase could be forming a 1:1 complex with dtc. The nature of the complex in the adsorbed phase may be inferred from the nature of various kinds of mercury complexes existing in the aqueous solution (2). The expected fractional concentrations of mercury complexes that are present in significant quantity in the experimental solutions were calculated (12) and are shown in Fig. 3. However, for obtaining this diagram all the other possible complexes of mercury with various anions (e.g., nitrate) present in the experimental solution were taken into account.

It can be seen from Fig. 3 that neutral chloro complexes predominate when the pH of the solution is less than 5.5. As the pH of the solution is increased, the concentration of the chloro complexes decrease and the formation of hydroxy

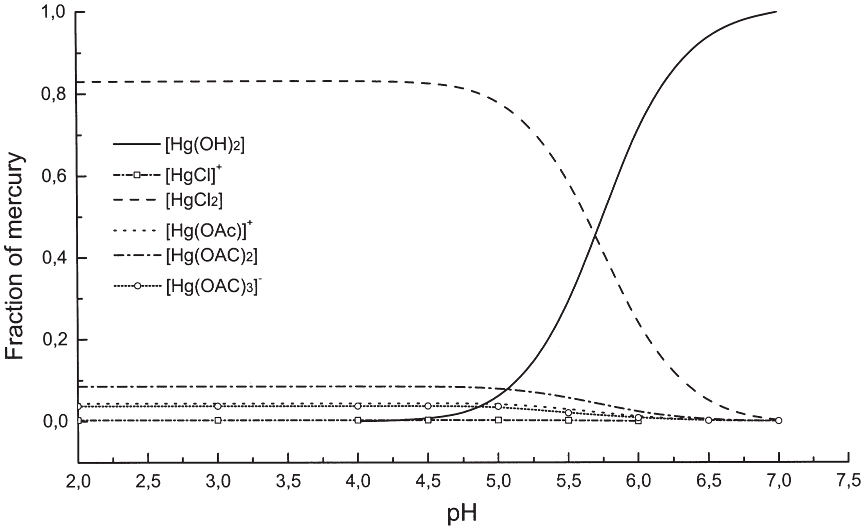


Figure 3. Variation of fractional concentration of mercury complexes with pH.

complex in aqueous solution increases. At pH 7, mercury exists fully in the form of $[Hg(OH)_2]$. The high Langmuir adsorption constant at $pH = 7$, indicates that dihydroxymercury(II) complex is more susceptible to the attack by the dtc ligands than the chloro complex present at pH less than 7. Further, in 0.1 *M* HCl medium, the calculated fraction of total anionic chloro complexes ($[HgCl_3]^- + [HgCl_4]^{2-} = 66\%$ of total mercury) is greater than the fraction of neutral chloro complex. These anionic species do not get attracted by the $-CS_2^-$ ligands of Si–dtc and also requires displacement of one or two Cl^- from the these complexes to form square planar complex, thus resulting in a low magnitude of sorption by Si–dtc at pH 1. This effect of chloro complexes in reducing the amount of mercury sorbed is consistent with literature reported earlier on the mercury sorption by various sorbents (13–15).

Figures 4 and 5 show the sorption of mercury as a function of time from solutions of pH 1 and 7, respectively. It can be seen that there is a very fast sorption in the early stages of the experiment followed by slower uptake. Nearly 70% of the total mercury is absorbed in the initial 5 min when the pH is 7 and in 30 min when pH is 1. The initial concentration of mercury does not have much impact on the percentage absorption. In all the cases, equilibrium is attained within 2 hr.

