Clay-Based Nanocomposites as Recyclable Adsorbent toward Hg(II) Capture: Experimental and Theoretical Understanding

Sankar Das,† Arnab Samanta,† Gautam Gangopadhyay,† and Subhra Jana*,‡,†

†Department of Chemical, Biological & Macro-Molecular Sciences and ‡Technical Research Centre, S. N. Bose National Centre for Basic Sciences, Block-JD, Sector-III, Salt Lake, Kolkata 700106, India

ABSTRACT: Here, we report the development of inorganic–organic hybrid nanocomposites through selective modification of the negative outer surfaces of halloysite nanoclays with two different organosilanes having primary or secondary amine sites to be explored them as novel and cost-effective adsorbents for the extraction of toxic inorganic contaminants from aqueous solution. They possess excellent selectivity for the adsorption of mercury, which shows monolayer molecular adsorption over the nanocomposites. The adsorption kinetics of Hg(II) is very fast and follows pseudo-second-order model compared to pseudo-first-order model. A combined experimental and theoretical study demonstrated that Hg(II) uptake by these nanocomposites is highly favorable and spontaneous up to 40 °C, and beyond this temperature, the uptake capacity gradually reduced. Temperature-dependent adsorption study exhibits endothermicity at low temperature (≤40 °C) and exothermicity beyond 40 °C. pH-dependent adsorption study showed their high uptake capacity until pH 7, which reduced at alkaline pH. All of the nanocomposites hold excellent adsorption capacity even at low concentration of adsorbate, along with multicycle sorption capability. The outstanding adsorption capacity as well as the easy synthetic route to achieve these nanocomposites may attract researchers to develop low-cost adsorbents to capture toxic metals, which in turn regulate the permissible limit of these toxic metals in drinking water.

1. INTRODUCTION

Contamination of toxic heavy-metal ions discharged from textile, fertilizer, mining, refining, and printing industries into water has been identified as a serious threat to not only public health but also the environment and natural ecosystems, as the toxic heavy metals present in liquid effluents are persistent, nonbiodegradable, and bioaccumulative.1–3 Among the several toxic heavy metals, mercury is the most harmful pollutant with a permissible limit of 2.0 ppb in drinking water. Mercury exposure via direct contact or gradual bioaccumulation leads to severe damage to human nerves, lungs, kidneys, and other organs. Currently, mercury has been excessively released into the environment through rapid discharge of industrial waste, including fossil fuel combustion, batteries, electronic materials, and chemicals. To date, several techniques have been adopted for heavy-metals removal, e.g., adsorption, precipitation, ion exchange, reverse osmosis, and nanofiltration.4–8

Among the various techniques, adsorption is fascinating to researchers owing to its simplicity, low cost, and a reliable chemical engineering process, which has potential to overcome the aforementioned environmental issues.9 For efficient mercury removal from water, several potential adsorbents have been reported in the literature, such as activated carbon,10,11 graphene,12 chelate-incorporated fibers,13,14 chitosan,15,16 cellulose,17,18 and porous silica.19,20 Although activated carbon is highly porous with large specific surface area and high adsorption efficiency, it is expensive to use and regenerate, thus limiting its large-scale synthesis for industrial application.19 Besides activated carbon, graphene-based adsorbents with large effective surface areas possess excellent adsorption capacity and selectivity, but the synthesis of such materials involves time-consuming steps to produce well-dispersed nanocarbon flakes and their functional derivatives.17 The potential toxicity of nanoscale adsorbents and difficulties in repossessing the adsorbents after metal-ions adsorption are the major limitations of some techniques.21 Again, adsorbents synthesized based on chelate-modified wool or polyester fibers involve either high-temperature processes or special instruments during their synthesis.13,14 An inherent drawback of the synthesis of template-based mesoporous silica materials is that it is not a cost-effective route owing to the use of expensive sacrificial templates like surfactants, block copolymers, etc., which in turn restricts their wide use as advanced adsorbents.22 The pressing need is therefore to develop environmentally friendly and reusable adsorbents in a large scale based on low-cost materials.
and simple synthetic route for efficient removal of toxic heavy-metal ions. Recently, inorganic–organic hybrid nanocomposites (NCs) consisting of clay materials have provided a new direction in the frontier area of materials science because of their high abundance in nature, together with high mechanical and thermal stabilities as well as diverse applications in the field of environmental remediation, which includes adsorption of toxic inorganic contaminants, since they possess good chemical affinity and excellent adsorption efficiency even at low concentration. Halloysite nanotubes (HNTs) are naturally occurring and economically sustainable two-layered aluminosilicate clay (Al₂Si₂O₅(OH)₄·nH₂O), containing tetrahedral SiO₂ sheets and octahedral AlO₆ sheets. HNTs having a hollow tubular structure demonstrate positive inner and negative outer surface charges, which regulate their physicochemical properties through control of the chemistry of these constituent elements. However, the disadvantages of such materials are less metal-loading capabilities and quite low metal-ion-binding constants, which can be resolved through functionalization of these materials using active organic functional groups immobilized over their surfaces. Thus, functionalization of HNTs by organosilanes gives rise to low-cost adsorbents for the adsorption of toxic heavy-metal ions, which in turn open a new route for the treatment of industrial heavy-metal-contaminated wastewater.

We have developed hybrid NCs consisting of different amine-functionalized HNTs and explored them as cost-effective sorbents for the removal of toxic heavy-metal ions from aqueous solution. Chemical analysis of the NCs was carried out by Fourier transform infrared (FTIR) and NMR spectroscopies, whereas morphological characterization was performed by scanning electron microscopy (SEM). Adsorption kinetics and isotherms for Hg(II) ions were studied using two different adsorbents. The adsorption capacities of all of the NCs were examined even at low concentration of adsorbate. A combined experimental and theoretical study was carried out to demonstrate the kinetics and thermodynamics of mercury adsorption process. pH-dependent sorption study was also performed to determine the effect of pH on the uptake efficacy. Subsequently, stabilities of these NCs were illustrated by their repetitive use and their efficacies were compared to those of the reported amine-based adsorbents.

