Adsorption of mercury from aqueous solution by nontronite, Aspergillus niger, and hybrid material
Denis L. Guerra, Ricardo A. R. Silva and Ivani Mello

ABSTRACT
A natural nontronite clay sample from the Amazon region (Tocantins State, Serra da Messa Group, Brazil) was utilized for synthesis of a new biomaterial produced by a hybridization process of inorganic and organic materials. The new biomaterial was composed of an Amazon nontronite and fungal mass obtained from the Aspergillus niger fungus. The natural clay, biomass, and biomaterial samples were used in batch studies for adsorption of Hg²⁺ ions from aqueous solution. The effects of stirring time, adsorbent dosage, and pH on the adsorption capacity demonstrated that 70 min is sufficient to reach equilibrium at room temperature and over a pH range of 6.0–8.0. The maximum number of moles adsorbed was 9.47, 17.8, and 18.7 mmol g⁻¹ for natural clay, biomass, and biomaterial, respectively. From the cation/basic center interactions for each material at the solid–liquid interface, by using calorimetry, the equilibrium constant and exothermic thermal effects were calculated. By considering the net interactive number of moles for mercury ion and the equilibrium constant, the enthalpy and negative Gibbs free energy could be calculated: ΔH = -6.8 ± 0.11 to -6.0 ± 0.22 kJ mol⁻¹; ΔG = -20.5 ± 0.25 to -23.2 ± 0.22 kJ mol⁻¹. The thermodynamic values indicated the existence of favorable conditions for interactions at the solid–liquid interface.

Key words | adsorption, Aspergillus niger fungus, mercury nontronite

NOMENCLATURE
N_l the maximum adsorption capacity of the adsorbent (mmol g⁻¹)
C_S metal concentration at equilibrium (mmol dm⁻³)
N_L amount of adsorbate adsorbed at the equilibrium – Langmuir (mmol g⁻¹)
K_L Langmuir affinity constant (dm⁻³ mmol⁻¹)
K_F Freundlich constant related to adsorption capacity [mmol g⁻¹ (mmol dm⁻³)⁻¹/n_F]
N_F dimensionless exponent of Freundlich equation
N_S amount of adsorbate adsorbed at the equilibrium – Sips (mmol g⁻¹)
K_S Sips constant related to the affinity constant [mmol dm⁻³)⁻¹/n_S]
A_RP the Redlich–Peterson constant (mmol dm⁻³)⁻g
g dimensionless exponent of Redlich–Peterson equation
K_RP Redlich–Peterson constants (dm⁻³ g⁻¹)
N_t amount of adsorbate adsorbed at time t (mmol g⁻¹)
N_E amount of adsorbate adsorbed at the equilibrium – kinetic (mmol g⁻¹)
k_AV Avrami kinetic constant (min⁻¹)
t time of contact (min)
k_f pseudo-first-order rate constant (min⁻¹)
k_s pseudo-second-order rate constant (g mmol⁻¹ min⁻¹)
α The initial adsorption rate (mg g⁻¹ h⁻¹) of Elovich equation
β Elovich constant related to the extent of surface coverage and also to the activation energy involved in chemisorption (g mg⁻¹)

INTRODUCTION
Contamination of water by mercury is of great concern due to the potentially toxic effects of elevated levels of this
pollutant in several ecosystems and human health. Industrial activities, such as the foundry process in steel production, solid waste incineration, the cracking of oil, and mining, are largely responsible for mercury pollution (Malm 1996). Numerous studies have reported that biological systems in some rivers of the Amazon region are contaminated with mercury species from illegal and inopportune mining operations (Nriagu et al. 1992). Pressure from environmental authorities has forced the establishment of discharge limits which, in turn, require the effective use of decontamination, purification, and separation methods. Nowadays, new reactive and porous materials and advanced methods have been sought to enable the removal of this pollutant from rivers and other water bodies such as lakes and groundwater aquifers (Diaz et al. 2007).

The methods employed for the uptake of Hg$^{2+}$ ions include precipitation, ion exchange and adsorption on various organic and/or porous materials, such as activated carbon, zeolites, pillared clay, and organoclay (Sharma & Forster 1995; Guerra et al. 2006). Attention has naturally been focused on the utilization of low-cost and abundant biomaterials (Sharma & Forster 1994, 1995; Aksu 2005). Numerous biomaterials such as the macroalga Cystoseira baccata (Herrero et al. 2005), various vegetal species such as bamboo (Tan et al. 2011), and fungus species (Saglam et al. 1999) have been tested for pollutant metals removal, and to elucidate important factors affecting the adsorption capacities of these materials for application on an industrial scale. In particular, fungal biomass can be easily acquired in significant quantities. Aspergillus niger (A. niger) is a filamentous ascomycete fungus and one of the most common species of the genus Aspergillus (Schuster et al. 2002). A. niger is economically important; this fungus species has been cultivated for the industrial application in systematic series of chemical operations that produce or manufacture several substances, e.g. in the preparation of citric acid, gluconic acid, and the production of enzymes by industrial fermentation processes (Schuster et al. 2002). A large number of reports addressing the biosorption of Hg$^{2+}$ ions with dead fungal biomass has been released recently and these studies concluded that mercury ions were removed from aqueous media by anionic adsorption (Svecova et al. 2006). An important viewpoint is that anionic adsorption by biomass of mercury ions depends on the pK values of the acidity of a medium solvated by divalent metal and the influence of a negative charge on the biomass surface (Svecova et al. 2006).

