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Adsorptive Demercuration by Virtue of an Appealing Interaction Involving Biopolymer Cellulose and Mercaptobenzothiazole

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ABSTRACT: In this work, we present an interesting method for the adsorption of Hg(II) involving its interaction with cellulose and mercaptobenzothiazole (MBT). This affinity could be realized with cellulose and MBT acting as host and guest in the first instance followed by the subsequent complexation of Hg(II) with MBT. The soft–soft interaction between Hg(II) and sulfur enhances the effective complexation with MBT. The favorable experimental conditions, isotherm models, mechanism of interaction, and thermodynamics are discussed. The negative values of free energy obtained at various temperatures and the endothermic adsorption process affirms the spontaneity of adsorption. FT-IR, SEM, EDS, and XRD techniques were utilized to characterize the MBT impregnated cellulose as well as the Hg(II)-loaded adsorbent. With a high adsorption capacity of 204.08 mg g^{-1} a sample volume of 500 mL could be quantitatively treated by column method. Potassium thiocyanate functions as a valuable reagent for the desorption of Hg(II). The practical application was tested for the adsorption of mercury vapor emanating from a used Compact Fluorescent Lamp (CFL).

1. INTRODUCTION

The rising concern for heavy metal pollution has triggered the development of effective adsorbent materials for their remediation.[1] Among the various heavy metals, focus toward alleviating Hg(II) pollution is important in view of its high toxicity.[2] The contamination of Hg(II) from coal combustion[3] is an important issue, since particulate Hg(II) that emanates from fly ash can cause considerable contamination to the atmosphere. Multifarious adsorbents with good potential are known to decontaminate Hg(II). Some of the noteworthy adsorbent materials include activated carbon,[4] chitosan,[5] mercaptothiazoline modified mesoporous silica,[6] microporous titanosilicate,[7] and silica grafted vinyl imidazole.[8] The interaction of Hg(II) with silver nano particles using amino propyl trimethoxy silane as the anchoring agent has been reported.[9] Pyrene based amphiphilic ligand[10] is also known for its potential toward sensing and separation of Hg(II).

The excellent ability of Hg(II) to behave as a typical soft acid[11] is well suited to interact with ligands containing sulfur as the heteroatom. Thiol functionalized silica[12] and ultra stable thiol containing ethane bridged mesoporous organo silica adsorbents[13] are known for their ability to bind Hg(II). Mercaptobenzothiazole is an excellent sulfur ligand known to adsorb and form strong complexes with transition metal ions.[14−16] Chelating 2-mercaptobenzothiazole loaded resin,[17] aminopropylbenzoylazo-2-mercaptobenzothiazole bonded to silica gel,[18] 2-mercaptobenzimidazole-clay,[19] and benzenedithiol modified cellulose resin[20] are some of the sulfur containing ligands used in conjunction with good solid supports for the adsorption of Hg(II). Cellulose grafted with glycidyl methacrylate and functionalized with thiosemicarbazide has been used for the effective adsorption of Cd(II), Hg(II), and acid fuchsin from aqueous solutions.[21]

Although an array of solid supports are in vogue, reports on the interaction of biopolymers with sulfur ligands are scarce. Furthermore, the interaction of cellulose with mercaptobenza-thiazole has not been reported. In order to seek a suitable host to this ligand, biopolymers such as cellulose prove to be a very good choice. Cellulose is a well-known biodegradable polymer and was first described in 1838 by Payen as a fibrous material. This naturally occurring polysaccharide, $(C_6H_{10}O_5)_n$, has anhydroglucose rings as the repeat unit with a β-1,4 glucosidic bond. The value of n varies with the source of cellulose and could range anywhere between 10000 and 15000. The biopolymer exhibits intermolecular hydrogen bonding between the chains, and this stabilizes the polysaccharide.[22,23] The strength of the cellulose fibrils could be attributed to the intra- as well as intermolecular hydrogen bonding. The stacking between the chains is also facilitated by van der Waals interaction. Crystalline cellulose exists as two distinct allomorphs I$_\alpha$ and I$_\beta$. The hydroxyl groups present in cellulose are vital in interacting with the metal cations. The excellent properties attributed to this polysaccharide[24] such as biodegradability, good stability, intramolecular hydrogen bonding, etc. prompted us to explore its potential for the effective interaction with mercaptobenzothiazole. This affinity leads to a subsequent secondary interaction with Hg(II) as the guest. Indeed, this triangular interaction between cellulose, MBT, and Hg(II) results in the effective adsorption of Hg(II), and the efforts directed toward the development of this methodology are reported in this paper.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Analytical grade reagents were used as such without further purification. Milli Q water (Elix 3) as used to prepare aqueous solutions of Hg(II) of varying concentrations. The biopolymer, cellulose, was obtained from Himedia, India.
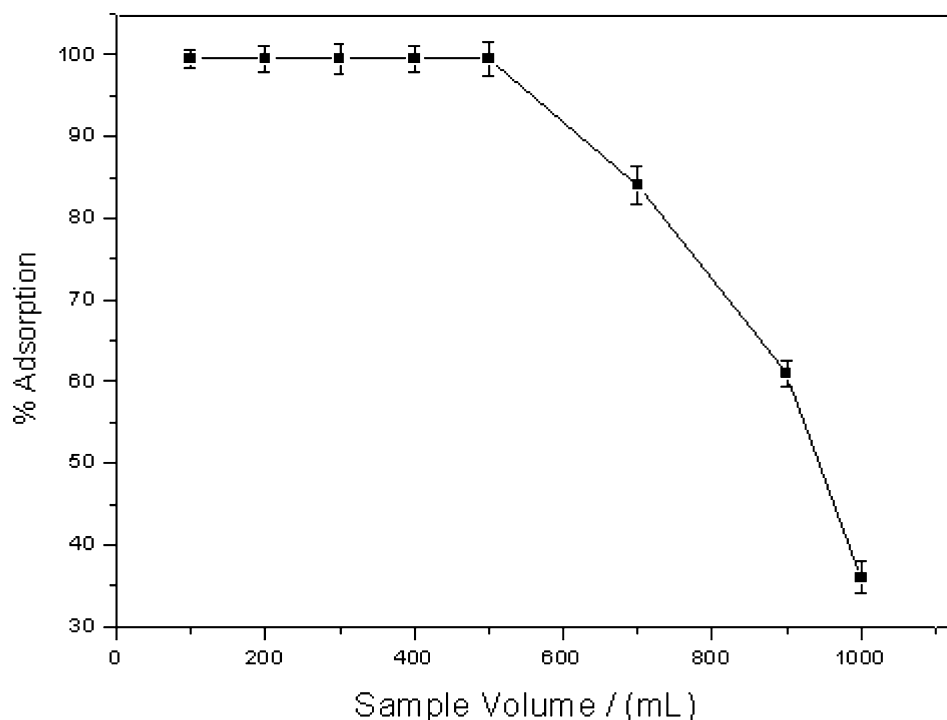
Figure 1. Variation of sample volume.

Hg(II) chloride was procured from Merck, India, and 2-mercaptobenzothiazole was obtained from Sigma Aldrich. A working solution of 100 mg L^{-1} Hg(II) was prepared by appropriate dilution from 1000 mg L^{-1} Hg(II). The other necessary reagents required for adsorption studies were procured from Merck, India.