2. RESULTS AND DISCUSSION

2.1. Characterization of P-HNTs and S-HNTs. The nanocomposites were synthesized based on the selective modification of the outer surfaces of HNTs using aminosilanes, having primary or secondary amine sites through the grafting of 3-(aminopropyl)triethoxysilane (P-HNTs) or trimethoxy[3-(methylamino)propyl]silane (S-HNTs), respectively, as ascribed in Scheme 1. The chemical modification of HNTs surfaces due to the grafting of aminosilanes was characterized by FTIR and NMR spectroscopies. Figure 1 represents FTIR spectra of HNTs, P-HNTs, and S-HNTs. The FTIR spectra of P-HNTs and S-HNTs demonstrate the presence of amino groups in the nanocomposites due to the grafting of aminosilanes onto the surface of HNTs.

![Scheme 1. Schematic Presentation of the Synthesis of P-HNTs and S-HNTs through Grafting of 3-(Aminopropyl)triethoxysilane and Trimethoxy[3-(methylamino)propyl]silane over the Outer Surfaces of HNTs, Respectively](image)

![Figure 1. FTIR spectra of HNTs, P-HNTs, and S-HNTs. The FTIR spectra of P-HNTs and S-HNTs demonstrate the presence of amino groups in the nanocomposites due to the grafting of aminosilanes onto the surface of HNTs.](image)
C−H and N−H, respectively, signifying grafting of aminosilanes.\textsuperscript{24,25} Additionally, we have performed solid-state $^{29}$Si NMR spectroscopy to further demonstrate the grafting of these aminosilanes over the surface of HNTs. $^{29}$Si cross polarization magic angle spinning (CP-MAS) NMR spectra of HNTs and P-HNTs are illustrated in Figure 2. In $^{29}$Si CP-MAS NMR spectra, the chemical shift at $-91$ ppm arises from the constituent silicon present in HNTs, P-HNTs, and S-HNTs. The appearance of a new peak at $-67$ ppm in both P-HNTs and S-HNTs (Figure S1 in the Supporting Information) is due to the tridentate (T$^{\text{3}}$)-bonded silicon, indicating the formation of a new chemical bond between the surface hydroxyl groups of HNTs and the organosilanes.\textsuperscript{26}

Field emission scanning electron microscopy (FESEM) images of HNTs, P-HNTs, and S-HNTs are shown in Figure 3. HNTs are composed of cylindrical-shaped tubes having lengths between 1.0 and 1.5 $\mu$m with outer and inner diameters of 50−100 and 15−20 nm, respectively, demonstrating polydispersity in their sizes. The morphologies of P-HNTs and S-HNTs are analogous to the morphology of pristine HNTs even after grafting of aminosilanes.\textsuperscript{26} X-ray diffraction pattern (XRD) of HNTs is similar to that of P-HNTs or S-HNTs (Figure S2). The characteristic (001) reflection remains unaltered after grafting of organosilanes, further demonstrating the absence of any intercalation of aminosilane into the interlayer of HNTs.\textsuperscript{26,27} The specific surface areas assessed by the Brunauer−Emmett−Teller (BET) method were found to be 22 and 19 m$^2$ g$^{-1}$ for P-HNTs and S-HNTs, respectively. The isotherms of the adsorbents are of type II with H3 hysteresis loops (Figure S3) according to IUPAC classification, representing the signature of mesoporous materials. Finally, CHN elemental analysis was carried out to achieve the exact concentration of grafted amino groups in P-HNTs and S-HNTs. The loaded N was assessed to be 0.51 and 0.53 wt % in P-HNTs and S-HNTs, respectively, under the present experimental condition. These organosilane-functionalized surfaces of HNTs are stable enough and impervious to remove the aminosilanes from the surface by any organic solvents or water.

Figure 2. $^{29}$Si CP-MAS NMR spectra of HNTs and P-HNTs.

Figure 3. FESEM images of (A) HNTs, (B) P-HNTs, and (C) S-HNTs, indicating that they are composed of cylindrical-shaped tubes with no change in their morphology even after grafting of aminosilanes.
2.2. Mercury Adsorption Study.

To explore the adsorption capacity of the NCs, mercury-containing aqueous solution was considered as a pollutant, since mercury has been established as one of the most harmful pollutants in the environment owing to its high toxicity, volatility, and bioaccumulation. The adsorption kinetics describing Hg(II) uptake rate was governed by the contact time during adsorption reaction, which in turn determines the efficiency of Hg(II) sorption of these adsorbents. To study the adsorption kinetics, the reaction mixture was equilibrated at room temperature and then the amount of Hg(II) ions adsorbed by P-HNTs and S-HNTs was estimated as a function of time. We found that the apparent adsorption equilibrium reached around 60 min of the adsorption process, after which no significant change in adsorption capacity was observed even up to 2 h (Figure 4).

The adsorption kinetics of Hg(II) ions was then studied based on the pseudo-first-order and pseudo-second-order rate equations\textsuperscript{28,29}

\begin{equation}
Q_t = Q_e - Q_e e^{-k_1 t}
\end{equation}

\begin{equation}
Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t}
\end{equation}

where $Q_e$ is the equilibrium adsorption capacity of an adsorbent (mg g\textsuperscript{-1}), $Q_t$ is the amount of adsorbate (mg g\textsuperscript{-1}) at time $t$, $k_1$ is the pseudo-first-order reaction rate constant (min\textsuperscript{-1}), and $k_2$ is the rate constant for pseudo-second-order reaction (g mg\textsuperscript{-1} min\textsuperscript{-1}). In Table 1, we have summarized kinetic parameters for Hg(II) adsorption based on the pseudo-first-order and pseudo-second-order models. On the basis of the extracted correlation coefficient ($R^2$), the adsorption kinetics of Hg(II) follows pseudo-second-order model for both P-HNTs and S-HNTs, where the chemical adsorption process is the rate-limiting step. Again, $Q_e$ values obtained from the pseudo-second-order model fitting are comparable to the experimental values, further suggesting pseudo-second-order adsorption kinetics of Hg(II).

