Sorption of humic acid from aqueous solutions by lanthana-alumina mixed oxide pillared bentonite

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This work aims to evaluate the sorbent power of pillared inter layer clay (PILC) for humic acid from aqueous solutions. PILC was prepared from natural bentonite clay with lanthana-alumina mixed oxide pillars and was found to be very effective in removing humic acid from water. Maximum adsorption of 97.3 and 88.8 % took place by PILC (pH 3.0) from an initial concentration of 15.0 and 30.0 µmol/l respectively. Lagergren first-order kinetic equation governed uptake process. Electrolyte (NaCl) compresses the diffuse double layer leading to the increased uptake of humic acid; this also showed that van der Waals attraction is an important part of the interactive forces between humic acid and PILC. According to Giles classification, adsorption isotherm may be classified as L-type. The applicability of Langmuir isotherm to PILC-humic acid system was tested. Adsorption capacity ‘Q’ (54.32 µmol/g) and binding constant ‘b’ (0.249 l/µmol) were maximum at 10°C and pH 3.0. Experiments conducted at different temperatures allowed for the calculation of isosteric heat of adsorption, revealing that the adsorption process was exothermic. About 94.6 % can be recovered from the spent clay using 0.01 M NaOH.

Keywords: Humic acid, Pillared clay, Bentonite, Adsorption, Isotherm, Kinetics, Desorption

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Introduction

Over permissible limits of organic compounds in the natural waters or drinking waters and effluents, poses a public health threat. Humic substances constitute a major fraction of the organic matter in the environment. The presence of humic acid (HA) in water and wastewater provides a yellow to brown colour; and also impart a high BOD load to the liquid waste\(^1\). HAs can be characterized as acidic and hydrophilic polymers with carboxylic, phenolic and hydroxyl groups in their structure. HAs are main precursors of trihalomethanes, which are highly toxic to human beings\(^2\). The non-biodegradability, persistent nature and high affinity for adsorbing various pollutants make HA a major threat to living organisms\(^3\). Activated carbon is an effective adsorbent for organic compounds, especially for phenolic compounds\(^4\). Other adsorbents include clays, zeolites, hydrated metal oxide gels and organo clays\(^5,6\). Pillared clays constitute a novel class of materials prepared by the exchange of an interlayer cation in swelling smectite type aluminosilicate bopolymeric hydroxy cation followed by dehydration and dehydroxylation\(^7\).

The adsorptive characteristics of soluble organic pollutants, particularly HAs, on pillared clays and their efficiency on the removal of HAs are known very little\(^8,9\). Bentonite is a smectite type of layered silicate having silicate tetrahedral and alumina octahedral (2:1), where Al-octahedron is sandwiched between two silicate tetrahedron layers. Present study assesses the ability of lanthana-alumina mixed oxide pillared clay prepared from natural bentonite clay to remove HA from aqueous solutions.

Experimental Procedure

Materials

Bentonite clay obtained from M/s Ashapura Clay Mines of Gujarat was used to prepare the pillared clay, which has following chemical composition: SiO\(_2\), 55.3; Al\(_2\)O\(_3\), 18.2; Fe\(_2\)O\(_3\), 9.3; TiO\(_2\), 0.7; Ca, 2.4; MgO, 4.9; Na\(_2\)O, 1.1; K\(_2\)O, 0.1; Moisture, 2.2; and ignition loss (1200°C), 5.4 wt %. The chemicals used throughout the study were of analytical grade. Stock solution of HA (500 µmol/l) was prepared in double distilled water using HA obtained from Fluka, Switzerland. Elemental analysis of HA\(^9\) was: C, 56.4; H, 6.1; N, 4.9; and O, 32.6 wt %.
Preparation of Lanthana-Alumina Mixed Oxide Pillared Clay (PILC)

The Na\(^+\) saturated bentonite was obtained by washing clay several times, first with 1.0 \(M\) NaCl and then with deionised water. Lanthana-alumina mixed oxide PILC was prepared\(^{10}\). Hydrolysed aluminium chloride was prepared by adding 0.5 \(M\) NaOH drop wise to 0.2 \(M\) AlCl\(_3\).6H\(_2\)O by vigorous stirring to an OH/Al ratio of 2.4. A pillaring precursor for PILC was obtained by refluxing a solution of hydrolyzed aluminium chloride (20 ml), LaCl\(_3\).6H\(_2\)O (4.55 g) and distilled water (17 ml) for 3 days. The pillaring solution containing La-Al was slowly added under vigorous stirring to bentonite suspension (1.0 % by wt) to a ratio of 20-meq Al/g bentonite. Slurry was kept for stirring for 3 h at room temperature and was aged overnight. PILC was separated by centrifugation and washed with deionised water until the supernatant was chloride free as indicated by AgNO\(_3\) test. The product was dried and calcined at 250°C for 2 h and subsequently at 500°C for another 2 h. PILC particles were sieved to obtain –80+230 mesh size particle (average diam, 0.096 mm).