2.2. Instrumentation. The analysis of Hg(II) was performed using a Hg(II) analyzer (MA 5840, ECIL India Ltd.) by the cold vapor atomic absorption technique wherein stannous chloride in acidic medium was used to reduce the Hg(II) to mercury vapor. The pH adjustments of the aqueous solutions were done using an Elico LI-127 pH meter supplied by Elico, India. An incubator shaker was procured from Biotechnics, India. A Jasco-4200 FT-IR spectrometer was used to characterize the functional groups in the cellulose-MBT adsorbent in the range 400−4000 cm^{-1}. A Philips PANalytical X'pert PRO diffractometer operating at 40 kV and 30 mA with a step size of 0.017° was utilized to record the characteristic changes in the diffraction pattern of the adsorbent material. A Hitachi S-3000H and JEOL JSM-6390 analyzer were used to observe the morphological changes in the adsorbent and record the energy dispersive X-ray spectrum (EDS) from batch studies after the adsorption of Hg(II). The release of mercury from CFL was ascertained from the EDS spectrum recorded using JEOL JSM-6390 analyzer.

2.3. Adsorbent Preparation, Pilot Batch, and Fixed Bed Column Study. The ligand 2-mercaptobenzothiazole (0.01 mol) was dissolved in 15 mL of acetone. Two g of cellulose was taken in a round-bottom flask, 15 mL of the ligand was added gradually, and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was filtered, washed with acetone, dried at room temperature, and used for adsorption studies. Batch adsorption tests were carried out by equilibrating (30 mL of 100 mg L^{-1} Hg(II) solution) adjusted to pH 4 with 0.2 g of the cellulose-MBT adsorbent material. The equilibration was carried out at 150 rpm for different time intervals using an orbital incubator shaker. The adsorption of Hg(II) was

ascertained by measuring the concentration left in the aqueous phase using Cold Vapor-Atomic Absorption Spectrophotometric (CV-AAS) method.[25] The difference between the initial Hg(II) concentration, C_o, and the aqueous phase concentration at equilibrium, C_e, was utilized in calculating the equilibrium amount (q_e) of Hg(II) adsorbed onto the cellulose-MBT adsorbent material. The relation between the above parameters, volume (V) of the aqueous phase in liters, and the weight (W) of the adsorbent material could be expressed as

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

The fixed bed column studies were also performed using a glass column (4 cm diameter, 25 cm length) loaded with 2.5 g of the prepared cellulose-MBT adsorbent at a packing height of 3.5 cm. Maintaining a flow rate of 5 mL min^{-1} and a bed height of 3.5 cm, a 100 mL volume of 30 mg L^{-1} Hg(II) was delivered onto the column, and the concentration after adsorption was measured using the CV-AAS technique. The adsorption of Hg(II) was quantitative (99.0%) with an average error of ±0.5% for three replicate measurements. An optimized flow rate of 5 mL min^{-1} at 30 mg L^{-1} Hg(II) ensured effective interaction of the cellulose-MBT adsorbent with Hg(II). The adsorption was also quantitative till a 500 mL sample volume (Figure 1). At a breakthrough volume of 500 mL and 100 mg L^{-1} Hg(II), the q_e value was found to be 15.2 mg g^{-1}, while the q_e value obtained experimentally by batch study was found to be 14.9 mg g^{-1}. Furthermore, in a fixed bed column operation, the rate of deactivation of the cellulose-MBT adsorbent can be expressed in terms of the adsorbent exhaustion rate (AER) which is defined as the ratio of the mass of the adsorbent (g) to the maximum volume treated (L). A low AER value signifies the effectiveness of the performance of the fixed bed column.[26] The AER value for the present system was found to be 5.0 g L^{-1}. At higher volumes, the effectiveness of adsorbent−adsorbate interaction decreases, thereby signifying the saturation of the adsorption bed.
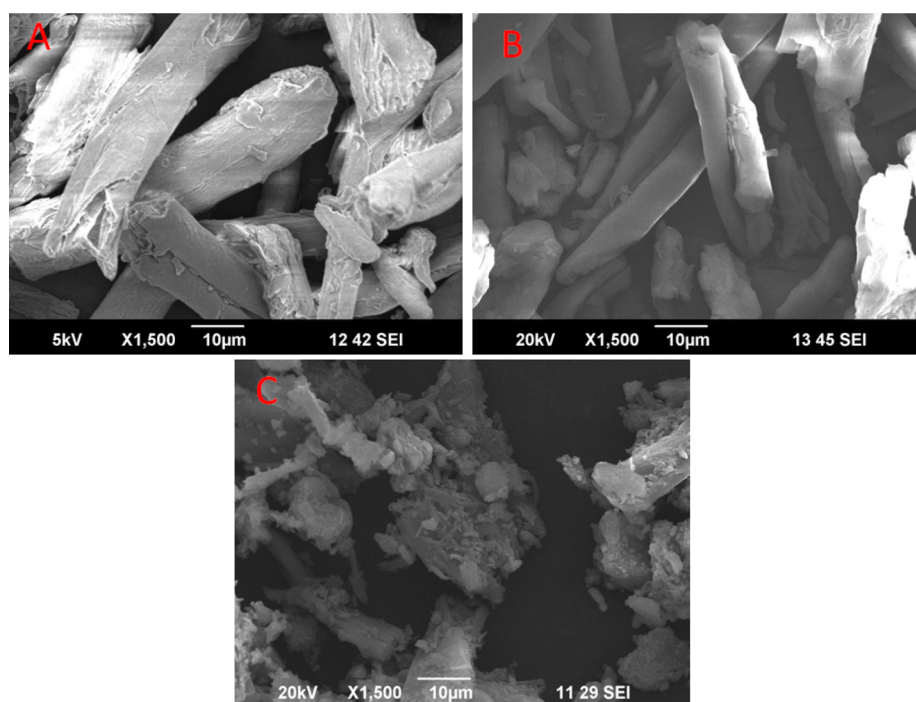
Figure 2. SEM images: (a) cellulose, (b) mercaptobenzothiazole impregnated cellulose adsorbent, and (C) after the adsorption of Hg(II).
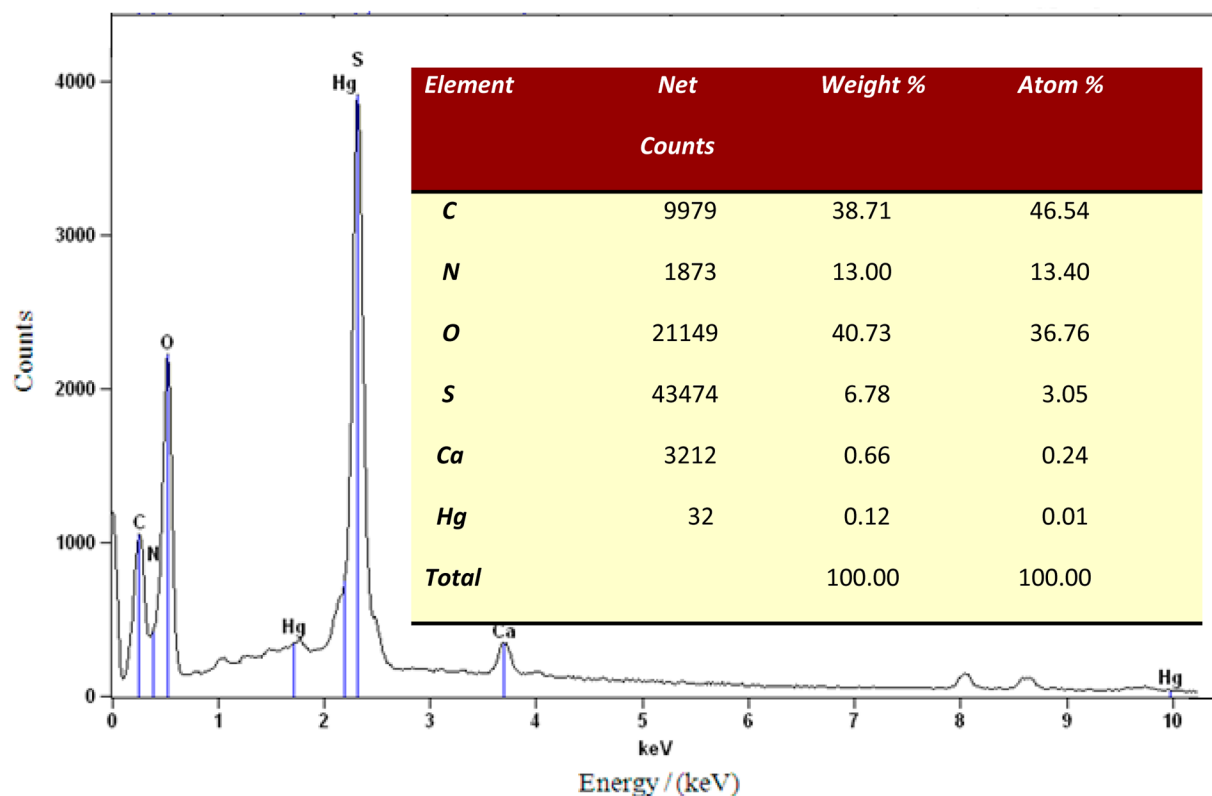