![Figure 4. Adsorption kinetics of Hg(II) for both (A) P-HNTs and (B) S-HNTs, representing that both P-HNTs and S-HNTs follow pseudo-second-order adsorption model.](image)

![Scheme 2. Schematic Presentation of the Probable Mechanism of the Binding of Toxic Hg(II) Ions with the Reactive Functional Groups (\textemdash\textsuperscript{\text{-NH2} or \textdash\textsuperscript{-NHR}) Present in the Adsorbents.](image)

| adsorbent | $Q_{e,exp}$ (mg g\textsuperscript{-1}) | $Q_{cal}$ (mg g\textsuperscript{-1}) | $k_1$ (min\textsuperscript{-1}) | $R^2$ | $Q_{cal}$ (mg g\textsuperscript{-1}) | $k_2$ (g mg\textsuperscript{-1} min\textsuperscript{-1}) | $R^2$ |
|-----------|---------------------------------|---------------------------------|-----------------|------|---------------------------------|-----------------|------|
| P-HNTs   | 52.18                           | 49.99                           | 0.575           | 0.71 | 52.18                           | 0.02181         | 0.99 |
| S-HNTs   | 21.50                           | 21.08                           | 1.029           | 0.69 | 21.52                           | 0.13614         | 0.98 |

\textsuperscript{28,29}
FTIR analysis was performed after the adsorption of Hg(II) ions over the surface of P-HNTs and S-HNTs (Figure S4), which demonstrated that the stretching and deformation vibrations of $\text{N}^-$ at 3453 and 1556 cm$^{-1}$ were shifted to 3438 and 1546 cm$^{-1}$, respectively, authenticating an interaction of Hg(II) ions with the adsorption sites ($\text{NH}_2$ or $\text{NHR}$) present in the adsorbents. The probable mechanism behind the binding of toxic Hg(II) ions is attributed to the metal–ligand complex formation between Hg(II) and the reactive functional groups ($\text{NH}_2$ or $\text{NHR}$) of the adsorbents, since they provide effective adsorption sites, as shown in Scheme 2. Again, Hg(II) ions prefer to coordinate with amine sites, resulting in a strong coordination with Hg(II) ions.

To demonstrate the adsorption isotherm of Hg(II), multiple sets of batch experiments were carried out at room temperature for P-HNTs and S-HNTs. The adsorption isotherm of Hg(II) was studied to indicate the binding properties, as shown in Figure 5. Both the adsorption isotherms initially showed a very sharp increase, signifying high-energy adsorption sites that facilitate strong adsorption at low equilibrium concentrations. The resultant data sets on mercury ion removal were fitted according to Langmuir and Freundlich isotherm models:\n
$$Q_e = \frac{Q_m C_e}{K_L C_e + 1}$$ \hspace{1cm} (3)\n
$$Q_e = K_F C_e^{1/n}$$ \hspace{1cm} (4)\n
where $Q_e$ is the equilibrium adsorption capacity of an adsorbent, $Q_m$ is the maximum adsorption capacity of that adsorbent (mg g$^{-1}$), $C_e$ is the equilibrium concentration of adsorbate (mg L$^{-1}$), $K_L$ is the Langmuir equilibrium constant (L mg$^{-1}$) associated to the free energy of adsorption, $K_F$ is the Freundlich equilibrium constant (mg g$^{-1}$)(L mg$^{-1}$)$^{1/n}$, and $n$ is the adsorption equilibrium constant. It is well known that Freundlich equilibrium isotherm demonstrates multilayer adsorption with interaction between adsorbed molecules and is related to the heterogeneous surfaces, whereas Langmuir isotherm describes the monolayer coverage of the adsorbate and valid for dynamic equilibrium adsorption over a homogeneous adsorbent surface.\n
Table 2. Langmuir and Freundlich Isotherm Models Fitting Parameters for the Adsorption of Hg(II) over the Adsorbents

| adsorbent | $Q_{exp}$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $Q_m$ (mg g$^{-1}$) | $R^2$ | $K_F$ (mg g$^{-1}$)(L mg$^{-1}$)$^{1/n}$ | $n$ | $R^2$ |
|-----------|----------------|-----------------|-----------------|------|--------------------------------|---|------|
| P-HNTs    | 71.4           | 0.00681         | 83.48           | 0.987| 8.505                          | 3.132 | 0.868 |
| S-HNTs    | 37.1           | 0.00522         | 45.22           | 0.991| 3.201                          | 2.73  | 0.901 |

Figure 5. Adsorption isotherms of Hg(II) ions over the surfaces of (A) P-HNTs and (B) S-HNTs, demonstrating monolayer coverage of the adsorbate.

Figure 6. (A) Plot of adsorption capacity of P-HNTs and S-HNTs as a function of temperature and (B) the corresponding ln $K_d$ vs 1/$T$ plot.
Table 2. It is interesting to note that the correlation coefficient obtained from the Langmuir model was better fitted than that from the Freundlich isotherm for mercury ions, suggesting a characteristic monolayer molecular adsorption of Hg(II) ions over the surfaces of P-HNTs and S-HNTs. The maximum adsorption capacities (Q_m) of P-HNTs and S-HNTs for Hg(II) were estimated to be 83.48 and 45.22 mg g⁻¹, respectively, indicating the higher adsorption capacity of P-HNTs for Hg(II) ions than that of S-HNTs. It should be pointed out that P-HNTs consist of primary amine sites, whereas S-HNTs are composed of secondary amine sites. Thus, the lower adsorption capacity of S-HNTs for Hg(II) ions is possibly due to the little interaction of the adsorbate with the secondary amines during the adsorption process, since amino groups present in the adsorbent are the effective adsorption sites.