Characterization

Brunauer Emmett and Teller (BET) surface area of Na-bentonite and PILC was calculated from \(N_2\) adsorption isotherm using quantasorb surface area analyser. X-ray diffraction patterns were obtained for oriented film samples using a Rigaku Geigerflex X-ray diffractometer with Ni filtered Cu \(k\alpha\) radiation (40 kV, 20 mA). FTIR spectra (400-4000 cm\(^{-1}\)) of original and modified clays were obtained using KBr pellet technique in a Bruker IFS 66V FTIR spectrophotometer. The porosity and density of clay samples were determined by a mercury intrusion porosimeter (Micrometrics model 9310) and by a specific gravity bottle respectively. TG plots of samples were obtained using a Metler Toledo ThermoFlex Instrument. Zero point charge (pH\(_{\text{zpc}}\)) is defined as pH of the dispersion at which the surface charge density on the adsorbent is zero. To determine pH\(_{\text{zpc}}\), potentiometric titration method was used\(^{11}\). Cation exchange capacity (CEC) of Na-bentonite and PILC was measured by MgCl\(_2\) saturation and subsequent displacement by CaCl\(_2\).

Adsorption Experiments

Adsorption studies in batch were carried in stoppered conical flasks (100 ml) with agitation (200 rpm) provided from a temperature controlled water bath shaker. Experiments were conducted with solutions (50 ml) containing a fixed concentration of HA; NaCl was added to adjust the background ionic strength of 0.1 \(M\) and then adsorbent (0.1 g) was added. The solution pH was adjusted to a desired value with 0.1 \(M\) NaOH and HCl. At predetermined time intervals, contents were centrifuged and unreacted HA concentrations in the supernatant solution were analyzed using a Shimadzu UV-Visible spectrophotometer at a wavelength of 350 nm. HA adsorbed by PILC was calculated by mass balance due to initial and final concentration in the solution.

Desorption Experiments

Experimental conditions for HA desorption were similar to those of batch sorption studies. After adsorption with HA for 6 h, HA loaded PILC was separated and washed with distilled water to remove any unadsorbed HA. The spent PILC was then resuspended in varying concentrations of NaOH solutions (50 ml). After being equilibrated for 6 h, solution mixture was centrifuged and the amount of desorbed HA in the supernatant solution was analyzed.

Results and Discussion

XRD pattern of the original clay indicated that the major mineral is bentonite (Fig. 1). The characteristic d spacing of 4.45, 2.54 and 1.49 Å confirms that the sample used in the work is bentonite. The peak at 4.45 Å further implies the 2:1 mineral type. The peaks at 2.02 and 1.69 Å represent the presence of iron oxide phase as impurity. X-ray pattern of the bentonite sample also indicates the presence of calcite (2.32 and 2.08 Å) and quartz (3.33 Å). X-ray patterns show a d (001)-value of 19.1 Å. Subtraction of the thickness of the 2:1 layer of 9.6 Å yields an interlayer separation of 9.1 Å.
The broad adsorption bands at 3418 cm$^{-1}$ for Na-bentonite and at 3423 cm$^{-1}$ for PILC correspond to fundamental stretching vibrations of different hydroxyl groups (Fig. 2). The band observed around 3623 cm$^{-1}$ for Na-bentonite is assigned to hydroxyl group vibration in Mg-OH-Al, Al-OH-Al and Fe-OH-Al in the octahedral layer\textsuperscript{12}. The bending mode of Al-OH-Al is confirmed by observing a peak at 916 cm$^{-1}$ and it also indicates the layer structure of clay. The presence of asymmetric stretching mode of O-Si-O was suggested by the absorption band at 1025 cm$^{-1}$. The very intense band observed at 1044 cm$^{-1}$ in the spectrum of PILC is assigned to Si-O-Si asymmetric stretching mode. The peak at 814 cm$^{-1}$ and the weak band at 684 cm$^{-1}$ could be due to low intense O-Si-O symmetric stretching. The asymmetric bending mode of O-Si-O is observed at 457 cm$^{-1}$ for PILC as in other silicate systems\textsuperscript{13}.