The present work was undertaken to investigate the feasibility of using the new geological occurrence of nontronite clay samples, fungal mass, and hybrid biomaterial for the adsorption of mercury ions from aqueous media by batch and column processes under several environmental conditions, and thermal effects involved in the adsorption process. The synthesis and chemical aspects related to the biomaterial composition with A. niger fungus on the layer and ferruginous structure of clay are presented in this study. The natural clay and new biomaterial were efficient at removing Hg$^{2+}$ ions from aqueous medium; the adsorption experimental data were analyzed by fitting them into the isotherm equilibrium model. Based on error function values, the experimental data were best fitted by the Sips isotherm model. The performance in adsorbing Hg$^{2+}$ ions from natural water under dynamic flow conditions was also studied and the results confirmed the batch experiments. The comparison of these two experiments was an important step to find the suitable theoretical isotherm model that can be used to design a removal process. Desorption of the mercury ions from materials was studied in 0.25 mol dm$^{-3}$ HNO$_3$ and very high desorption rates, approximately 97%, were achieved in three adsorption systems. The energetic effect at the solid–liquid interface that was caused by the aggregation of Hg$^{2+}$ ions in the reactive center on the surface of materials was determined through the calorimetric titration procedure.

**EXPERIMENTAL**

**Raw material and reagents**

The clay was sampled in the Amazon region, in northern Brazil. The natural nontronite sample, named NON-1, with particles less than 2.0 μm in size, was prepared by separating the silt and sand by sedimentation. The cation-exchange capacity (CEC) was measured in order to evaluate the potential use of clay for intercalation by A. niger, following the ammonium acetate method with concentration of 2.0 mol dm$^{-3}$ at 315 ± 1 K and pH 8.0 (Schollenberger &
The result obtained was 98.0 meq/100 g of clay on an air-dried basis. Chemical characterization was also carried out, using analytical techniques that will be described below. The natural phyllosilicate sample was activated in a stream of dry nitrogen by heating at 423 ± 1 K over 10 h and used immediately.

The A. niger fungus ATCC 9142 was provided by FAT (André Tosello Foundation-SP/Brazil). An aqueous solution was prepared with a concentration of 1,500.0 mg dm\(^{-3}\) and pH was adjusted by the addition of 0.10 mol dm\(^{-3}\) of HNO\(_3\) (Aldrich) or NaOH (Aldrich). Fresh dilutions were used for each adsorption experiment. Double distilled deionized water (DDW) was used where required for the preparation of solutions.

**Chemical preparation of biomaterials**

The chemical modification was developed in three steps. (i) Culture of A. niger (Figure 1); the A. niger fungus ATCC 9142 was cultivated in medium containing 22.0 g dm\(^{-3}\) of malt extract, 22.0 g dm\(^{-3}\) of 2-deoxyglucose, and 1.5 g dm\(^{-3}\) of peptone (Vela & Rosenthal 1972) on a rotary shaker at 298 ± 1 K; pH was basic. After 9 days of incubation, the fungal biomass was washed with DDW and then dried at 298 ± 1 K (Kapoor & Viraraghavan 1995; Park et al. 2004, 2005). The resulting biomass was preserved in a desiccator and named BIO-AN. The mass of approximately 10 g of BIO-AN was maintained in another desiccator for utilization in the following synthesis with nontronite clay.

(ii) NON-1 was submitted an atmosphere of solvated ethylene glycol. The mass of approximately 5 g of NON-1 was suspended with 10.0 cm\(^3\) of 2-deoxyglucose and 5.0 cm\(^3\) of peptone, under reflux at inert nitrogen atmosphere and mechanical stirring over 130 min; the resulting solution was called NON-1\(_{\text{AQS}}\). (iii) For the intercalation reaction, approximately 10 g of biomass obtained in the first step (BIO-AN) was added in the solution obtained in the second step (NON-1\(_{\text{AQS}}\)); this intercalation reaction for obtaining hybrid biomaterial was processed over 3.5 days with mechanical stirring at 298 ± 1 K; the resulting solution was filtered through glass and the solid was dried under vacuum for 12 h to yield the respective hybrid biomaterial named NON-1/AN.

**Batch adsorption study**

Firstly, the effect of pH on adsorption for NON-1, BIO-AN, and NON-1/AN samples was evaluated by varying this parameter over a pH range of 1.0 to 12.0, with the addition of 0.10 mol dm\(^{-3}\) of nitric acid or sodium hydroxide. The pH of the solutions was measured using a pH/Ion, model 450 M, Analyzer, SP, Brazil.

The adsorption experiments were performed by a batch-wise method, i.e. by suspending 20.0 mg of each material in an aqueous solution (25.0 cm\(^3\)) of the divalent mercury at concentrations varying from 0.125 to 3.50 mmol dm\(^{-3}\), under orbital stirring over 24 h at 298 ± 1 K (Kanaan & Malar 2005; Sari & Tuzen 2009). The materials were separated by centrifugation and supernatant solutions were carefully transferred to glass flasks to determine the concentrations of mercury ions present in each supernatant solution. The final concentrations of the mercury ions were determined using a PerkinElmer Flame Atomic Absorption (AA) Spectrometer model Analyst 200 operating with an air-acetylene flame and a mercury cathode lamp (\(\lambda_{\text{Hg(I)}} = 253.60\) nm). The Hg\(^{2+}\) adsorption capacities \((N_f)\) of the phyllosilicate and biomaterials were calculated from Equation (1), for a series of isotherms, and revealed that the adsorption process conforms to the equilibrium theoretical models. The isotherm equations corresponding to the Langmuir (1918), Freundlich (1906), and Sips (1948) models are presented in Table 1. The kinetic equations corresponding to the Avrami, pseudo-first-order,
and pseudo-second-order models (Lagergren 1898) are given in Table 1.

\[ N_f = \frac{N_i - N_e}{m} \]  

(1)

where \( N_i \) is the initial number of moles of \( \text{Hg}^{2+} \) ions added to the adsorbent, \( N_e \) is the amount remaining after the equilibrium is reached and \( m \) is the mass in grams of the adsorbent. Profiles of the adsorption isotherms that were obtained experimentally are represented by the number of moles per gram adsorbed (\( N_i \)), versus the number of moles at equilibrium per volume of solution (\( C_g \)).