Element	Net Counts	Weight %	Atom %
C	9979	38.71	46.54
N	1873	13.00	13.40
O	21149	40.73	36.76
S	43474	6.78	3.05
Ca	3212	0.66	0.24
Hg	32	0.12	0.01
Total		100.00	100.00

Figure 3. EDS spectral analysis showing the presence of adsorbed Hg(II).

3. RESULTS AND DISCUSSION

3.1. Surface Morphological Changes and XRD Pattern of the Adsorbent. The SEM images taken prior and after the adsorption of Hg(II) exhibits (Figure 2) some observable changes in the surface morphology of the cellulose-MBT adsorbent with regard to the porosity and surface homogeneity.

The adsorption of Hg(II) on the surface of 2-mercaptobenzo-thiazole impregnated the cellulose adsorbent was also confirmed through the energy dispersive X-ray (EDS) spectral analysis (Figure 3). The adsorption of Hg(II) was evident from the characteristic peak in the range 1−3 keV along with C, O, N, and S typical of the adsorbent.[27] The X-ray diffraction pattern of the adsorbent gives valuable insight into the crystalline or

amorphous nature of the adsorbent. The initial amorphous feature of the adsorbent assumes a slight crystalline nature as evident from the sharpening of the peaks after the adsorption of Hg(II). The XRD pattern of the cellulose shows peaks (Figure 4)
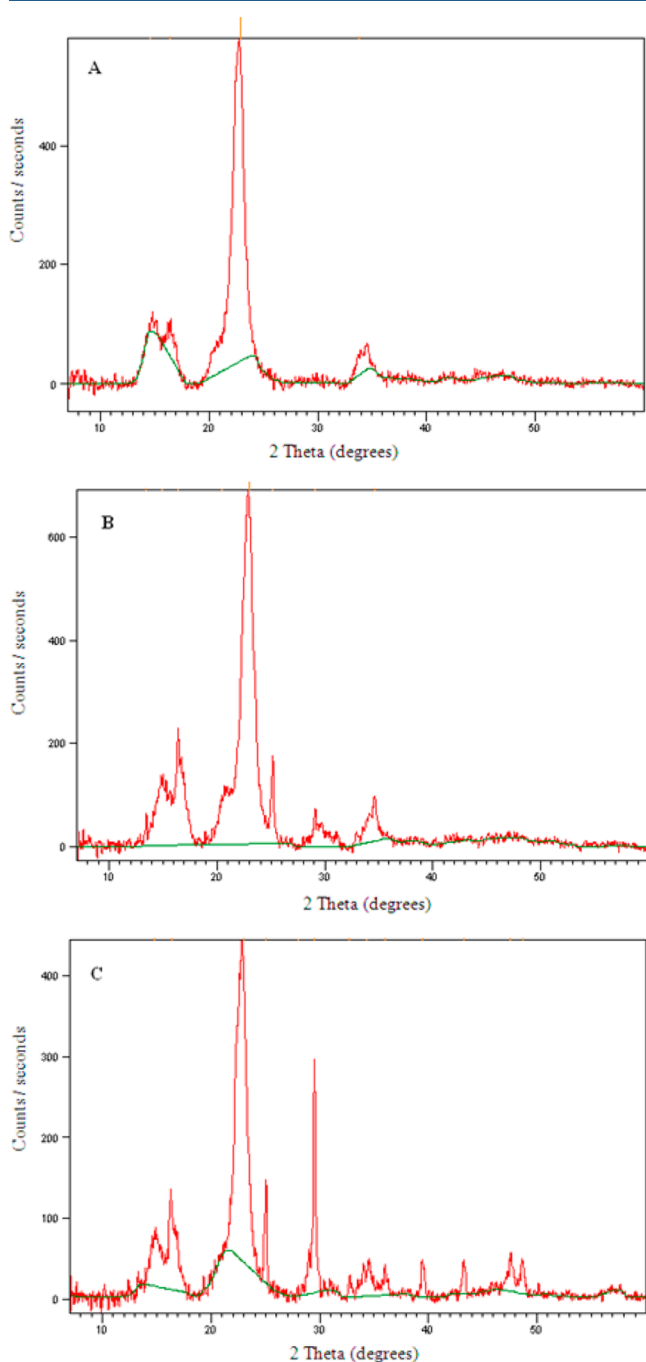

Figure 4. XRD pattern: (a) cellulose, (b) mercaptobenzothiazole impregnated cellulose adsorbent, and (c) after the adsorption of Hg(II).

corresponding to 2θ values 14.77°, 16.44°, 22.71°, and 34.62°, respectively.[28] The interaction of 2-mercaptobenzothiazole with cellulose yields new peaks at 13.41°, 15°, 15.56°, 25.19°, 29°, and 34.86°, respectively. The average crystallite size of this adsorbent was calculated using the Debye-Scherer's eq $(0.9\lambda/\beta \cos \theta)$ where 'λ' is the wavelength of X-ray and β is the full width half-maximum of the diffraction peak. The average crystallite size of the cellulose-MBT adsorbent was found to be 24.45 nm. The

secondary interaction of Hg(II) with the cellulose-MBT adsorbent gives characteristic peaks at 29.50°, 39.44°, 47.67°, and 48.85°. These results indicate that the metal ion can penetrate easily onto the adsorbent surface and interact effectively with the functional groups present in cellulose as well as the hetero atoms present in the ligand.

3.2. Mechanism, FT-IR Analysis and Thermodynamics of the Adsorption Process. The interaction of Hg(II) with MBT on the cellulose matrix depends on the pH of aqueous medium. The pH for effective complexation was observed to be greater than 90% in the range (3−4.0). Nevertheless, pH 4.0 gave higher adsorption efficiency, and beyond this value (Figure 5),
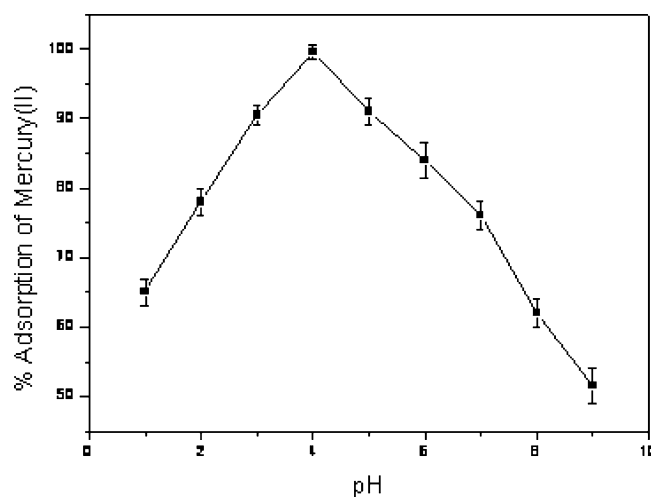

Figure 5. Effect of pH.