2.3. Temperature Dependence of Adsorption Capacity: Kinetic and Thermodynamic Study. Temperature-dependent adsorption kinetics of these adsorbents was performed by carrying out the adsorption experiment in different temperatures, keeping all other experimental conditions unaltered. Figure 6A presents the change in the temperature. The maximum adsorption was noted around 40°C. To determine spontaneous adsorption process, it is necessary to consider both the enthalpy and free-energy change. The free-energy change can be obtained from the equilibrium constant (K_d), which is estimated experimentally. The overall reaction equilibrium constant (K_d) can be obtained from the experiment as

\[ K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{W} \]  

(5)

where \( V \) is the working volume in milliliter, \( W \) is the adsorbent mass in grams, and \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of the adsorbate, respectively.

The plot of \( \ln K_d \) vs \( 1/T \) is shown in Figure 6B, from which one can subsequently measure the enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)), as shown in Tables 3 and 4. How the free-energy change is affected due to endothermicity and disorderliness of a process can be determined by the following equation

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]  

(6)

\[ \Delta G^0 = -RT \ln K_d \]  

(7)

| Table 3. Thermodynamic Parameters of Hg(II) Adsorption onto P-HNTs and S-HNTs as a Function of Temperature (283–313 K) |
|---|---|---|---|---|---|
| adsorbent | \( T \) (K) | \( Q_e \) (mg g⁻¹) | \( \Delta G^0 \) (kJ mol⁻¹) | \( \Delta H^0 \) (kJ mol⁻¹) | \( \Delta S^0 \) (J mol⁻¹ K⁻¹) |
| P-HNTS | 283 | 46.98 | -15.80 | 12.87 | 101.37 |
| | 293 | 50.10 | -16.84 | | |
| | 298 | 52.18 | -17.35 | | |
| | 303 | 52.20 | -17.86 | | |
| | 313 | 53.80 | -18.84 | | |
| S-HNTs | 283 | 19.29 | -11.55 | 6.9 | 65.23 |
| | 293 | 20.70 | -12.21 | | |
| | 298 | 21.50 | -12.55 | | |
| | 303 | 22.10 | -12.88 | | |
| | 313 | 23.5 | -13.50 | | |

where \( R \) is the gas constant (8.314 J mol⁻¹ K⁻¹), \( T \) is the absolute temperature in kelvin (K), and \( K_d \) is the equilibrium constant in mL g⁻¹. As equilibrium constant (\( K_d \)) can be obtained experimentally from \( K_d = Q_e/C_e \) for various temperatures, one can find \( -\Delta H^0/R \) as the slope and \( \Delta S^0/R \) as the intercept from ln \( K_d \) vs \( 1/T \) plot.

For a spontaneous process, \( \Delta G^0 \) is negative, which is a result of \( \Delta H^0 \) and \( T\Delta S^0 \), where \( \Delta H^0 \) as positive means endothermcity and \( \Delta S^0 \) as positive as an increase in randomness happens. This is due to the fact that Hg(II) adsorbs to the primary or secondary amine structure relative to its standard state. At higher temperatures above 40°C, the surface adsorption of Hg actually governs the overall temperature dependence of rate.

2.4. Relation between Kinetics and Thermodynamics. The pseudo-second-order rate of the overall adsorption reaction, \( r_d \), can be written as

\[ r_d \propto \frac{r_e}{r_e + K_d} \]  

(8)

where \( r_e \) is the rate proportional to the number of Hg atoms adsorbed on the surface and \( r_e \) is the rate proportional to the number of Hg atoms involved in the primary or secondary amine complexation. Usually, adsorption of Hg on the surface of an adsorbent is an adsorption process governed by the rate

\[ r_e = r_e^0 e^{-\Delta G_e^0/RT} \]  

(9)

\[ r_e = r_e^0 e^{\Delta G_e^0/RT} \]  

(10)

where \( \Delta G_e^0 \) is change in free energy of activation of adsorption process, \( r_e^0 \) depends on the number of Hg atoms on the adsorbent, \( \Delta G_e^0 \) is the amount of energy of interaction due to amine complexation with Hg, and \( r_e^0 \) is proportional to the number or size of Hg–amine complexes.

However, the critical size of the amine complexation actually controls the lowering of the thermal activation energy barrier of the adsorption process from the adsorbent. So, the overall adsorption rate, \( r_d \), can be written from the collision theory as

\[ r_d = f \left( \frac{k_B T}{h} \right) r_e^0 \frac{r_e}{r_e + K_d} e^{-\left(\Delta G_e^0 - \Delta G_e^0/RT\right)} \]  

(11)

where \( f \) is a proportionality constant, which depends on the frequency factor of collision of Hg with the adsorbent and includes other approximate rate factors independent of temperature. The breaking of Hg–amine complex is also a thermally activated process, where the activation energy is negative of the interaction energy to make the appropriate size of the Hg–amine complex formation. We consider the overall process as

| Table 4. Thermodynamic Parameters of Hg(II) Adsorption onto P-HNTs and S-HNTs as a Function of Temperature (313–343 K) |
|---|---|---|---|---|---|
| adsorbent | \( T \) (K) | \( Q_e \) (mg g⁻¹) | \( \Delta G^0 \) (kJ mol⁻¹) | \( \Delta H^0 \) (kJ mol⁻¹) | \( \Delta S^0 \) (J mol⁻¹ K⁻¹) |
| P-HNTS | 313 | 53.80 | -18.84 | -39.15 | -64.54 |
| | 323 | 49.15 | -18.37 | | |
| | 333 | 43.63 | -17.85 | | |
| | 343 | 34.93 | -16.84 | | |
| S-HNTs | 313 | 23.30 | -13.50 | -27.32 | -44.31 |
| | 323 | 18.10 | -12.95 | | |
| | 333 | 14.34 | -12.50 | | |
| | 343 | 11.10 | -12.18 | | |
Hg(II) + adsorbent $\rightleftharpoons \frac{k_r}{k_b}$ adsorbed Hg–amine complex on the adsorbent so that

$$K_d = \frac{k_r}{k_b}$$

(12)