Kinetic data for the sorption of metal ions by various sorbents are normally described by first-order or second-order rate equation (16). However, the present

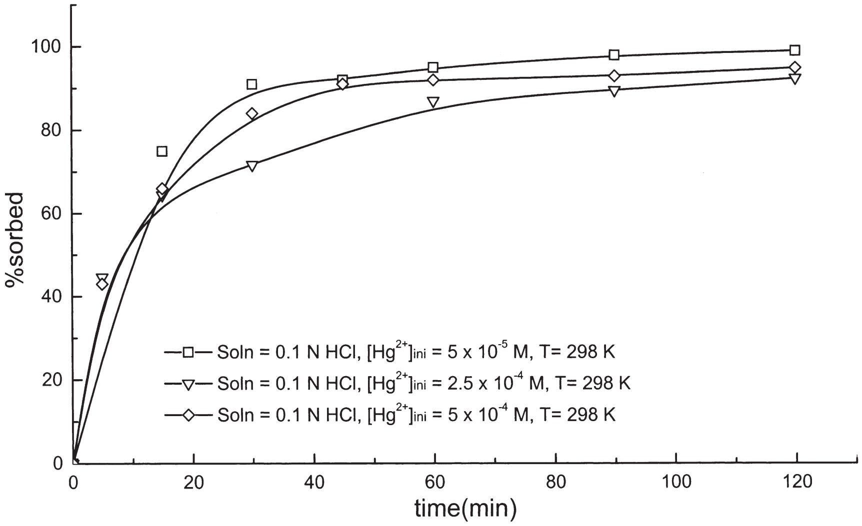


Figure 4. Variation of percentage sorption of Hg(II) with time (pH 1).

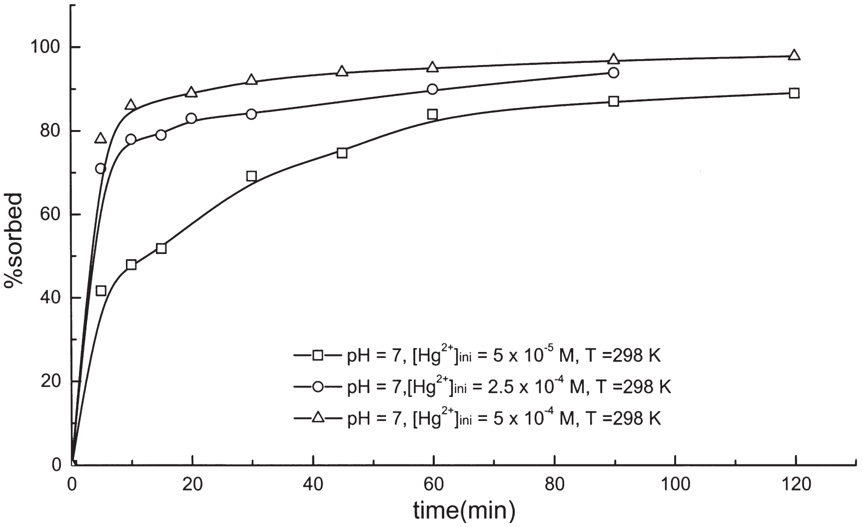


Figure 5. Variation of percentage sorption of Hg(II) with time (pH 7).

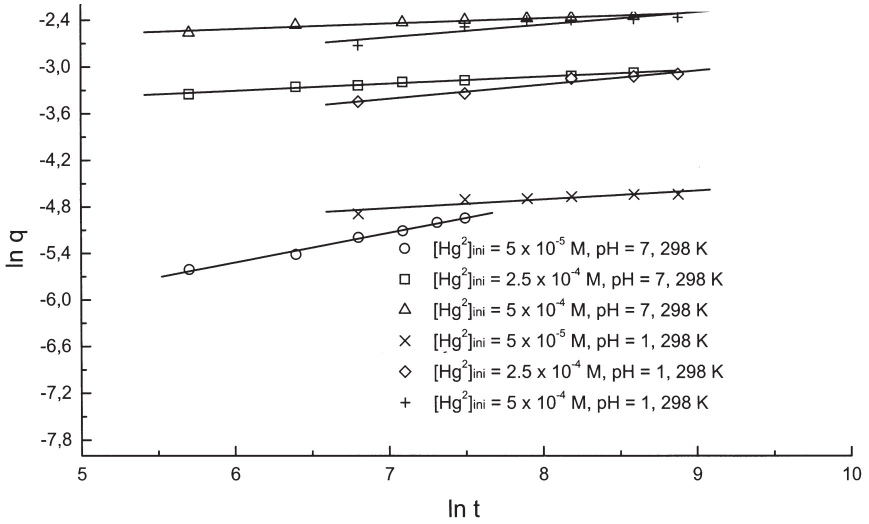


Figure 6. Variation of $\ln q$ with $\ln t$ for the sorption of mercury as a function of $[Hg^{2+}]_{ini}$ with pH.