there was an apparent decrease in the percentage adsorption. This could be ascribed to the formation of hydroxy species of Hg(II) such as $Hg(OH)_2$, $Hg(OH)^+$ at higher pH range.[29] The sorption of heavy metals involves the interaction of the functional groups on the sorbent through ion exchange, complexation, and electrostatic interaction. The overall interaction involves affinity between the three species (Figure 6). The primary interaction would involve the hydrogen bonding between the hydroxyl
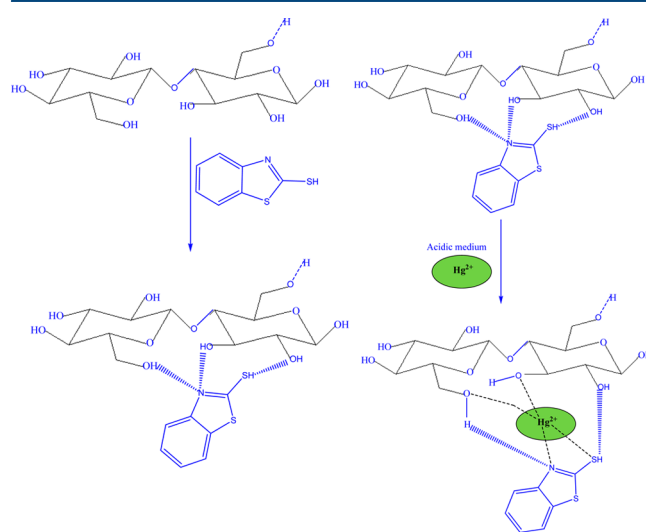

Figure 6. Conceptual illustration portraying the interaction of cellulose, MBT, and Hg(II).

groups in cellulose and the S as well as N atoms present in the ligand. The lone pair directionality is quite important in the hydrogen bonding[30] involving the N···H−O and S−H···O interactions. Herein, cellulose acts as an effective host, and the guest MBT can enter the voids present in the cellulose polymeric chain as well as physically adsorb through van der Waals, hydrogen bonding, and dipole−dipole interactions onto the surface of the biopolymer. The subsequent interaction would involve the affinity of Hg(II) with the biopolymer as well as the ligand. The mechanism of Hg(II) adsorption onto mercapto-benzothiazole-impregnated cellulose involves intermolecular hydrogen bonding, chelation (co-ordination), and electrostatic interaction.[28] Hg(II) being a typical soft acid has the ability to coordinate with sulfur and nitrogen in MBT to form a stable metal chelate-complex. The lone pair of electrons in the cellulose hydroxyl groups could also interact with the metal ion through ion-dipole interactions. The FT-IR spectra (Figure 7) of
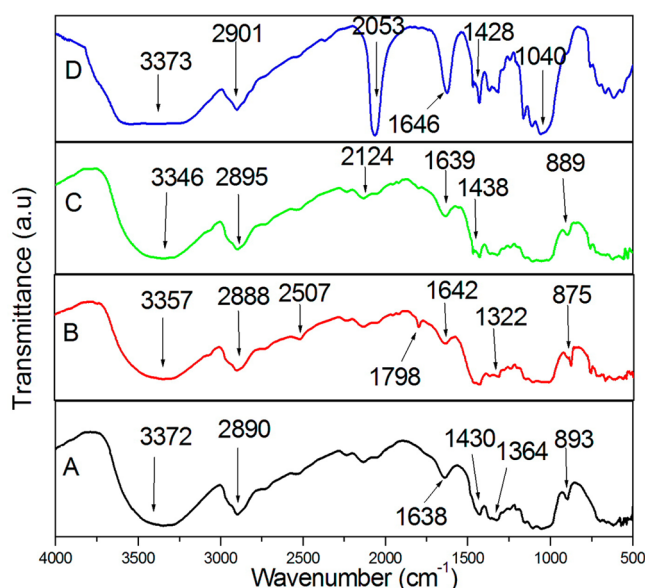

Figure 7. FT-IR spectrum of (a) cellulose, (b) cellulose-MBT adsorbent, (c) after the adsorption of Hg(II), and (d) after the desorption of Hg(II).

cellulose, mercaptobenzothiazole impregnated cellulose, and Hg(II)-treated adsorbent were examined in order to understand the interaction. The FT-IR spectrum of the polysaccharide cellulose which fundamentally comprises of several D-glucose units shows prominent peaks characteristic of O−H, C−O, and glycosidic linkages.[31] The peaks at 2890 cm^{-1} and 3372 cm^{-1} could be attributed to the C−H and O−H stretching, respectively. An O−H deformation peak was observed at 1430 cm^{-1} and 1364 cm^{-1}. The peaks in the range 889−893 cm^{-1} could be assigned to the C−O−C stretching in the glycosidic linkages of the polysaccharide. The ring stretching of glucose was observed at 1112 cm^{-1}. The peak due to C−O stretching vibrations in cellulose was observed at 1035 cm^{-1}. The cellulose-MBT adsorbent shows characteristic peaks in the range 2500−2600 cm^{-1} attributed to the polarizable S−H stretching,[32] and the peak at 1642 cm^{-1} could be ascribed to the C=N stretching vibration. The C−N (phenyl carbon−nitrogen bond) stretching frequency was observed at 1322 cm^{-1}.[33] It has been reported through density functional theory calculations that the C−S stretching frequency in the IR spectrum of MBT could range

between 572 and 876 cm^{-1}, and notably the significant peak observed at 875 cm^{-1} could be attributed to the C−S region. The partial oxidation of cellulose could lead to the introduction of the carbonyl functional group observed[34] at 1798 cm^{-1}. After the adsorption of Hg(II), the changes are reflected by the appearance of new peaks at 889 cm^{-1}, 1639 cm^{-1}, and 3346 cm^{-1}. These changes indicate that the chelation of Hg(II) with MBT could occur through the sulfur and nitrogen atoms. The change in the O−H stretching frequency also indicates the plausible electrostatic interaction of Hg(II) with the lone pair of electrons present in the oxygen atom of cellulose hydroxyl groups.[35] The ligand MBT could be conformationally oriented in the cis or trans form depending on whether the S−H bond eclipses the C=N or the C=S bond.[36] It is more probable that in cis form the interaction of Hg(II) would be more facile with the hetero atoms sulfur and nitrogen. Furthermore, when 2-mercaptobenzothiazole approaches the host biopolymer in the reaction medium, a disorder accompanied by translational entropy gain[36] results in the positive entropy in this primary interaction. Essentially, the biopolymer has to be conveniently oriented in order to hold the ligand in the layer between the polymeric chains and promote good interaction with the hetero atoms present in the ligand. This could be further corroborated by taking into account the respective Gibb's free energy changes[29] associated with cellulose, 2-mercaptobenzothiazole, and Hg(II).

$$\Delta G_{biopolymer} = \Delta H_{biopolymer} - T\Delta S_{biopolymer} \qquad (2)$$

$$\Delta G_{(MBT)} = \Delta H_{(MBT)} - T\Delta S_{(MBT)} \qquad (3)$$

$$\Delta G_{Hg(II)} = \Delta H_{Hg(II)} - T\Delta S_{Hg(II)} \qquad (4)$$

$$\Delta G_{adsorption} = \Delta H_{adsorption}$$
$$- T(\Delta S_{biopolymer} + \Delta S_{(MBT)} + \Delta S_{Hg(II)}) \qquad (5)$$

The entropy factor on the whole depends on the contribution that stems from the corresponding entropy changes associated with cellulose, 2-mercaptobenzothiazole, and the metal ion. Hence, the $T\Delta S$ term becomes more positive, and this implies that the physicochemical adsorption process is spontaneous. The study of the adsorption of Hg(II) onto the cellulose-MBT adsorbent at different temperatures gives the valuable thermodynamic parameters and also aids in further corroborating the adsorption mechanism. The Van't Hoff equations relate the equilibrium constant to the Gibb's free energy, entropy, and enthalpy of adsorption as follows[37]

$$\Delta G^0 = -RT \ln K \qquad (6)$$

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{-\Delta S^0}{R} \qquad (7)$$

The standard reaction Gibb's energy is negative when the adsorption process is endothermic and $T\Delta S_{ads}$ is fairly large and positive. Hence, for an endothermic adsorption process to be spontaneous, the reaction entropy has to be positive,[38] and furthermore the temperature should be high enough for $T\Delta S_{ads}$ to be greater than ΔH_{ads} The spontaneity of the adsorption process is linked to the equilibrium constant (K) and the free energy values. If $\Delta G^0 < 0$, then $K > 1$ is in accordance with eq 6, and this implies that the adsorption of Hg(II) is effective and spontaneous at a given temperature. As evident from Table 1, K

values were found to increase with temperature with a corresponding decrease in the free energy.