The desorption process of mercury ions was achieved by using 25.0 cm\(^3\) of the eluent, i.e. 0.25 mol dm\(^{-3}\) of HNO\(_3\) (Arpa et al. 2000). The NON-1, BIO-AN, and NON-1/AN samples were reutilized after adsorption with the mercury ions, i.e. the material samples were loaded with the mercury ions, under the following conditions: initial concentration of \( \text{Hg}^{2+} \) ions, 100.0 mg dm\(^{-3}\); amount of materials, approximately 5 g; volume of the adsorption medium, 25.0 cm\(^3\); pH 4.0; temperature, 273 ± 1 K; and adsorption time, 180 min. Then, the three adsorption systems were placed in the desorption medium and stirred at 600 rpm for up to 60 min.

### Column adsorption study

A 15.0 cm long glass column with a 0.50 cm internal diameter, a porous sintered glass disk at the bottom and a Teflon stopcock was packed with 1.00 g of NON-1, BIO-AN, and NON-1/AN samples for each experiment in the dynamic adsorption system, which occupied 5.0 cm\(^3\) of this column. The column was then filled from the top with 1.85 × 10\(^{-4}\) mol dm\(^{-3}\) of \( \text{Hg}^{2+} \) ions at pH 4.0 and a feed flow rate of 3.0 cm\(^3\) min\(^{-1}\). The column effluent flow-rate was adjusted to 3.5 cm\(^3\) min\(^{-1}\) using the stopcock, and the solution depth or hydraulic head at the top was kept constant by feeding the column at the same flow rate as the effluent rate using a peristaltic pump (Model 601, SP, Brazil). The column effluents were collected in 50.0 cm\(^3\) intervals using a fraction collector, and \( \text{Hg}^{2+} \) ions were determined as above using Flame Atomic Absorption Spectrometry (Analyst 200, PerkinElmer). The column adsorption capacity (\( N_{cd} \)) was calculated by Equation (2), which is expressed as (Xu et al. 2009):

\[
N_{cd} = \frac{(C_0V_0 - \Sigma C_nV_n)}{m}
\]  

(2)

where \( N_{cd} \) (mg g\(^{-1}\)) is the mass of \( \text{Hg}^{2+} \) ions adsorbed per gram of NON-1, BIO-AN, and NON-1/AN at saturation, \( C_0 \) (mg dm\(^{-3}\)) is the original concentration of mercury, \( V_0 \) (dm\(^3\)) is the volume of the effluent solution, \( C_n \) (mg dm\(^{-3}\)) is the concentration of sample \( n \), \( V_n \) (dm\(^3\)) is the volume of sample \( n \), and \( m \) (g) is the amount of material.

In order to evaluate material samples as possible adsorbents for the wastewater treatment of mercury-containing effluents, breakthrough curves for \( \text{Hg}^{2+} \) ions using various materials as adsorbents were obtained; the values were determined by analyses of the BP1 (lower breakpoint) and BP2 (higher breakpoint), both of which were obtained after passing an effluent volume of 1.85 × 10\(^{-4}\) mol dm\(^{-3}\) of \( \text{Hg}^{2+} \) ions through the column of adsorbent.

Due to the continuous adsorption, the flow of \( \text{Hg}^{2+} \) solution creates a wave front as it flows through the bed composed of materials. This wave front is known as the mass transfer zone (MTZ). In order to determine the MTZ, the amount of \( \text{Hg}^{2+} \) put into the column and the total amount removed were calculated; they correspond to...
the adsorption capacity until the breakthrough point \( (q_U) \), which is BP2, and the saturation point \( (q_T) \), respectively. Equations (3) and (4) were obtained through a mass balance in the column using its saturation data based on its breakthrough curves, where the area below the curve \( (1 - C/C_0) \) up to the breakthrough point is proportional to \( q_U \), and up to the point of exhaustion of the bed is proportional to \( q_T \) (Ernest et al. 1997).

\[
q_U = \frac{C_0 V}{1,000 \text{m}} \int_0^{t_b} (1 - C_t / C_0) \, dt
\]

(3)

\[
q_T = \frac{C_0 V}{1,000 \text{m}} \int_0^{t_{tot}} (1 - C_t / C_0) \, dt
\]

(4)

where \( q_U \) (mg g\(^{-1}\)) is the amount of adsorbent metal per unit of adsorbent mass up to the breakthrough point, \( C_t \) (mg dm\(^{-3}\)) is the metal concentration in a solution in the column outlet, \( C_0 \) (mg dm\(^{-3}\)) is the initial metal concentration in the liquid state, \( m \) (g) is the bentonite mass, \( t_b \) (min) is time until breakthrough point, and \( t_{tot} \) (min) is the time for total removal and limit of concentration in a solution column outlet \((z_L)\).