experimental data do not fit into either of these rate equations. Kinetic data exhibiting a very rapid absorption at the beginning of the experiment followed by slower uptake was described by Ungarisch and Aharoni (17) and by others (7,15). The linearized form of the equation describing the amount of metal ion sorbed and time is shown in Eq. (3).

$$\ln q = \ln k + \frac{1}{\nu} \ln t \tag{3}$$

where q is the amount of mercury adsorbed at time t, and k and ν are constants. Figure 6 shows a plot of $\ln q$ against $\ln t$ and the constants obtained from this plot are shown in Table 1, which indicates that the constant (k) increases with increase in the initial concentration of mercury.

Figure 7 shows the plot of distribution coefficient as a function of fractional loading (the ratio of amount of mercury sorbed to maximum amount that can be sorbed) of mercury on Si–dtc. It indicates that the distribution coefficient decreases with the increase in mercury loading. At low fractional loadings, where most of the sites are not occupied by the mercury ion, a slight increase in the temperature results in a large increase in the distribution coefficient. As the sites are occupied progressively, the distribution coefficient for the sorption of Hg(II) decreases due to the decrease in the concentration of unoccupied sites. Thus, there is only a marginal increase in the distribution coefficient with temperature,

Table 1. Fitting Constants (k and ν) for the Sorption of Hg(II) from Solution of pH 1 and 7

$[Hg]_{ini}$ (M)	pH	k (mmol/g sec) $\times 10^2$	ν
5.0×10^{-5}	1	0.3596	8.6083
2.5×10^{-5}	1	0.9125	5.4262
5.0×10^{-4}	1	2.3008	6.0631
5.0×10^{-5}	7	0.0427	2.6055
2.5×10^{-5}	7	2.1108	10.8084
5.0×10^{-4}	7	5.2812	13.9938

which is observed at higher fractional loadings. Figure 8 shows the plot of $\log K_d$ against $1/T$ for the sorption of Hg(II) from $0.1\,M$ HCl. The nature of the straight lines suggests that the sorption process is endothermic and the enthalpy change (ΔH) for the sorption of mercury from $0.1\,M$ HCl solution by Si–dtc can be calculated approximately from the slopes of these straight lines using Eq. (4).

$$\log K_d = \left(\frac{-\Delta H}{2.303RT}\right) + \text{Constant} \tag{4}$$

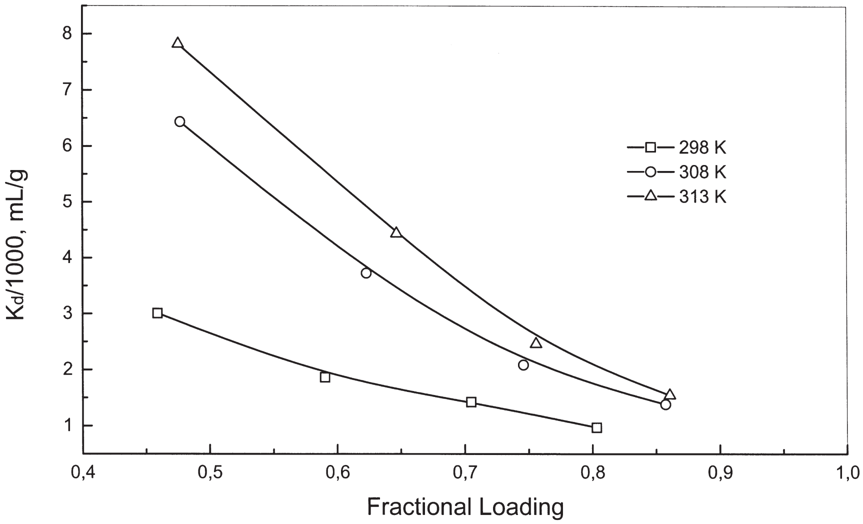


Figure 7. Variation of K_d with fractional loading of Hg(II) at pH 1.