Table 1. Thermodynamic Parameters for the Adsorption of Hg(II)

temp (K)	ΔG^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	ΔH^0 (kJ mol^{-1})
303	−4.17	279	81
313	−5.86		
323	−7.63		
333	−13.71		

The equilibrium constant K was acquired from the ratio of concentration of Hg(II) adsorbed on the 2-mercaptobenzothiazole impregnated cellulose adsorbent to that in the aqueous phase. The positive and negative values of ΔH^0 would give an insight into the exo- or endothermic nature of adsorption. The Van't Hoff plot (Figure 8) with a correlation coefficient value of
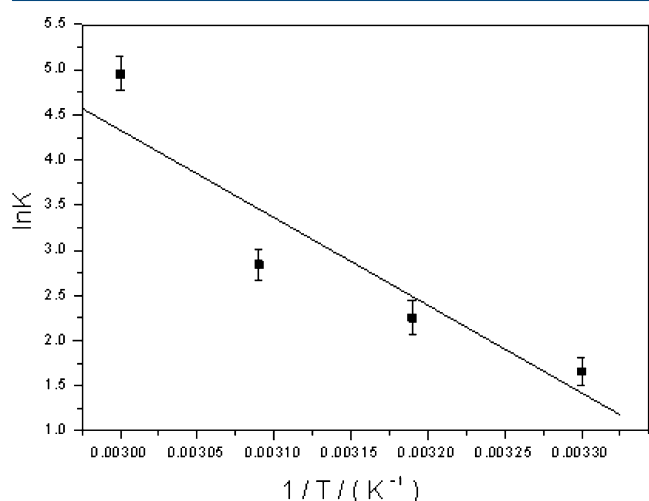

Figure 8. Variation of equilibrium constant with temperature.

0.92 yields the ensuing enthalpy and entropy changes associated with the adsorption process. The ΔG^0 values were observed to be negative with varying temperatures thereby leading to the rational conclusion that the adsorption is indeed spontaneous and endothermic (Table 1). Since, Hg(II) is a typical soft acid, it interacts effectively with sulfur and nitrogen atoms of the ligand. The negative free energy (ΔG^0) values confirms the effectiveness of the affinity between cellulose, 2-mercaptobenzothiazole, and Hg(II). The magnitude of ΔH^0 is generally less than 80 kJ mol^{-1} for physisorption, while for chemical adsorption it is in the range 80−400 kJ mol^{-1}.[39] The positive entropy and enthalpy changes associated with the adsorption also reflect the randomness at the adsorbent-solution interface, endothermic adsorbent−adsorbate interaction, and the decrease in the hydration of the ions. This process augments the total degrees of freedom thereby ensuring the effective interaction between the metal ion and the cellulose-MBT adsorbent.

3.3. Adsorption Kinetics and Isotherm Models. The experimental data obtained from the adsorption of Hg(II) onto the MBT-cellulose adsorbent were assessed using the familiar Lagergen[40] and Ho[41] first- and second-order kinetics.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \qquad (9)$$

The plot of log ($q_e - q_t$) against t (Figure 9a) and t/q_t against t (Figure 9b) would yield the required kinetic parameters. It was observed that the pseudo-second-order model gave a good fit to the experimental data, and this was also corroborated from the higher regression coefficient value. Another characteristic fact to augment this feature was ascertained from the equilibrium adsorption capacity values. The $q_{e\ calculated}$ and $q_{e\ exp}$ values were found to be 15.11 mg g^{-1} and 14.91 mg g^{-1}, and this confirms the utility of pseudo-second-order kinetics (Table 2) in fitting the experimental data. Pore, surface and intraparticle diffusion[42] could be the possible modes of adsorption of Hg(II) onto the MBT-cellulose adsorbent surface. The likelihood of intraparticle diffusion also is fairly inherent in understanding the adsorption process. The Weber−Morris[43] diffusion model describes this reasonably well and correlates the amount of Hg(II) adsorbed to the diffusion rate constant (k_{int})