The MTZ can be calculated based on the \( q_U/q_T \) ratio according to Equation (5), and MTZ has a maximum value which corresponds to the bed height \((H_L)\).

\[
\text{MTZ} = H_L \left( 1 - \frac{q_U}{q_T} \right)
\]

(5)

**Thermal effect interactions**

The thermal effects from mercury ions interacting on NON-1, BIO-AN, and NON-1/AN surfaces were followed by calorimetric titrations using an isothermal calorimeter, Model LKB 2277. In this titration, the mercury solution was added to a suspension of about 20 mg of the solid sample in 2.0 cm\(^3\) of water, under stirring at 298 ± 1 K. A series of increments of 10.0 dm\(^3\) of metal solutions was added to the solid materials to obtain the thermal effect of interactions \( (\sum Q_d) \). Two other titrations are needed to complete the full experiment: (i) the thermal effect due to hydration of NON-1, BIO-AN, and NON-1/AN samples \( (\sum Q_h) \), which normally gives a null value, and (ii) the dilution effect of metal solution in water, without sample in the vessel \( (\sum Q_d) \). The resulting thermal effect is given by Equation (6) (Guerra et al. 2011a, b).

\[
\sum Q_t = \sum Q_i - \sum Q_d - \sum Q_h
\]

(6)

**Analytical procedure**

The natural phyllosilicate sample was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), using a PerkinElmer 3000 DV instrument. The oven-dried powdered sample weighing 250.0 mg was placed separately on a weighed glass dish and transferred quantitatively to pre-cleaned nitric acid digestion bottles.

The natural phyllosilicate and biomaterials were analyzed by scanning electron microscopy (SEM) in a JEOL microscope, model JEOL JSM 6360LV, using an acceleration voltage of 20 kV and magnification ranging from 300- to 370-fold.

**RESULTS AND DISCUSSION**

**Characterization of clay, biomass, and hybrid materials**

The bulk geologic material used for this study was a massive yellowish sample consisting of 32.5% nontronite clay, 58.1% silt, and 9.4% sand; this coloration can be attributed to the presence of high perceptual of iron in the oxidation state in the bulk geologic material. Elemental analysis by ICP-OES of the original clay sample, NON-1, gave results that were consistent with nontronite, with silicon being the major element as a structural component. The total mineralogical composition was 45.69, 24.67, 9.35, 3.15, 1.34, 0.24, 0.07, 0.03, 0.02, and 0.01% of SiO\(_2\), Fe\(_2\)O\(_3\), Al\(_2\)O\(_3\), MgO, CaO, K\(_2\)O, MnO, ZnO, CuO, and ZrO, respectively, and 15.41% of the mass was lost in the ignition process. The percentages of Mg(II), Ca(II), and K(I) indicate variable amounts of cations, which can be suitable for the intercalation and adsorption processes. A blank and a set of elemental standards were run to calibrate the instrument:

\[
\text{SiO}_2 \quad [(\text{NH}_4)_2\text{SiF}_6/\text{H}_2\text{O}/1,000 \text{ ppm}], \quad \text{Fe}_2\text{O}_3 \quad (\text{Fe}/\text{HNO}_3/100 \text{ ppm}), \quad \text{Al}_2\text{O}_3 \quad (\text{Al}/\text{HCl}/100 \text{ ppm}), \quad \text{MgO} \quad (\text{Mg}/\text{HNO}_3/
Typical SEM images of smectite type nontronite (also called smectite of iron) and fungal morphology of biomaterials samples are presented in Figures 2(a)–2(c). Foliated morphology as well as structural ordering of the original nontronite can be seen in Figure 2(a). The heterogeneous nature of the surface morphology of the NON-1 sample was revealed in this micrograph, which also shows that nontronite crystals present considerable variation in size. This observation may suggest the existence of other minerals as accessories or secondary minerals, such as feldspar, hematite, and goethite, the last two minerals with high iron content, such as nontronite and common soil altered by intense leaching (Tazaki et al. 1987). The microcrystals revealed some fissures and holes (Figure 2(a)) in the surfaces, which indicated the presence of a macroporous structure; the microcrystals had dark yellow tonality, which can be attributed to high iron content in the nontronite structure. This morphology may contribute a little to the diffusion of the large molecules to the adsorbent surfaces of phyllosilicate. In Figure 2(b) the classical morphology for the genus Aspergillus can be observed; ‘septate’ cells are created by internal cross-walls and are usually perforated by large pores. This type of randomly developed modification is denominated hyphae; the hyphae, developed with the culture method described above, have an elongated form; the typical morphology of branching filamentous structures and a significant density of septate hyphae were also observed in the SEM micrograph of BIO-AN (Corner 1932). This morphology can be considered evidence of the success of the fungal biomass that was obtained with the culture method utilized in this study, principally in the use of the density of the culture medium. The classification, such as heterogeneous surface nature, can also be applied for NON-1/AN, with conidia formations in the clay inorganic surface observed in Figure 2(c). This formation may prove that NON-1 was a favorable medium for the development of conidiophores and the resulting biomaterials can be potentially reactive in the adsorption process.

**Batch adsorption and thermodynamic studies**

The Hg$^{2+}$ ions were examined over a pH range of 1.0 to 12.0. Figure 3(a) shows the influence of pH in adsorption process of Hg$^{2+}$ ions onto the surfaces of NON-1, BIO-AN, and NON-1/AN. The equilibrium data reveal maximum values of $N_f^{\text{max}}$ around pH 5.0 for NON-1, 8.0 for BIO-AN, and 6.0 for NON-1/AN. As can be seen from Figure 3(a), the adsorption of Hg$^{2+}$ ions on NON-1 mainly occurs at $5.0 < \text{pH} < 9.0$. The adsorption of Hg$^{2+}$ ions increases quickly at $\text{pH} < 8.0$ for BIO-AN and NON-1/AN. The results emphasize that with an increase in the pH of the solution, the $N_f^{\text{max}}$ adsorbed increased for the three systems. Therefore, the efficiency of Hg$^{2+}$ ions with NON-1, BIO-AN, and NON-1/AN can be controlled by the initial pH of the reactions at the solid–liquid interface. The reason for a small adsorption capacity at high pH level is the competition between the excess of OH$^{-}$ species in the metal solutions (Guerra et al. 2009). Also, greater acid concentrations suppress hydrolysis of Hg$^{2+}$ ions. In addition, the adsorption