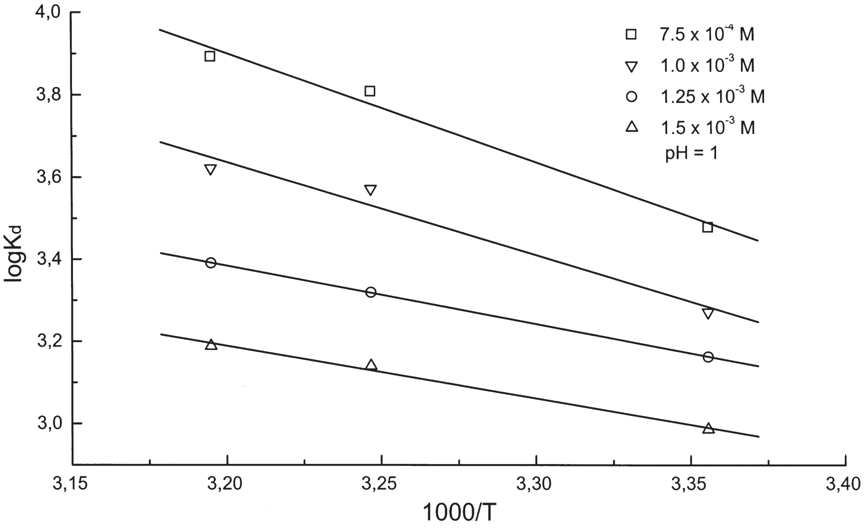


Figure 8. Variation of log K_d with $1/T$.

It is found that, when the initial concentration of mercury is increased from 7.5×10^{-4} to $1.5 \times 10^{-3}\,M$, ΔH decreases from 44.7 to 24.4 kJ/mol.

Table 2 shows the effect of additives on the distribution coefficient (K_d) of mercury. It is observed that the distribution coefficient of mercury in the presence of iodide, a soft-base ligand, is the lowest. This could be due to the formation of $[HgI_4]^{2-}$, which is inextractable by Si–dtc, as it was observed in the case of

Table 2. Effect of Various Complexing Agents on the Distribution Coefficient of Mercury

Complexing Agents (1 *M*)	K_d (mL/g)
Sodium acetate (pH = 7)	1653
Sodium fluoride (pH = 7)	1721
Sodium chloride (pH = 7)	568
Sodium iodide (pH = 7)	90
Sodium nitrate (pH = 7)	1688
Sodium citrate (pH = 7)	428
Sodium sulfate (pH = 7)	1425
Potassium thiocyanate (pH = 7)	660
Ascorbic acid (pH = 3)	283
Thiourea (pH = 7)	1645

choride ion. High uptake of mercury was observed even in solutions containing thiourea, suggesting that Si–dtc–Hg complex is more stable than Hg–thiourea complex.

CONCLUSIONS

Si–dtc, a sorbent grafted with soft-base ligand, can be used efficiently for the removal of mercury from the waste solutions containing various complexing agents. The maximum mercury sorption capacity by Si–dtc was found to be $\sim 61\,\mathrm{mg/g}$. This indicated that mercury in the sorbent phase may be forming a 1:1 complex with dtc. The sorption of mercury was seen to be rapid in the early stages. Nearly 70% of total mercury was absorbed from pH 7 solution within 5 min. The fitting constant (k) for the sorption process was found to increase with the increase in the initial concentration of mercury. The enthalpy change for the sorption of mercury from 0.1 M HCl medium was found to decrease from 44.7 to 24.4 kJ/mol when the initial concentration of mercury was increased from 7.5×10^{-4} to $1.5 \times 10^{-3}\,M$.