As the $k_b$ is not affected by the Hg–amine complexation interaction energy, $K_d$ is affected only by $\Delta G^\circ_{ads}$ in $\Delta G^\circ$. The free energy of activation for the adsorption of Hg–amine complex is given by

$$\Delta G^\theta_{a} = \Delta G^\circ_{a} - \Delta G^\circ_{c}$$

(13)

But the backward activation process, $\Delta G^\theta_{b}$, does not depend on the complexation so that

$$\Delta G^0 = \Delta G^\theta_{a} - \Delta G^\theta_{b} = \Delta G^\theta_{ads} - \Delta G^\theta_{c}$$

(14)

where $\Delta G^\theta_{ads}$ is the free-energy change only due to the Hg(II) surface adsorption process. The mechanism of temperature-dependent adsorption process is very similar in primary and secondary amine cases except the fact that the primary amine complexation is more favored than the secondary one at any temperature by the obvious reason of steric hindrance on the surface.

At lower temperatures below 40 °C, one can find $\Delta G^\circ_{c} > \Delta G^\circ_{e}$. At 40 °C, $\Delta G^\circ_{e}$ is almost zero and the value of $\ln K_d$ falls on the normal adsorption straight line with $1/T$ at higher temperature. Below 40 °C, $\Delta G^\circ_{c}$ is negative, so $\ln K_d$ increases with increasing $1/T$. However, it is beyond our limit to demonstrate the temperature dependence of decomplexation or decrease in size of the Hg–amine complex with increase in temperature from the present experiment. In the high-temperature range (>40 °C), from the straight line curve with positive slope, one finds $\Delta H^0$ as negative. Hg adsorption is an exothermic process and $\Delta S^0$ is negative, i.e., disorderness decreases. Therefore, the decrease in the adsorption capacity of our adsorbents at high temperature is possibly due to the weakening of the interaction between the active sites of the adsorbents and adsorbate. However, in the lower-temperature range (<40 °C), straight line curve with negative slope $\Delta H^0$ of the amine–Hg complexation is positive, indicating an endothermic process, whereas $\Delta S^0$ is positive, so disorderness increases due to the complexation process, which is also supported by the experimental data (Tables 3 and 4).

2.5. Adsorption of Different Toxic Metals. In addition to Hg(II), we have studied the adsorption kinetics of P-HNTs and S-HNTs for several toxic metals [Cd(II), Pb(II), and Cu(II)] present in the aqueous solution, keeping all of the experimental conditions unaltered. The functional groups of the adsorbent and the adsorbate (metal ions) play an important role in the adsorption process, which in turn regulate the adsorption efficiency of the adsorbent. From Figure 7A, it can be found that the uptake of Hg(II) from aqueous solution by both P-HNTs and S-HNTs is remarkably higher than that of other metal ions, demonstrating insignificant adsorption of these metal ions possibly due to the physicochemical properties of the metal ions, such as electronegativity and ionic radius. Hence, we may conclude that P-HNTs has exceptional...
Scheme 3. Schematic Presentation of the Sorption of Hg(II) Ions by These Clay-Based Nanocomposites Leaving Behind Clean Water Free from Toxic Metal Ions

selectivity for Hg(II) adsorption and is capable of removing them from aqueous solution. The stability and recyclability of P-HNTs and S-HNTs were demonstrated by carrying out a number of adsorption/desorption experiments using 10% thiourea in 0.05 M HCl solution as an eluent. After successive regeneration, the uptake efficiencies of these adsorbents were found to be almost the same up to six cycles (Figure 7B). After the sixth cycle, a slight decrease in adsorption efficacy was observed both for P-HNTs and S-HNTs, which is possibly due to the irreversible adsorption of Hg(II) or may be due to the oxidation of amino groups during repetitive adsorption experiments.

2.6. Effect of Solution pH. It is important to note that the solution pH imparts a significant role during the adsorption process of Hg(II). To demonstrate pH-dependent adsorption capacity of both P-HNTs and S-HNTs, we have carried out the adsorption study in the pH range of 2−11, as shown in Figure 8A. With increasing solution pH from 2 to 7, the adsorption capacity of these adsorbents for Hg(II) ion increased notably and became the highest at pH 7. This is possible due to the higher concentration of hydrogen ions at lower pH, which results in the protonation of the amino groups, leading to the weak binding ability of amino groups toward Hg(II) ions at lower pH. Additionally, a competitive adsorption between Hg(II) ions and hydrogen ions with the amine-binding sites of the adsorbents occurs at low pH, which further encumbers the sequestration of Hg(II) ions. At higher pH (>7), an increase in the adsorption efficiency of the adsorbents should occur since the deprotonated amines are available for binding with Hg(II). This observation has also been corroborated with our experimental findings for zero-point-charge pH (pHzpc). It should be noted that pHzpc is an important factor during adsorption of ionic species, where the adsorbent surface has net electrical neutrality. Figure 8B depicts the pHzpc of both P-HNTs and S-HNTs. The pHzpc of P-HNTs was estimated to be 7.6, whereas it is 7.2 for S-HNTs. Therefore, pH > pHzpc, and the surface of the adsorbents should be negatively charged, which may facilitate the adsorption of cationic species. However, a decrease in adsorption efficacy was observed for both the adsorbents. This may be due to the formation of Hg(OH)δ− complex with increasing concentration of hydroxyl ions in the solution, resulting in an electrostatic repulsion between the lone pair of nitrogen of amino groups with the negatively charged metal complexes and leading to the lowering of the Hg adsorption efficiency of the adsorbents.