TGA curves of Na-bentonite and PILC (Fig. 3) show difference in decomposition pattern. The total mass loss at 800°C, for bentonite (22.1 %) and PILC (26.4 %), can be mostly attributed to the dehydroxylation reaction at 450-545°C associated with a weight loss of Na-bentonite (10.2 %) and PILC (12.3 %). The higher weight loss observed in PILC may be due to the presence of hydrated intercalated species in the interlayer region. The first decomposition (a weight loss of 7.8 % for bentonite and 10.1 % for PILC), which starts around 40°C and extend up to 180°C, may be due to loss of adsorbed water of intercalated species in PILC. Major decomposition takes place above 400°C, when weight loss is as follows: Na-bentonite, 11.9; and PILC, 13.2 %.
Scanning electron micrograph (SEM) shows that Na-bentonite before pillaring appears as thin cornflake like crystal with fluffy appearance revealing the extremely fine platy structure (Fig. 4). After pillaring, clay has become more porous and fluffy, probably due to the change in surface charge of the particle as a result of pillaring and the reduction in certain amorphous phase originally associated within the Na–bentonite.

A variation in porosity, density and pH <sub>zpc</sub> was also observed after pillaring (Table 1). The increase in surface area after pillaring indicates the easy accessibility of N<sub>2</sub> to the interstitial cavities where lanthana and alumina oxides were intercalated into the cavities. The cation exchange capacity of the Na–bentonite was reduced from 0.87 to 0.69 meq/g owing to partial occupation of permanently charged sites by polyhydroxocations and migration of protons from the pillars into the octahedral sheet of the bentonite<sup>14</sup>.

### Effect of pH on HA Adsorption

Adsorption of HA was maximum at pH 3 (Fig. 5) as follows: PILC (15 µmol/l), 97.3; and PILC (30 µmol/l), 88.8%. This trend is consistent with other studies on the adsorption of natural HA on iron oxide<sup>15,16</sup>. Lai & Chen<sup>17</sup> reported maximum adsorption of HA in iron coated sand at pH 3.0. Increasing pH increases the ionization of HA (\(\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-\)) and hence the concentration of the negatively charged ion \(\text{A}^-\). The increasing electrostatic repulsion between \(\text{A}^-\) and negatively charged clay particles would lead to reduced adsorption of HA at high pH. Undissociated HA molecules dominating at low pH are more hydrophobic and more absorbable than ionized form.

### Effect of Contact Time and Initial Concentration

Equilibrium time (5 h) is independent of initial concentration (Fig. 6). Increasing solute concentration (pH 3.0) from 15 to 60 µmol/l, HA uptake decreased from 97.3% (7.30 µmol/g) to 68.2% (20.46 µmol/g). However, uptake per unit weight of adsorbent increased. In industrial application, higher removal at low concentration is important.

### Adsorption Kinetics

Predicting sorption rate for a given system is probably the most important factor for sorber design with sorbate residence time and the reactor dimensions controlled by system’s kinetics. A simple kinetic analysis of adsorption is pseudo-first-order equation<sup>18</sup>.

\[
\log (q_e - q_t) = \log q_e - \frac{k_{ad} t}{2.303}
\]  

... (1)

where \(k_{ad}\) is the adsorption rate constant (min<sup>-1</sup>), \(q_e\) is the amount adsorbed (µmol/g) at equilibrium and \(q_t\) is the amount adsorbed (µmol/g) at time ‘t’.

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Fig. 5 — Effect of pH on the adsorption of HA on bentonite clay and PILC.

Fig. 6 — Effect of initial concentration on the adsorption of HA on PILC.
The straight-line plots of \( \log(q_e - q_t) \) vs \( t \) for different concentrations (Fig. 7) indicate the applicability of the above equation for the present system and explain that the process follows pseudo-first-order kinetics. At 30°C and pH 3.0, the adsorption rate constants at initial concentrations of 15, 30, 45 and 60 µmol/l were found to be 1.11 x 10^-2, 1.09 x 10^-2, 1.08 x 10^-2 and 0.98 x 10^-2 min^-1 respectively. The values \( k_{ad} \) at different initial concentrations clearly indicate that these parameters are totally independent of initial concentration.

**Effect of Ionic Strength**

At pH 3 and initial concentration of HA (15 µmol/l) with different ionic strengths (0.001, 0.005, 0.01, 0.05, 0.1 M), the adsorption of HA increased (74.5 – 97.3 %) with increase in ionic strength (0.001 – 0.1 M). The presence of electrolyte compresses the electrical diffuse double layer leading to the increased uptake of organic pollutants such as HA. Adsorption is sensitive to the change in ionic strength if electrostatic attraction is a significant mechanism for sorption process.