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REFERENCES

1. Cheremisinoff, N.P. *Handbook of Industrial Toxicology and Hazardous Materials*; Marcel Dekker, Inc.: New York, 1999; 399.
2. Fergusson, J.E. *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*; Pergamon Press: New York, 1990; 533.
3. Takizawa, Y. Epidemiology of Mercury Poisioning. In *The Biogeochemistry of Mercury in the Environment*; Nriagu, J.O., Ed.; Elsevier: North Holland, 1979; 325.
4. Goel, P.K.; Sharma, K.P. *Environmental Guidelines and Standards in India*; Technoscience Publications: India, 1996; 15.
5. Fatunmbi, H.O.; Bruch, M.D.; Wirth, M.J. ^{29}Si and ^{13}C NMR Characterization of Mixed Horizontally Polymerized Monolayers on Silica Gel. Anal. Chem. **1993**, *65*, 2048–2052.
6. Bulman, R.A.; Szabo, G.; Clayton, R.F.; Clayton, C.R. Investigation of the Uptake of Transuranic Radionuclides by Humic and Fulvic Acids

Chemically Immobilized on Silica Gel and Their Competitive Release by Complexing Agents. Waste Manag. **1997**, *17*, 191–199.

7. Mattigod, S.V.; Feng, X.; Fryxell, G.E.; Liu, J.; Gong, M. Separation of Complexed Mercury from Aqueous Wastes Using Self-assembled Mercaptan on Mesoporous Silica. Sep. Sci. Technol. **1999**, *34*, 2329–2345.
8. Dias Filho, N.L.; Gushikem, Y. 2-Mercaptoimidazole Covalently Bonded to a Silica Gel Surface for the Selective Separation of Mercury(II) from an Aqueous Solution. Sep. Sci. Technol. **1997**, *32*, 2535–2545.
9. Venkatesan, K.A.; Srinivasan, T.G.; Vasudeva Rao, P.R. Cobalt Extraction Studies on Dithiocarbamate Grafted on Silica Gel Surface. Colloids Surf. A: Physicochem. Eng. Aspects **2001**, *180*, 277–284.
10. Coucouvanis, D. The Chemistry of Dithioacid and 1,1-Dithiolate Complexes. Prog. Inorg. Chem. **1970**, *11*, 233–371.
11. Mahmoud, M.E. Selective Extraction of Mercury(II) by Silica Gel-Immobilized-Dithiocarbamate Derivatives. Anal. Chim. Acta **1999**, *380*, 297–304.
12. Venkataramani, B.; Gupta, A.R. Sulfate Complexes of Hydrolyzed Uranyl Species in Solution: Formation Constant of $(UO_2)_2(OH)_2SO_4$. Indian J. Chem. **1990**, *29A*, 373–375.
13. Chen, X.; Feng, X.; Liu, J.; Fryxell, G.E.; Gong, M. Mercury Separation and Immobilization Using Self-assembled Monolayers on Mesoporous Supports. Sep. Sci. Technol. **1999**, *34*, 1121–1132.
14. Forbes, E.A.; Posner, A.M.; Quirk, J.P. The Specific Adsorption of Inorganic Hg(II) Species and Co(III) Complex Ions on Goethite. J. Colloid Interface Sci. **1974**, *49*, 403–406.
15. Ansari, M.H.; Deshkar, A.M.; Kelkar, P.S.; Dharmadhikari, D.M.; Hasan, M.Z.; Paramasivam, R. Mercury Removal from Waste Water by Steamed Hoof Powder. Water Sci. Technol. **1999**, *40*, 109–116.
16. Sparks, D. *Kinetics of Soil Chemical Processes*; Academic Press, Inc.: CA San Diego, California, 1989; 4.
17. Ungarisch, M.; Aharoni, C. Kinetics of Chemisorption: Deducing Kinetics Laws from Experimental Data. J. Chem. Soc., Faraday Trans. **1981**, *77*, 975–985.

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