Finally, we have compared Hg(II) the uptake efficiency of P-HNTs to that of the reported amine-based adsorbents (Table S1), illustrating significant adsorption efficacy of the former. Thus, exceptional sorption capacity together with easy synthetic route to achieve these nanocomposites may be an alternative pathway for developing prospective adsorbents to capture toxic metals present in drinking water (Scheme 3).

3. CONCLUSIONS

In conclusion, we have fabricated two hybrid nanocomposites containing primary or secondary amine site to explore them as cost-effective sorbents for the removal of toxic heavy-metal ions from aqueous solution. The adsorption kinetics of Hg(II) ions follows pseudo-second-order rate equation compared to the pseudo-first-order model. The adsorption isotherms were well fitted with the Langmuir isotherm model with a high value of correlation coefficient compared to the Freundlich isotherm model, confirming monolayer adsorption of the mercury ions on the surface of amine-functionalized clay nanomaterials. With increasing solution pH, the adsorption efficiencies of these adsorbents for Hg(II) ion increased up to pH 7, followed by a gradual decrease in alkaline pH. Thermodynamic analysis indicates that Hg(II)-ion adsorption by these adsorbents is highly favorable, spontaneous, and endothermic in nature at low temperature, further corroborated by theoretical study. All of the adsorbents showed excellent adsorption capacity even at low concentration and multicycle Hg(II) uptake capability; however, P-HNTs possess the highest uptake capability among them. Owing to the outstanding adsorption efficiency and good recyclability, these nanocomposites may be explored as an adsorbent for industrial heavy-metal-contaminated wastewater treatment, which in turn may find application in the field of environmental remediation.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Inorganic–Organic Hybrid Nanocomposites. Inorganic–organic hybrid NCs were synthesized by grafting of organosilanes over the outer surfaces of HNTs. The grafting reaction was performed under nitrogen atmosphere by a standard air-free technique. A 50 mL three-necked round-bottom flask containing 15.0 mL of toluene was fixed with a rubber septum, condenser, and a thermocouple adapter.
And 3.0 g of HNTs was added to the flask. The reaction mixture was deaerated for 30 min under nitrogen at room temperature, followed by heating with a heating mantle. Then, aminosilane (6.0 mmol) was injected into the flask at 60 °C under stirring condition, and subsequently, the reaction mixture was heated to 120 °C and refluxed for 20 h at that temperature. Finally, the as-synthesized product was collected through filtration, washed several times with toluene and ethanol separately to remove unreacted aminosilanes, if any, and then dried at 100 °C overnight under vacuum. The products were abbreviated as P-HNTs and S-HNTs for 3-(aminopropyl)-triethoxysilane- and trimethoxyl[3-(methylamino)propyl]silane-functionalized HNTs, respectively, and explored them as adsorbent to capture toxic metal ions.

4.2. Batch Adsorption Study Using Nanocomposites.
To demonstrate the adsorption capacity of these NCs toward toxic metal ions from aqueous solution, Hg(II) solution was taken in a beaker containing P-HNTs or S-HNTs. Adsorption experiments were carried out taking different concentrations of Hg(II) solution, and the adsorbent concentration was maintained at 3.0 g L⁻¹. The solution was stirred on a magnetic stirrer up to a desired time and then the solution was filtered off once the adsorption was over and collected for further study. The resulting solutions were analyzed by inductive coupled plasma optical emission spectroscopy (ICP-OES). The amount of unbound Hg(II) ions present in the filtrate was also estimated using diphénylthiocarbazone (dithizone), which formed a complex with Hg(II) ions. The adsorption spectra of mercury–dithizone complexes were recorded using a UV–visible spectrophotometer in a standard quartz cuvette of 1 cm path length. pH-dependent adsorption analysis was performed for both P-HNTs and S-HNTs in the pH range of 2–11, and the solution pH was adjusted to the desired value by adding either HCl or NaOH. All of the isotherms and kinetics were carried out at pH 4 at 25 °C. For adsorption kinetics and pH study, the initial concentration of Hg(II) solution was taken to be 200 mg L⁻¹ with an adsorbent concentration of 3.0 g L⁻¹. For the regeneration and reuse of the NCs, the used P-HNTs and S-HNTs were treated with 10% thiourea in 0.05 M HCl solution for 2 h and then washed with plenty of water. After being regenerated, the adsorbents were added into the Hg(II) solution to check their reusability. Keeping all of the experimental conditions unaltered, we have also studied the adsorption capacities of these NCs for other heavy-metal ions [Cd(II), Pb(II), and Cu(II)] present in the aqueous solution.

4.3. Determination of pH at Zero Point Charge (pH_{ZPC}). The zero point charge pH (pH_{ZPC}) values of P-HNTs and S-HNTs were calculated by the pH drift method. In this method, the pH_{ZPC} of the adsorbent was estimated by adding 10 mL of 0.05 M NaCl solution to several vials (15 mL) and the pH was adjusted to a desired value (range, 2–12) by adding aqueous solutions of either HCl or NaOH. Then, 0.03 g of the adsorbent was added to each vial and closed properly and mixed well using a vortexer for 30 min. After that, the vials were allowed to equilibrate for 48 h at room temperature. The suspensions were centrifuged to measure the final pH of the supernatant. The difference between the final and initial pH (ΔpH) was plotted against initial pH. The point of intersection of the resulting curve at which ΔpH = 0 gives rise to the exact value of pH_{ZPC} of an adsorbent.