![Figure 2](https://iwaponline.com/wqrj/article-pdf/48/2/155/379954/155.pdf)
of $\text{Hg}^{2+}$ ions on the surface of this material type (organic–inorganic structure) is principally dominated by ion-exchange or outer-sphere complexation at low pH values, and by inner-sphere complexation at high pH (Guerra et al. 2013). Consequently, the number of moles of $\text{Hg}^{2+}$ ions adsorbed may decrease at low pH.

The interaction of cations with surfaces of the nontonite structure and the fungal biomass is governed by the microenvironment around each arrangement, which is usually composed of reactive centers, mainly in the internal hydrated structure. Such hydroxyl groups act as bridgings that favor the nontronite interaction process with fungal biomass.

From the adsorption isotherm for $\text{Hg}^{2+}$ ions, represented by a $C_S$ versus $N_f$ plot, the theoretical curves were obtained with a non-linear method, as shown in Figure 3(b), whose data were adjusted to the Langmuir, Freundlich, Sips, and Redlich–Peterson models (Figure 3(c)), as before. The Sips adsorption model can be used to explain the significant capacity of the NON-1/AN to quantify divalent metal interactions by complexation reactions. The four theoretical models present a significant advantage in

![Graphs and Figures]

**Figure 3** | Effect of pH on $\text{Hg}^{2+}$ adsorption (a) and effect of concentration of $\text{Hg}^{2+}$ adsorption onto nontronite samples (b): NON-1, BIO-AN, and NON-1/AN. Isotherms calculated with non-linear method: Sips, Langmuir, Freundlich, and Redlich–Peterson (c) and separation factor of $\text{Hg}^{2+}$ ions adsorbed at six different temperatures (d).
comparing the experimental data; it allows quantifying the capacity of retaining cations within the structure of the matrix and to evaluate the constant related to the bonding energy.

One of the essential characteristics of the Langmuir model and derivative models, such as the Sips model, could be expressed by a dimensionless constant called an equilibrium parameter or dimensionless separation factor, $R_L$, which can be calculated using the following equation (Malkoc et al. 2006):

$$ R_L = \frac{1}{(1 + K_L C_0)} $$

where $C_0$ (mmol dm$^{-3}$) is the highest initial solute concentration. The parameters of the Langmuir equation may be utilized to represent the affinity in the adsorption process between adsorbent and adsorbate surfaces using the dimensionless separation factor. The criteria for separation factor and characteristics of Langmuir isotherms, respectively, are: $R_L > 1$ is unfavorable, $R_L = 1$ is linear, $0 < R_L < 1$ is favorable, and $R_L = 0$ is irreversible (Padmesh et al. 2005). As seen in Figure 3(d), the values of $R_L$ for adsorption of Hg$^{2+}$ ions on NON-1, BIO-AN, and NON-1/AN surfaces at six different temperatures ($T_n = 298, 323, 348, 373, 393$, and $413 \pm 1$ °K) were between 0 and 1, which indicates the favorable adsorption of mercury ions on the surface of materials that were utilized in this study.

For a series of calorimetric titrations, the number of increments and the volumes of Hg$^{2+}$ ions needed to saturate the mass of the NON-1, BIO-AN, and NON-1/AN samples (Lazarin & Airoldi 2009) are listed in Table 2. The adsorption process was evaluated from the results obtained, by considering the adsorption isotherms and the molar fraction of the Hg$^{2+}$ ions in solution. The experimental data were better adjusted to a Sips model ($R^2 \sim 0.99$), in which it was assumed that monolayer of Hg$^{2+}$ ions is formed on the NON-1, BIO-AN, and NON-1/AN surfaces. The maximum adsorption capacities for Hg$^{2+}$ ions onto materials used in this work are listed in Table 3, the values of which are highest for BIO-AN and NON-1/AN. This behavior can be attributed to the optimization of the physical–chemical properties of the materials obtained by the synthesis method, and consequently, to the larger surface capacity.
The molar fraction of Hg\(^{2+}\) ions in the supernatant in equilibrium for each point of the calorimetric titration (X) was calculated by considering the number of moles of the solute (N\(_S\)) and the number of moles of water (N\(_{Wat}\)) expressed by Equation (8) (Lazarin & Airoldi 2009):

\[
X = \frac{N_S}{(N_S + N_{Wat})}
\]

(8)

The thermodynamic values obtained were adjusted by the Levenberg–Marquardt criteria and interaction calculated by the Simplex methods to the modified Langmuir model (Guerra et al. 2014a, b) are given in Equation (9).