**Adsorption Isotherm**

Adsorption isotherm studies are of fundamental importance in determining the adsorption capacity of HA on PILC and it diagonises the nature of adsorption. Adsorption isotherm corresponds to the isotherm of the L-type, which indicates the higher affinity of adsorbate for the adsorbent. The adsorption density increases with increasing solution temperature. To determine adsorption capacity of PILC, adsorption isotherm study was attempted by analyzing adsorption data by computer simulation techniques to fit the Langmuir isotherm model which can be represented as

\[
q_e = \frac{bC_eQ^o}{1 + bC_e} \quad \ldots (2)
\]

where \( q_e \) and \( C_e \) are the equilibrium concentration of HA in the adsorbent phase and liquid phase respectively. \( Q^o \) and \( b \) are Langmuir constants related to the maximum adsorption capacity corresponding to complete coverage of available adsorption sites (µmol/g) and intensity of adsorption respectively.

The above equation can be rearranged to the following linear form:

\[
\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \quad \ldots (3)
\]

The values of \( Q^o \) and \( b \) were calculated from the slope and intercept of the linear plots of \( C_e/q_e \) vs \( C_e \) for different temperatures. The good fit of the experimental and the correlation coefficients \( (R^2) \) higher than 0.98 indicated the applicability of the Langmuir isotherm model. The validity of the isotherm model is tested by comparing the experimental and calculated isotherm data (Fig. 8). \( Q^o \) values from the plots were 54.32, 52.68, 50.80 and 48.31 µmol/g at 10, 20, 30 and 40°C respectively; the corresponding \( b \) values were 0.249, 0.153, 0.098 and 0.060 l/µmol. The values of \( Q^o \) and \( b \) decreased with the temperature showing that adsorption capacity and intensity of adsorption are enhanced at lower temperatures.
Thermodynamic Consideration

The standard free energy, $\Delta G^0$ for the adsorption of HA on PILC was calculated as:

$$\Delta G^0 = - RT \ln b$$  \hspace{1cm} \ldots (4)$$

The values of $\Delta G^0$ were found to be -29.23, -29.08, -28.95 and -28.66 kJ/mol at 10, 20, 30 and 40°C respectively. The amount adsorbed at equilibrium must decrease with increasing temperature, because the negative value of $\Delta G^0$ decreases with increase in temperature. Isothermal data at four different temperatures were obtained to estimate the isosteric heat of the process. Isosteric heats of adsorption ($\Delta H_x$) for various loadings were calculated using Clausius-Clapeyron relationship

$$\frac{d(\ln C_e)}{dT} = - \frac{\Delta H_x}{RT^2}$$ \hspace{1cm} \ldots (5)$$

Equilibrium concentration, $C_e$ at constant amount of adsorbed HA are obtained from the isotherm data (Fig. 8) at different temperatures. A linear regression of $\ln C_e$ as a function of $1/T$ yields a single value of $\Delta H_x$ at constant loading. $\Delta H_x$ for the present system were about -18.44 kJ/mol and almost constant regardless of the amount adsorbed (Fig. 9). These results suggest that PILC exhibits an energetically homogeneous surface due to the absence of lateral interactions between adsorbed molecules$^{20}$.

Desorption Studies

Application of PILC for the removal and recovery of HA from aqueous solutions may require that the adsorbent be regenerated efficiently so that the adsorbent can be reused. In the present study, attempts were made to regenerate the adsorbent as well as desorbed HA from the spent adsorbent using NaOH. The total desorbed amount was calculated and compared to the initial sorbent amount. Desorption increased (34.1 – 94.6 %) with increase in concentration of NaOH (0.001 to 0.01 M). The results clearly show that the quantitative removal of HA from PILC and regeneration of the adsorbent can be done efficiently at higher pH. The results also indicate that HA is adsorbed by the adsorbent through physisorption.

Conclusions

The present study establishes lanthana-alumina mixed oxide PILC a very effective adsorbent for removal of HA from aqueous solutions. Amount of HA adsorption increases by lowering pH and increasing the ionic strength of the system. The process follows pseudo-first-order kinetics. The L-type isotherm obtained in the sorbent indicated a favourable process and fitted Langmuir equation model well. The adsorption capacity calculated by Langmuir adsorption isotherm gave 54.32 µmol/g of HA removal at 10°C and pH 3.0. The isosteric heat of adsorption was also determined at various surface loadings of the adsorbent. About 94.6 percent of HA can be recovered from the spent adsorbent using 0.01 M NaOH.

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References