4.4. Characterization. Fourier transform infrared (FTIR) spectra were recorded in the range of 500–4000 cm⁻¹ using JASCO FT/IR 6300. The number of scans was fixed to 50 with a resolution of 2 cm⁻¹. All of the FTIR spectra were recorded in the transmission mode. The solid-state ²⁹Si cross-polarization magic angle spinning (CP-MAS) NMR spectra were obtained using a JEOL JNM-ECX400II spectrometer. Powder X-ray diffraction (XRD) analysis was carried out using a Rigaku MiniFlex II powder diffractometer using Cu Kα radiation with a beam voltage of 35 kV and a beam current of 15 mA. The morphology of HNTs was characterized by field emission scanning electron microscopy (FESEM: FEI QUANTA FEG 250) after drop-casting a solution on silicon wafer. Specific surface area was estimated by the BET method using nitrogen adsorption/desorption isotherms at 77 K with a 3Flex Micromeritics analyzer. CHN analysis was done using a PerkinElmer 2400 Series II CHNS Elemental Analyzer. UV–visible absorption spectroscopy was conducted at 25 °C using Shimadzu spectrophotometer UV-2600 to estimate the concentration of metal ions present in the solutions. Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements were also carried out using the PerkinElmer ICP-OES instrument (PerkinElmer, Inc., Shelton, CT) to verify the result obtained from UV–visible spectroscopy. pH-dependent adsorption study was carried out using a Mettler Toledo FEP20 pH Meter.

ASSOCIATED CONTENT

S Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00789.

Materials; ²⁹Si CP-MAS NMR spectrum of S-HNTs; XRD patterns of the adsorbents; nitrogen adsorption–desorption isotherms; FTIR spectra of the adsorbents after adsorption of Hg(II) ions; comparison of Hg(II) uptake efficiency with the reported amine-based adsorbents (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: subhra.jana@bose.res.in. Tel: +9133 2335 5706.

ORCID
Subhra Jana: 0000-0002-7105-7106

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by SERB Women Excellence Award (SB/WEA/08/2016) and Nano Mission Research Grant (SR/NM/NS-18/2014) funded by Department of Science and Technology (DST), Government of India, and S. N. Bose National Centre for Basic Sciences, Kolkata, India.

REFERENCES

(1) McNutt, M. Mercury and Health. Science 2013, 341, 1430.
(2) Krabbenhoft, D. P.; Sunderland, E. M. Global Change and Mercury. Science 2013, 341, 1457–1458.
(3) Boening, D. W. Ecological Effects, Transport, and Fate of Mercury: A General Review. Chemosphere 2000, 40, 1335–1351.
(4) Aguado, J.; Arsuaga, J. M.; Arenchía, A.; Líndo, M.; Gascón, V. Aqueous Heavy Metals Removal by Adsorption on Amine-Functionalized Mesoporous Silica. J. Hazard. Mater. 2009, 163, 213–221.
(5) Prabhu, V.; Lee, S.; Clack, H. L. Electrostatic Precipitation of Powdered Activated Carbon and Implications for Secondary Mercury
Adsorption within Electrostatic Precipitators. Energy Fuels 2011, 25, 1010–1016.

(6) Babel, S.; Kurniawan, T. A. Low-Cost Adsorbents for Heavy Metals Uptake from Contaminated Water: A Review. J. Hazard. Mater. 2003, 97, 219–243.

(7) Oehmen, A.; Vergel, D.; Fradinho, J.; Reis, M. A. M.; Crespo, J. G.; Velizarov, S. Mercury Removal from Water Streams through the Ion Exchange Membrane Bioreactor Concept. J. Hazard. Mater. 2014, 264, 65–70.

(8) Samanta, A.; Das, S.; Jana, S. Exploring b-FeOOH Nanorods as an Efficient Adsorbent for Arsenic and Organic Dyes. ChemistrySelect 2018, 3, 2467–2473.

(9) Benhamou, A.; Baudu, M.; Derriche, Z.; Basly, J. P. Aquous Heavy Metals Removal on Amine-Functionalized Si-MCM-41 and Si-MCM-48. J. Hazard. Mater. 2009, 171, 1001–1008.

(10) Morris, E. A.; Kirk, D. W.; Jia, C. Q.; Morita, K. Roles of Sulfuric Acid in Elemental Mercury Removal by Activated Carbon and Sulfur-Impregnated Activated Carbon. Environ. Sci. Technol. 2012, 46, 7905–7912.

(11) Fischer, C.; Oschatz, M.; Nickel, W.; Leistenschneider, D.; Kaskel, S.; Brunner, E. Biospired Carbide-Derived Carbons with Hierarchical Pore Structure for the Adsorptive Removal of Mercury from Aqueous Solution. Chem. Commun. 2017, 53, 4845–4848.

(12) Chandra, V.; Kim, K. S. Highly Selective Adsorption of Hg\(^{2+}\) by a Polypyrrole—Reduced Graphene Oxide Composite. Chem. Commun. 2017, 47, 3942–3944.

(13) Monier, M.; Nawar, N.; Abdel-Latif, D. A. Preparation and Characterization of Chelating Fibers Based on Natural Wool for Removal of Hg(II), Cu(II) and Co(II) Metal Ions from Aqueous Solutions. J. Hazard. Mater. 2010, 184, 118–125.

(14) Monier, M.; Abdel-Latif, D. A. Modification and Characterization of PET Fibers for Fast Removal of Hg(II), Cu(II) and Co(II) Metal Ions from Aqueous Solutions. J. Hazard. Mater. 2013, 250–251, 122–130.

(15) Miretzky, P.; Cirelli, A. F. Hg (II) Removal from Water by Chitosan and Chitosan Derivatives: A Review. J. Hazard. Mater. 2009, 167, 10–23.

(16) Zhang, A.; Xiang, J.; Sun, L.; Hu, S.; Li, P.; Shi, J.; Fu, P.; Su, S. Preparation, Characterization, and Application of Modified Chitosan Sorbents for Elemental Mercury Removal. Ind. Eng. Chem. Res. 2009, 48, 4980–4989.