$$q_t = k_{int}\sqrt{t} + C \qquad (10)$$

The experimental data when fitted to this model yield the k_{int} from the slope of q_t versus $\sqrt{t}$ linear plot (Figure 9c). If this plot passes through origin, it could be interfered that intraparticle diffusion is the only process that affects the adsorption. However, the experimental data in the present system yield a plot with a nonzero intercept, and this indicates that the boundary layer effect[44] could also influence the adsorption kinetics of Hg(II) onto the MBT-cellulose adsorbent. Furthermore, the fact that q_t increases with the time of adsorption t shows that at the outset the external surface diffusion could influence the adsorption kinetics followed by intraparticle diffusion as the step that defines the rate of adsorption of Hg(II). The well established Langmuir, Freundlich, and other typical isotherm models (Table 3) were utilized to fit the experimental adsorption data.[45−48] Each of these models gives certain distinctive isotherm constants (Table 4), and various empirical equations were employed in calculating these parameters. The maximum adsorption capacity (q_o) and the adsorption energy b could be calculated from the Langmuir isotherm plot of C_e/q_e against C_e (Figure 9d). A high Langmuir adsorption capacity of 204.08 mg g^{-1} signifies the ability of 2-mercaptobenzothiazole impregnated cellulose as an excellent adsorbent for Hg(II). The separation factor ($R_L = 1/1+bC_o$) obtained from this model was found to be <1 which further justifies the effectiveness of triangular interaction.[49] The fact that the experimental data could also be elucidated based on Langmuir model is evident from the value of the exponent g which was near unity as obtained from the Redlich−Peterson isotherm model ((Figure 9e). The Freundlich isotherm plot of log q_e versus log C_e (Figure 9f) was used to calculate the adsorption intensity n and the adsorption capacity K_F. The adsorption intensity n and the high regression coefficient of 0.97 indicates the effective uptake of Hg(II) by the cellulose-MBT adsorbent. Since, $1/n$ was less than unity, it also indicates an ordinary L type Langmuir isotherm.[50] The various isotherm data plots of q_e against C_e (Figure 9g) also show that the experimental data connect well with the Freundlich isotherm model. The efficacy of the triangular interaction between cellulose, MBT, and Hg(II) was evident from the rising portion of this plot and the saturation obtained at higher values of C_e. The mean free energy of adsorption, E_{DR} value, obtained from the Dubinin−Raduksveich model (Figure 9h) is indicative of the physical
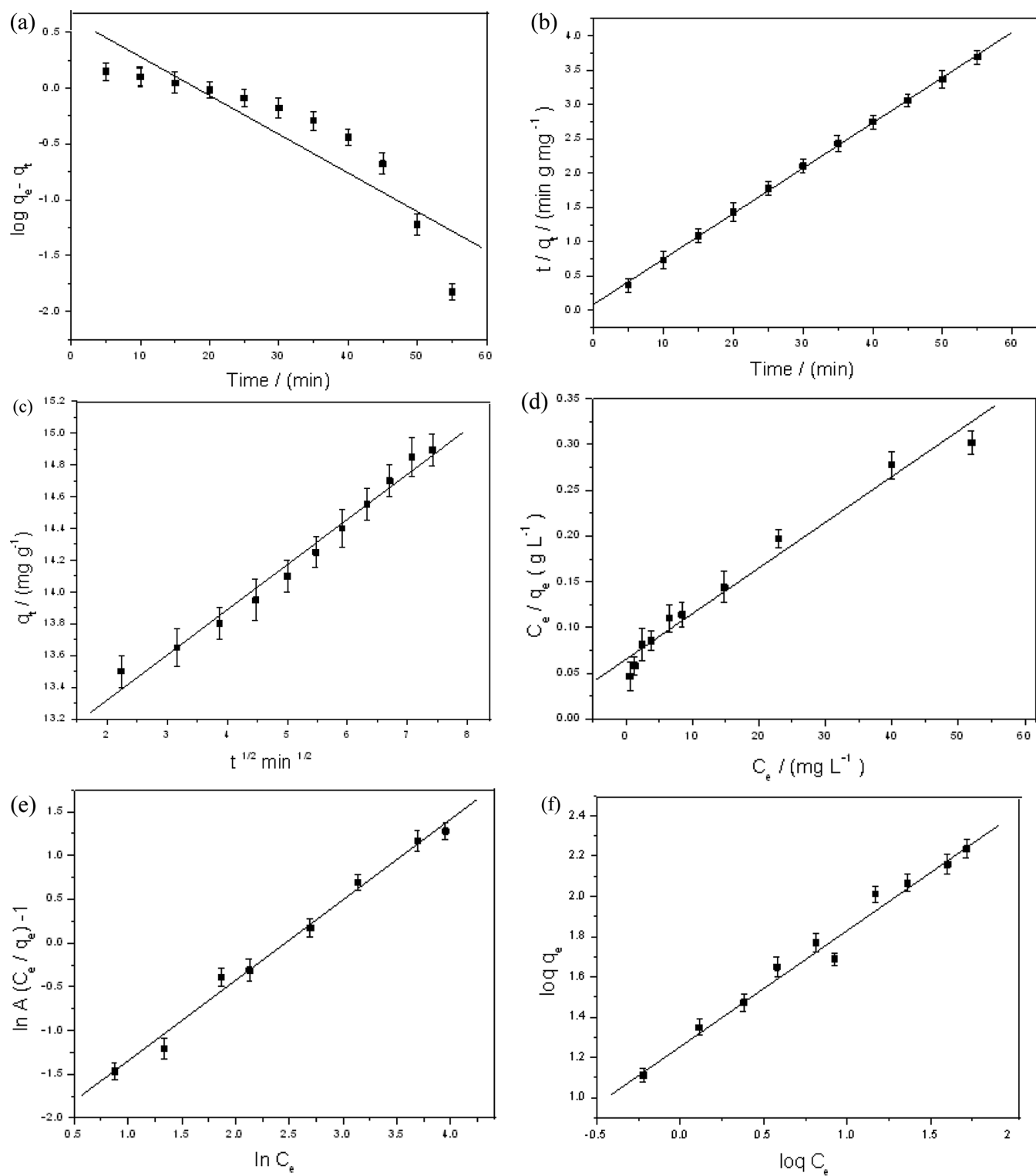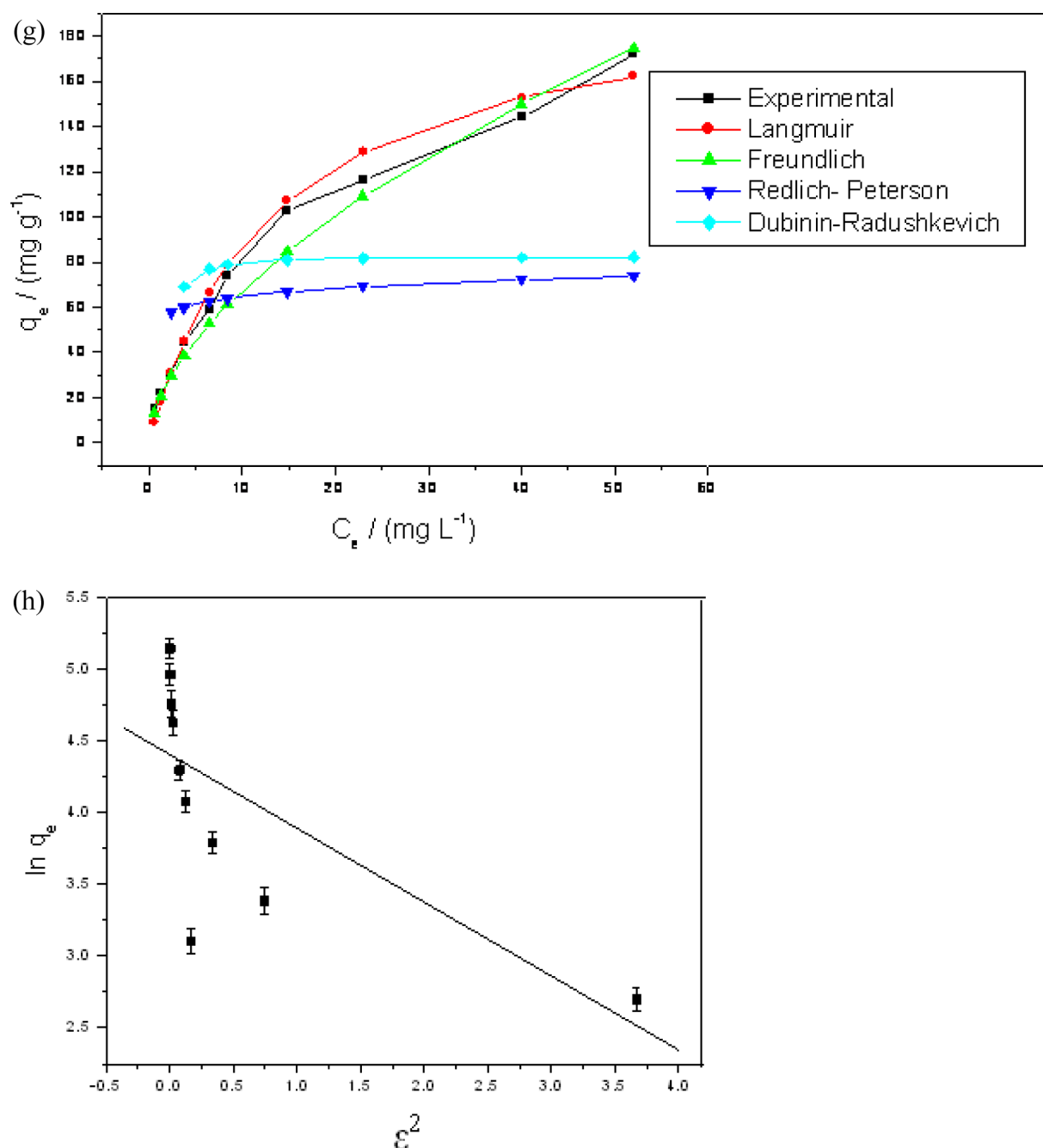
Figure 9. continued

Figure 9. (a) Pseudo-first-order kinetic plot, (b) pseudo-second-order kinetic plot, (c) Weber−Morris plot of q_t against $t^{1/2}$, (d) Langmuir isotherm, (e) Redlich−Peterson isotherm, (f) Freundlich isotherm, (g) plot of q_e against C_e for various isotherms, and (h) Dubinin−Radushkevich isotherm.

Table 2. Kinetic Parameters Associated with the Adsorption of Hg(II)

k_2 (g mg^{-1} min^{-1})	regression coefficient	k_1 (min^{-1})	regression coefficient	k_{int} (mg g^{-1} min$^{-1/2}$)
0.0496	0.99	0.079	0.80	0.284

adsorption between Hg(II) and the 2-mercaptobenzothiazole impregnated cellulose adsorbent.