The calorimetric results obtained for three systems are presented in Figure 4(a) and are listed in Table 2.

\[
\sum X = \frac{1}{(K_L - 1)\Delta_{int}h} + \sum X
\]

(9)

where \(\Sigma X\) is the sum of the mole fraction of each mercury cation in solution, after adsorption, obtained for each experimental point of titrand addition. \(\Sigma \Delta h\) is the integral enthalpy of adsorption for each point of the calorimetric titration obtained by dividing the thermal effect resulting from adsorption by the number of moles of adsorbate measured; \(K_L\) is the proportionality constant which also includes the equilibrium constant. \(\Delta_{int}h\) is the thermal effect of the formation of a monolayer on the surface. A plot of \(\Sigma X/\Sigma \Delta h\) versus \(\Sigma X\) gave the values of \(\Delta_{int}h\) and \(K_L\), respectively, obtained from non-linear fitting of the calorimetric isotherms. The enthalpy of adsorption, \(\Delta_{int}H\), was calculated using Equation (10) (Lazarin & Airoldi 2009; Guerra et al. 2011a, b):

\[
\Delta_{int}H = \frac{\Delta_{int}h}{N_S}
\]

(10)

Change in free energy (\(\Delta_{int}G\)), enthalpy (\(\Delta_{int}H\)), and entropy (\(\Delta_{int}S\)) are important thermodynamic parameters that were determined using the following equations (Equations (11) and (12)), taking these values into account (Malkoc & Nuhoglu 2003):

\[
\Delta_{int}G = -RT \ln K_L
\]

(11)
where $K_L$ is the equilibrium constant obtained from the Langmuir isotherm equation, $T$ ($K$) is the absolute temperature, and $R$ is the universal gas constant ($8.314 \times 10^{-3}$ kJ K$^{-1}$ mol$^{-1}$). Equation (12) relates to the energy of adsorption systems:

$$\Delta_{\text{int}}G = \Delta_{\text{int}}H - T\Delta_{\text{int}}S \tag{12}$$

The thermodynamic cycle for this series of adsorptions involving suspension (susp) of NON-1, BIO-AN, and NON-1/AN (N/B/N) in aqueous solution (aq) with Hg$^{2+}$ ions (M$^{n+}$) can be represented by the following calorimetric reactions. Reactions (13)–(15) represent calorimetric titration experiments carried out in duplicate for each determination:

\begin{align*}
N/B/N_{(\text{susp})} + M^{n+}_{(aq)} & \rightarrow N/B/N \cdot M^{n+}_{(\text{susp})} \sum Q_t \tag{13} \\
N/B/N_{(\text{susp})} + nH_2O & \rightarrow N/B/N \cdot nH_2O_{(aq)} \sum Q_b \tag{14} \\
M^{n+}_{(aq)} + nH_2O & \rightarrow M^{n+} \cdot nH_2O_{(aq)} \sum Q_d \tag{15}
\end{align*}

The thermal effects of reactions (13)–(15) for each experimental point of the calorimetric titration were considered in the calculation of the net thermal effect ($\Sigma Q_r$) of these interactions, as represented by reaction (16):

$$N/B/N \cdot nH_2O_{(aq)} + M^{n+} \cdot nH_2O_{(aq)} \rightarrow N/B/N \cdot M^{n+}_{(\text{susp})} + 2nH_2O \sum Q_r \tag{16}$$
A resume of the thermodynamic data is listed in Table 2. From the thermodynamic point of view, the obtained exothermic and positive entropic values establish the set of favorable results for the thermodynamics of mercury–materials interactions. Thus, the spontaneity of such reactions is expressed by the negative Gibbs free energy with a considerable contribution of the positive entropy. These values suggest that during interactions of Hg\(^{2+}\) ions and *A. niger* biomass/nontronite, the desolvation disturbs the structure of the reaction medium to promote the disorganization of the system and, consequently, leads to an increase in entropy (Lazarin & Airoldi 2009; Guerra et al. 2011a, b). The relationship between thermodynamics adsorption values for three systems is presented in Figure 4(b). In conclusion, all thermodynamic values are favorable, and exothermic enthalpy, negative free Gibbs energy and positive entropy data corroborate with Hg\(^{2+}\)/NON-1, BIO-AN, and NON-1/AN interactions at the solid–liquid interface.

**Kinetic adsorption**

The adsorption experimental data for Hg\(^{2+}\) ions uptake versus contact time for fixed adsorbent amounts are presented in Figure 5(a), giving identical abrupt increases in adsorption at low times before reaching the plateaus in the experimental isotherms. According to these data, equilibrium is achieved at around 70, 90, and 100 min for the systems Hg\(^{2+}\)/NON-1, Hg\(^{2+}\)/BIO-AN, and Hg\(^{2+}\)/NON-1/AN, respectively. However, to be sure of the best adsorption conditions at higher concentration levels, and to obtain equilibrium at the solid–liquid interface, all of the experiments were carried out within 210 min of contact time. This short time period required to attain equilibrium suggests an excellent affinity of the mercury for these materials, principally in the adsorption process with BIO-AN and NON-1/AN from aqueous solution. When the rate of reaction of an adsorption reaction is controlled by a chemical exchange, a pseudo-second-order model can be better adjusted to the experimental kinetic data (Yeddou & Bensmaili 2005), as expressed in Table 3. Carrying out a set of experiments at constant temperature (273 ± 1 K) and monitoring the amount adsorbed over time, the kinetics of the adsorption process could be identified. The rate of metal uptake during the entire period of adsorption was found to be independent of the initial metal concentration used. The correlation coefficient of the pseudo-second-order rate equation \(R^2\) for the non-linear regression was approximately 0.99, which suggest that the kinetic adsorption can be described by the pseudo-second-order rate equation with a satisfactory approximation of the experimental kinetic curve.

Based on the second-order model, the initial adsorption rate and half-adsorption time are estimated by the following
Equations (17) and (18) (Yeddou & Bensmaili 2005):

\[ h = k_2 N_{EQ}^2 \]  
\[ t_{1/2} = \frac{1}{k_2 N_{EQ}} \]

The half-adsorption time, \( t_{1/2} \), is another parameter and is defined as the time required for the adsorption to take up half as much Hg\(^{2+}\) ions as its equilibrium values for three systems. Thus, the initial adsorption rate and half-adsorption time are usually a measure of adsorption rate.