(17) Hanif, Z.; Lee, S.; Qasim, G. H.; Ardinginsih, I.; Kim, J. A.; Seon, J.; Han, S.; Hong, S.; Yoon, M. H. Polypyrrole Multilayer-Laminated Cellulose for Large-Scale Repeatable Mercury Ion Removal. J. Mater. Chem. A 2016, 4, 12425–124334.

(18) Zhou, Y.; Hu, X.; Zhang, M.; Zhuo, X.; Niu, J. Preparation and Characterization of Modified Cellulose for Adsorption of Cd (II), Hg (II), and Acid Fuchsin from Aqueous Solutions. Ind. Eng. Chem. Res. 2013, 52, 876–884.

(19) Da’na, E. Adsorption of Heavy Metals on Functionalized-Mesoporous Silica: A Review. Microporous Mesoporous Mater. 2017, 247, 145–157.

(20) Yantasee, W.; Rutledge, R. D.; Chouyoyok, W.; Sukwato, V.; Orr, G.; Warner, C. L.; Warner, M. G.; Fryxell, G. E.; Wiacek, R. J.; Timchalk, C.; Addleman, R. S. Functionalized Nanoporous Silica for the Removal of Heavy Metals from Biological Systems: Adsorption and Application. ACS Appl. Mater. Interfaces 2010, 2, 2749–2758.

(21) Liao, K. H.; Lin, Y. S.; Macosko, C. W.; Haynes, C. L. Cytotoxicity of Graphene Oxide and Graphene in Human Erythrocytes and Skin Fibroblasts. ACS Appl. Mater. Interfaces 2011, 3, 2607–2615.

(22) Walcarus, A.; Mercier, L. Mesoporous Organosilica Adsorbents: Nanoengineered Materials for Removal of Organic and Inorganic Pollutants. J. Mater. Chem. 2010, 20, 4478–4511.

(23) Jana, S.; Das, S. Development of Novel Inorganic–Organic Hybrid Nanocomposites as a Recyclable Adsorbent and Catalyst. RSC Adv. 2014, 4, 34435–34442.

(24) Das, S.; Samanta, A.; Jana, S. Light-Assisted Synthesis of Hierarchical Flower-Like MnO\(_2\) Nanocomposites with Solar Light Induced Enhanced Photocatalytic Activity. ACS Sustainable Chem. Eng. 2017, 5, 9086–9094.

(25) Das, S.; Jana, S. A Facile Approach to Fabricate Halloysite/Metal Nanocomposites with Preformed and In Situ Synthesized Metal Nanoparticles: A Comparative Study of their Enhanced Catalytic Activity. Dalton Trans. 2015, 44, 8906–8916.

(26) Hor, Y.-S.; Souton, P.; Dinh, A.; Liu, Z.; Green, M. E. R.; Hook, J. M.; Antill, S. J.; Keptet, C. J. Functionalization of Halloysite Clay Nanotubes by Grafting with γ-Aminopropyltriethoxysilane. J. Phys. Chem. C 2008, 112, 15742–15751.

(27) Das, S.; Ghosh, C.; Jana, S. Moisture Induced Isotopic Carbon Dioxide Trapping from Ambient Air. J. Mater. Chem. A 2016, 4, 7632–7640.

(28) Ho, Y. S.; McKay, G. The Sorption of Lead (II) Ions on Peat. Water Res. 1999, 33, 578–584.

(29) Ho, Y.-S. Review of Second-Order Models for Adsorption Systems. J. Hazard. Mater. 2006, 136, 681–689.

(30) Thomas, J. M.; Thomas, W. J. Introduction to the Principles of Heterogeneous Catalysis; Academic Press, 1967.

(31) Antochshuk, V.; Oikhovoy, O.; Jaroniec, M.; Shin, H. J.; Ryoo, R. Benzylthioiuore-Modified Mesoporous Silica for Mercury (II) Removal. Langmuir 2003, 19, 3031–3034.

(32) Niu, Y.; Qu, R.; Sun, C.; Wang, C.; Chen, H.; Ji, C.; Zhang, Y.; Shao, X.; Bu, F. Adsorption of Pb (II) from Aqueous Solution by Silica-Gel Supported Hyperbranched Polyamidoamine Diamers. J. Hazard. Mater. 2013, 244–245, 276–286.

(33) Song, X.; Niu, Y.; Qiu, Z.; Zhang, Z.; Zhou, Y.; Zhao, J.; Chen, H. Adsorption of Hg (II) and Ag (I) from Fuel Ethanol by Silica Gel Supported Sulfur-Containing PAMAM Dendrimers: Kinetics, Equilibrium and Thermodynamics. Fuel 2017, 206, 80–88.

(34) Niu, Y.; Qu, R.; Chen, H.; Mu, L.; Liu, X.; Wang, T.; Zhang, Y.; Sun, C. Synthesis of Silica Gel Supported Salicylaldheyde Modified PAMAM Dendrimers for the Effective Removal of Hg (II) from Aqueous Solution. J. Hazard. Mater. 2014, 276, 267–278.

(35) Perry, R. H.; Green, D. Perry’s Chemical Engineering Handbook, 6th Ed.; McGraw-Hill: New York, 1984.

(36) Kabiri, S.; Tran, D. N. H.; Azari, S.; Losic, D. Graphene-Diatom Silica Aerogels for Efficient Removal of Mercury Ions from Water. ACS Appl. Mater. Interfaces 2015, 7, 11815–11823.

(37) Das, S.; Maity, A.; Pradhan, M.; Jana, S. Assessing Atmospheric CO\(_2\) Entrapped in Clay Nanotubes using Residual Gas Analyzer. Anal. Chem. 2016, 88, 2205–2211.