3.4. Regeneration and Recycle of the Adsorbent. Regeneration and recycling of the adsorbent are two parameters that are imperative in any adsorption. This would reflect the stability of the adsorbent in the presence of other constituents present in real samples. The reagents such as potassium thiocyanate (KSCN) (2 mol L^{-1}), EDTA (3 mol L^{-1}), thiourea

Table 3. Isotherms and the Relevant Expressions

isotherm	equation
Langmuir[45]	$\dfrac{C_e}{q_e} = \dfrac{1}{q_o b} + \dfrac{C_e}{q_o}$
Freundlich[46]	$\log q_e = \log K_F + \dfrac{1}{n}\log C_e$
Redlich−Peterson[47]	$\ln(A C_e/q_e - 1) = g \ln(C_e) + \ln(B)$
Dubinin−Radushkevich[48]	$\ln q_e = \ln q_m - \beta \varepsilon^2$

(4 mol L^{-1}), potassium iodide (1 mol L^{-1}), and potassium chloride (2 mol L^{-1}) were employed to study the for the potential desorption of Hg(II) from the adsorbent column.

Table 4. Langmuir, Freundlich, Redlich−Peterson, and Dubinin−Radushkevich

isotherm model	parameters	values
Langmuir	q_o (mg g^{-1})	204.08
	b (L mg^{-1})	0.0745
	R_L	0.11
	r^2	0.97
Freundlich	K_F (mg$^{1-1/n}$ g^{-1} L$^{1/n}$)	17.93
	n	1.73
	r^2	0.97
Redlich−Peterson	g	0.92
	B (L mg^{-1})	0.103
	A (L g^{-1})	15.20
	r^2	0.99
Dubinin−Radushkevich	q_m (mg g^{-1})	82.12
	β (mol^2 kJ^{-2})	0.515
	E (kJ mol^{-1})	0.985
	r^2	0.50

Thiocyanate, EDTA, and thiourea[29] are known for their ability to complex Hg(II) through the heteroatoms sulfur, nitrogen, and oxygen. Potassium iodide and chloride could assist in desorbing Hg(II) as their respective tetrahalo complexes. The ability of the above-mentioned reagents in the desorption of Hg(II) were found to be KSCN (98.5%) > EDTA (89.0%) > thiourea (83%) > potassium iodide (71%) > potassium chloride (63%), respectively. In the proposed method involving the adsorption of Hg(II) onto the cellulose-MBT adsorbent, it was found that 20 mL of 2.0 mol L^{-1} KSCN was most effective in quantitative desorption (98.5 ± 0.35%) of Hg(II). This was also confirmed through the FT-IR spectrum (Figure 7) obtained after desorption. The IR spectrum obtained after desorption shows similarity with the original adsorbent with an additional intense peak at 2053 cm^{-1} attributed to C≡N band.[51] Apparently, thiocyanate has the ability to link Hg(II) through the soft sulfur atom more effectively (Figure 10). The high stability constant favors the elution as tetrathiocyanatomercury(II) complex effectively. The biopolymer-MBT adsorbent was stable for 5 adsorption−desorption cycles (Figure 11) without any obvious decrease in the efficacy of the adsorbent column.

3.5. Diverse Ion Effect. The presence of N and S atoms in the MBT ligand could prove to quite conducive for a variety of transition metal ions to chelate and interfere with the adsorption process. In order to investigate the adsorption selectivity of the cellulose-MBT adsorbent, studies were conducted in the presence of metal ions such as Mn^{2+} (250 mg L^{-1}), Al^{3+} (250 mg L^{-1}), Cd^{2+} (100 mg L^{-1}), Ni^{2+} (300 mg L^{-1}), Co^{2+} (200 mg L^{-1}), Fe^{2+} (200 mg L^{-1}), Pb^{2+} (100 mg L^{-1}), Zn^{2+} (250 mg L^{-1}), and Cu^{2+} (200 mg L^{-1}) independently in a 200 mL sample volume containing 30 mg L^{-1} Hg(II). Pb^{2+}, Cd^{2+}, and Zn^{2+} interfered by reducing the adsorption of Hg(II) by 20−25% at the levels mentioned above, and this could be ascribed to their competition for the ligand and the active adsorption sites. Anions such as SO$_4^{2-}$ (200 mg L^{-1}), NO$_3^-$ (250 mg L^{-1}), PO$_4^{3-}$ (200 mg L^{-1}), and Cl$^-$ (100 mg L^{-1}) did not decrease the adsorption capacity of Hg(II).

3.6. Adsorption Capacities of Other Metal Ions. The biopolymer cellulose along with different modifiers/chelating agents have been utilized to study the adsorption of other metal ions such as copper, lead, nickel, etc. A comparison of the adsorption capacities[52−56] (Table 5) shows that mercaptobenzothiazole has high adsorption efficiency for Hg(II).
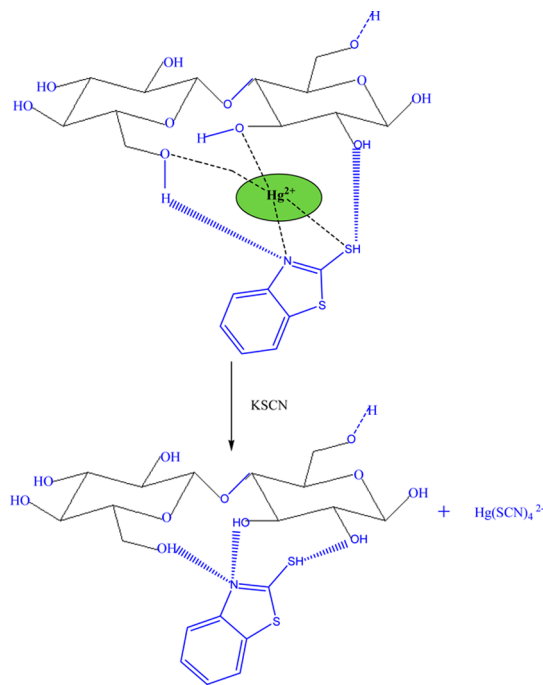
Figure 10. Scheme representing the regeneration of the cellulose-MBT adsorbent.
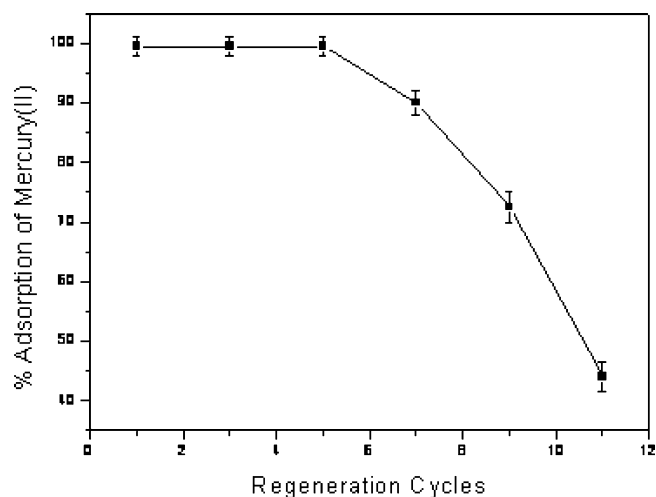
Figure 11. Regeneration of the adsorbent.

Table 5. Adsorption Capacities of Some Common Metal Ions Reported in the Literature

adsorbent material	modifier	metal ion	adsorption capacity (mg g^{-1})
cellulose	sodium hydroxide[52]	Cu(II)	70.5
cellulose	glycidyl methacrylate[53]	Cu(II)	68.5
cellulose powder	acrylic acid[54]	Pb(II)	55.9
cellulose powder	cysteine[55]	Ni(II)	8.0
porous cellulose	polyethyleneimine[56]	Zn(II)	27.0
cellulose	mercaptobenzothiazole (present study)	Hg(II)	204.08

3.7. Performance Assessment against Other Sorbents. The significant feature to take cognizance in solid phase

extraction is the adsorption capacity, and biopolymers impregnated with chelating agents are known for their high sorption characteristics. The efficacy of 2-mercaptobenzothiazole impregnated cellulose adsorbent was evaluated with regard to its adsorption capacity against other sorbents.[4,6,14,19,20,57,58] The comparison given in Table 6 exemplifies the fact that the cellulose-MBT adsorbent shows very good prospect in adsorbing Hg(II).