For the determination of activation energy \( E_a \) (kJ mol\(^{-1}\)) for Hg\(^{2+}\) ions adsorption reaction, the pseudo-second-order rate constant \( k_s \) (g mmol\(^{-1}\) C\(_0\) \(1\) min\(^{-1}\)) was expressed as a function of five different temperatures \( T_n \) (298, 323, 348, 373, 393, and 413 ± 1 K) by an Arrhenius type relationship (Equation (19)) (Yeddou & Bensmaili 2005):

\[ k_s = k_0 \exp \left( \frac{E_a}{RT} \right) \]

where \( k_0 \) (g mol\(^{-1}\) min\(^{-1}\)) is the temperature independent factor. From this equation and the non-linear method, the rate constant values of adsorption, \( k_0 \) and the activation energy values can be calculated and are presented in Table 2. These values show that the adsorption processes of Hg\(^{2+}\) ions by adsorbent surfaces of materials used in this work are exothermic. These results may be explained by the fact that the adsorption phenomena are exothermic and are spontaneous processes in three systems, confirming the conclusion obtained by the calorimetric method, where the values of determination coefficient (\( R^2 \)) for both calculated curves were approximately 0.999. The pseudo-second-order kinetic constant decreased with increasing temperature (Figure 5(b)).

**Column Hg\(^{2+}\) adsorption**

In order to evaluate clay and biomaterials as absorbents for wastewater treatment of Hg\(^{2+}\) ions containing effluents, breakthrough curves of this divalent metal using NON-1, BIO-AN, and NON-1/AN samples as absorbents were obtained, as illustrated in Figure 6. The layer structure of the hybrid material, NON-1/AN, is less stable than the natural nontronite, as indicated by the formation of and fragmentation of clusters of particles during the adsorption tests in column-flow conditions. Smaller breakthrough points (BP) were determined when the mercury ion effluents from the column attained concentrations of \( >0.010 \) mg dm\(^{-3}\), with the curve showing an S-type model (Han et al. 2006).

The surface reaction theory was the foundation for the Adams–Bohart equation and assumes non-spontaneous equilibrium of reactions in the adsorbent surfaces; therefore, the rate of the adsorption is considered proportional to the fraction of adsorption capacity still remaining on the adsorbent. The Adams–Bohart model (Equation (20)) is utilized for the analysis of the initial part of the breakthrough experimental curves (Malkoc et al. 2006).

\[ \frac{C_t}{C_0} = \exp \left[ k_{AB} C_0 t - k_{AB} N_0 Z \right] \frac{Z}{U_0} \]

where \( C_0 \) and \( C_t \) (mgdm\(^{-3}\)) are the inlet and effluent Hg\(^{2+}\) ions concentrations, respectively. \( Z \) (cm) is the height of the column, \( U_0 \) (cm min\(^{-1}\)) is the superficial velocity, \( N_0 \) (mg dm\(^{-3}\)) is the saturation concentrations in this model, and \( k_{AB} \) (dm\(^3\) mg\(^{-1}\) min\(^{-1}\)) is the mass transfer coefficient. The range of \( t \) should be considered from the beginning to the final part of the breakthrough.

**Figure 6** | Effect of variation in effluent concentration on the breakthrough curves, NON-1 (○), BIO-AN (□), and NON-1/AN (○) and curves calculated with a non-linear method by the Adams–Bohart equation (△).

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The BP₁ value is related to the ability of the adsorbents to retain the Hg²⁺ ions from aqueous solutions. The large breakpoints (BP₂) were related to the complete saturation of the materials with the mercury ions. Using an adsorption column packed with adsorbent reactive sites in which an inert carrier flows at a steady rate (dynamic system), the BP₁ value clearly indicated that the nontronite, biomass and hybrid material would be efficient adsorbents assisting in the decontamination of effluents of the toxic metal mercury. A single volume of the adsorbent is capable of completely removing least 2.25 mmol g⁻¹ of mercury as observed for NON-1/AN. The values for mercury adsorption in a dynamic system were similar to values obtained in batch experiments (Table 3). Using a dynamic adsorption system, the maximum saturation of the materials by Hg²⁺ ions is very close to the values obtained in the batch adsorption experiments for the three systems.

**Comparison with other adsorbents**

The same examples of different adsorbents focusing on the available mercury extraction data from aqueous solutions were listed for comparison with adsorbents utilized in this investigation (Table 4). Of the 13 different adsorbents investigated, none had a greater adsorption capacity than the natural or modified materials for Hg²⁺ ion uptake, indicating that these adsorbents could be used in the removal of Hg²⁺ ions from aqueous solutions. In addition, evaluation is complex because the efficiency depends on solution pH, adsorbent mass, initial adsorbate concentration, contact time, temperature of the experimental systems, and other solution conditions. Therefore, comparisons were made in terms of the most essential parameter, the maximum adsorption capacity. The most relevant observation was that the tested nontronite exhibit a greater adsorption capacity than most of the activated carbon from furfural (Yardim et al. 2005) and biomass and that hybrid material have higher capacities than the macroalga sample Cystoseira baccata (Herrero et al. 2005). According to the results, NON-1, BIO-AN, and NON-1/AN may be suitable for use in the treatment of contaminated drinking water where Hg²⁺ is at low concentrations, e.g. 2.5 × 10⁻⁴ mol dm⁻³.