Table 6. Comparison of Adsorption Capacity against Other Sorbent Materials

adsorbent material	adsorption capacity (mg g^{-1})
activated carbon[4]	151.51
2-mercaptothiazoline modified mesoporous silica[6]	140
mercaptobenzothiazole − clay[14]	2.71
mercaptobenzimidazole- clay[19]	102.49
O-benzenedithiol-modified cellulose[20]	23.0
dithiocarbamate-anchored polymer/organosmectite composites[57]	157.3
chitosan -azacrown ether[58]	116.4
mercaptobenzothiazole impregnated cellulose (present study)	204.08

3.8. Application To Study the Adsorption of Mercury from a Used CFL. As a prelude to an interesting application, the effectiveness of cellulose-MBT sorbent was tested to adsorb mercury vapor emanating from a used compact fluorescent lamp. Indeed, sulfur impregnated adsorbents[59] are quite effective in the in situ capture of mercury from compact fluorescent lamps. Preliminary studies were conducted to explore the prospective application of the biopolymer-thiol ligand for the in situ adsorption of mercury. The CFL was broken carefully, and the fractured pieces were transferred to a short sealed polypropylene tube containing the adsorbent. The adsorbent powder was left in contact with the fractured lamp overnight (approx. 24 h), and the broken pieces were removed cautiously and separated from the powdered adsorbent material. The mercury vapor was adsorbed onto the surface of the adsorbent, and this was ascertained from the EDS peak (Figure 12) obtained for mercury after the adsorption.

4. CONCLUSIONS

The legacy of biopolymer cellulose finely woven as an effective adsorbent by interaction with MBT has enhanced the adsorption of Hg(II). The pivotal role played by the ligand and the biopolymer has fostered effective soft−soft interaction of the heteroatom sulfur and the lone pair-ion dipole interactions of the surface hydroxyl groups of cellulose with Hg(II). The pH for effective adsorption was found to be 4.0. The ΔH and ΔS values were found to be 81 kJ mol^{-1} and 279 J mol^{-1} K^{-1}, and this indicates the adsorption process to be endothermic with
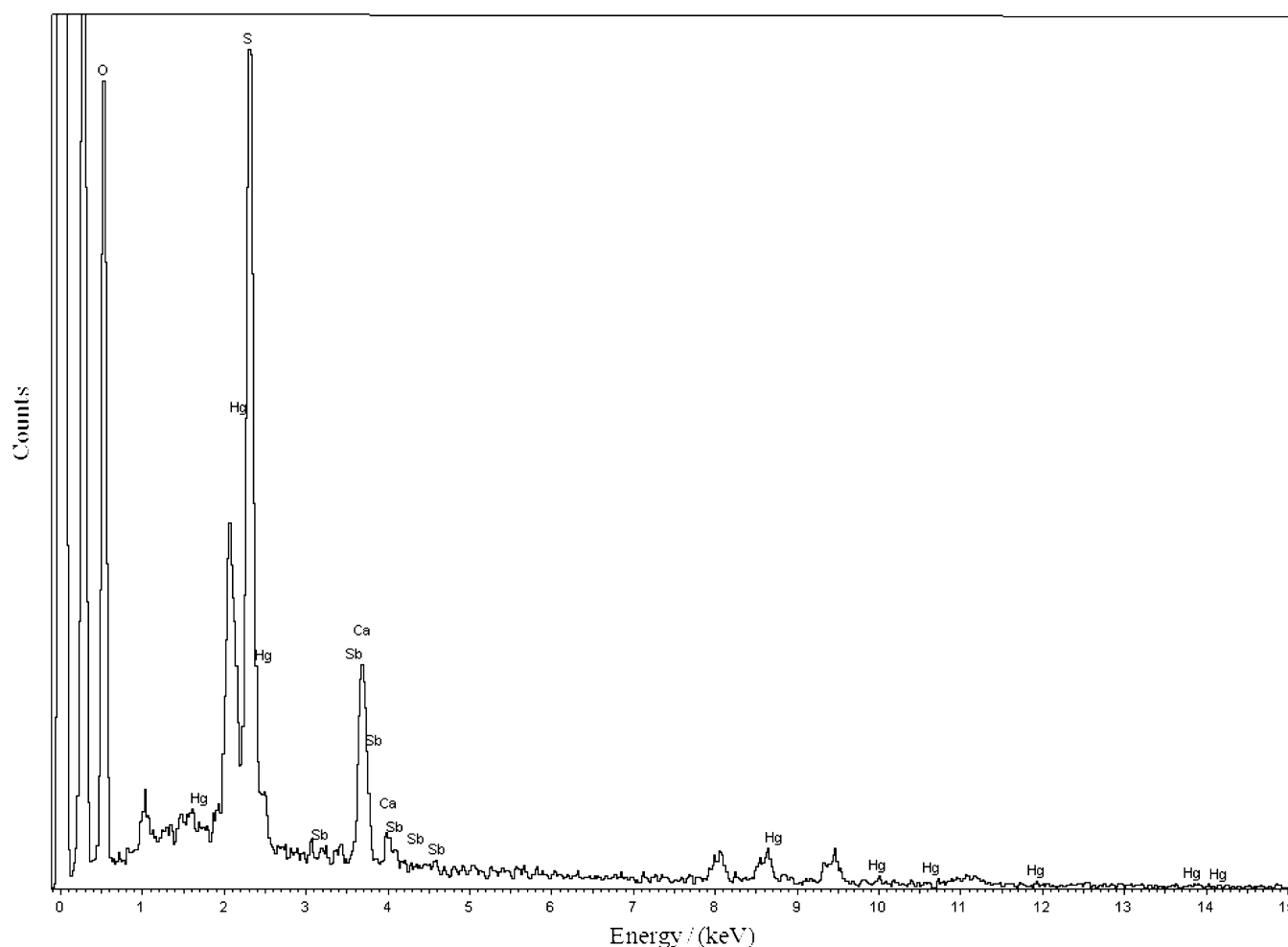
Figure 12. EDS spectrum of the adsorbent after insitu entrapment of Hg(II) vapor from CFL.

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increased randomness at the adsorbent-solution interface. The $q_{e\ calculated}$ and $q_{e\ exp}$ values were found to be 15.11 mg g^{-1} and 14.91 mg g^{-1}, and this shows the applicability of pseudo-second-order kinetics (Table 2) in fitting the experimental data. Among the various isotherm models, Langmuir and Freundlich isotherms yield a high regression coefficient value. The high Langmuir sorption capacity (204.8 mg g^{-1}) that could be realized using this adsorbent is another high point of this method. Effective regeneration of the adsorbent using potassium thiocyanate with good efficiency up to 5 adsorption−desorption cycles and a breakthrough volume of 500 mL could be attained through column studies. The fixed bed column studies gave an adsorbent exhaustion rate of 5.0 g L^{-1}. The adsorbent is quite effective toward adsorption of Hg(II) from aqueous phase in the presence of diverse cations and anions. In addition, the adsorbent also shows considerable promise in adsorbing mercury vapor from a used CFL which could certainly lead to fascinating and diverse applications of this sulfur ligand impregnated biopolymer adsorbent. Indeed, this cellulose-MBT adsorbent could also be effective toward the decontamination of Hg(II) from other anthropogenic sources of pollution as well.

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Notes
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