**Table 4** Comparisons of the maximum adsorption capacity of Hg²⁺ ions in the materials studied in the current research with some natural and synthetic adsorbents studied in recent research

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Hg²⁺ (mg g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroalga Cystoseira baccata</td>
<td>329.00</td>
<td>Herrero et al. (2005)</td>
</tr>
<tr>
<td>Amazon montmorillonite clay (Pará state, Brazil)</td>
<td>246.00</td>
<td>Guerra et al. (2009)</td>
</tr>
<tr>
<td>BEN₇-PVNSY₇</td>
<td>109.14</td>
<td>Guerra et al. (2010a, b)</td>
</tr>
<tr>
<td>Activated carbon from furfural</td>
<td>174.00</td>
<td>Yardim et al. (2003)</td>
</tr>
<tr>
<td>Amazon Soil</td>
<td>3.96</td>
<td>Miretzky et al. (2005)</td>
</tr>
<tr>
<td>SBA-15 functionalized with MTZ</td>
<td>220.65</td>
<td>Pérez-Quintanilla et al. (2006)</td>
</tr>
<tr>
<td>Camel bone charcoal</td>
<td>28.24</td>
<td>Hassan et al. (2008)</td>
</tr>
<tr>
<td>Dithiocarbamate-anchored polymer/organosmectite</td>
<td>157.30</td>
<td>Say et al. (2008)</td>
</tr>
<tr>
<td>Laterite (Guizhou Province, China)</td>
<td>3.33</td>
<td>Xiaohong et al. (2008)</td>
</tr>
<tr>
<td>Powdered activated carbon PAC-derived from walnut shell</td>
<td>101.00</td>
<td>Zabihi et al. (2009)</td>
</tr>
<tr>
<td>Polyacrylamide aerogel</td>
<td>17.63</td>
<td>Ramadan et al. (2010)</td>
</tr>
<tr>
<td>Silica aerogel</td>
<td>11.60</td>
<td>Ramadan et al. (2010)</td>
</tr>
<tr>
<td>Polyacrylamide-silica aerogel</td>
<td>13.69</td>
<td>Current research</td>
</tr>
<tr>
<td>NON-1</td>
<td>189.37</td>
<td>Current research</td>
</tr>
<tr>
<td>BIO-AN</td>
<td>355.06</td>
<td>Current research</td>
</tr>
<tr>
<td>NON-1/AN</td>
<td>374.44</td>
<td>Current research</td>
</tr>
</tbody>
</table>
Desorption

Desorption is an adsorbent’s recuperation technology that utilizes a removal agent to increase the removal possibility of metal anchored in the material surfaces that was used in a subsequent adsorption process, providing the reuse of adsorbent matrices in other decontamination processes. Desorption of the adsorbed mercury ions onto materials was also studied by a batch-wise method. The desorption capacities obtained in this study were comparable to those reported for smectite clay from northern Anatolia, Turkey (Arpa et al. 2000). The maximum desorption capacities found were 96.86% for NON-1, 96.30% for BIO-AN, and 96.02% for NON-1/AN (Figure 7). The experimental data reveal a decrease of perceptual of mercury desorbed for biomaterials; this conclusion can be attributed to the presence of reactive groups with major powers of immobilization in the reactive sites (power chelating) for mercury ions in the organic species that were components of biomass of BIO-AN, and NON-1/AN samples. This significant chelating power can be attributed to the influence of outer-sphere complexation and by inner-sphere complexation at the interface of materials.

In desorption and reuse studies, very high desorption rates, greater than ~97%, were achieved. Because of the substantially lower cost, the materials used have great potential for the removal of mercury from polluted aquatic ecosystems (Ford et al. 2001).

CONCLUSION

The principal objective of the current research was to study the influence of the adsorption process on adsorbents and divalent metal characteristics by means of both batch-wise and dynamic flow conditions. A summary of the current investigation follows.

(i) The results obtained in the present investigation indicate that the removal of Hg$^{2+}$ by NON-1, BIO-AN, and NON-1/AN is a complex phenomenon, principally in the surfaces of BIO-AN, and NON-1/AN. The uptake of mercury from aqueous medium strongly depends on solution pH, temperature, adsorbent dose, initial concentration of Hg$^{2+}$ ions, and contact time of the solid–liquid interface. The most appropriate condition was over a pH range of...
6.0–8.0 at 298 ± 1 K. The maximum adsorption capacity was observed at pH 4.0.

(ii) The Langmuir, Freundlich, Sips, and Redlich–Peterson theoretical isotherms were utilized to interpret the experimental data, which fitted very well to the Sips model. The pseudo-second-order model provided the best correlation of the experimental kinetic data.

(iii) The adsorption results were confirmed through stable complexes formed between cations and reactive groups disposed on the biomaterial surfaces, whose behavior was checked by the thermodynamic values obtained by calorimetric investigation at the solid–liquid interface to give favorable sets of data. Thermodynamic values calculations showed that the Hg²⁺ adsorption process by materials has an exothermic and spontaneous nature, such as exothermic enthalpy, negative Gibbs free energy, and positive entropic values.

(iv) Dynamic flow tests showed that the adsorption of mercury onto material surfaces with regard to the flow rate of adsorbate, inlet feed Hg²⁺ ion concentrations and solid–liquid permanence time as well as the experimental data are well fitted by the Adams–Bohart equation. Comparing the batch-wise method and column experiments, the batch-wise method effectively exploited the adsorbent divalent metal binding capacity rather than the fixed bed column. Of the 13 different adsorbents mentioned in the specialized literature, none had a greater adsorption capacity than the hybrid material for the uptake of Hg²⁺ ions, indicating that these adsorbents could be used in the removal of Hg²⁺ from aqueous medium. The employed adsorbents are more economical than commercially available adsorbents and were applied industrially for the batch and dynamic flow method.

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REFERENCES


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