Adsorption of Humic Acid from Aqueous Solution on Different Modified Bentonites

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The main objective of this work is the preparation and the characterization of a modified bentonites based adsorbents by intercalation with DMSO and DMF. Modified bentonites were analyzed using thermal analysis (TGA), infra-red analysis (FTIR) and X-ray diffraction. The X-ray results indicate that the geometry of the interlayer space was modified for all bentonites, and the interlayer distances observed are in the order of 1 to 1.41 nm. The adsorption ability and efficiency of different bentonites was tested for the removal of humic acid HA in aqueous solutions. In fact, batch adsorption experiments were carried out under different conditions including the adsorbent dose, the contact time, the initial humic acid concentration, the solution pH, in order to investigate their effects on the retention capacity of the modified bentonites. The maximum adsorption capacity of HA was found to be 16.97 mg/g, 14.65 mg/g, and 11.2 mg/g for DMF-bentonite, DMSO-bentonite and bentonite respectively. In conclusion Modified bentonites showed quite good capabilities in removing HA from aqueous solutions.

1. Introduction

Humic acid (HA) is one of the major components of humic substances which arise from the microbial degradation of biomolecules, and it is ubiquitous in surface water and ground water. The existence of HA in drinking water can lead to colour, taste and odour problems, and to biological instability of drinking water in distribution system. Furthermore, HA can bind various pollutants including toxic heavy metals and synthetic organic chemicals, and carry them through water treatment facilities and distribution systems. The adsorption remains one of the most effective methods to remove humic acid from water.

This work focuses on the preparation and characterization from modified bentonite by DMSO and DMF. The resulting adsorbent is tested humic acid removal from water and adopted the optimal parameters to remove humic acid.

2. Materials and methods

2.1. Preparation of organo-clay

The Na-exchanged form of the bentonite was prepared by stirring 1 M NaCl solution containing a sample of the clay for 24 hours at ambient temperature. Next, the solution was filtered and the clay was washed with distilled water to remove NaCl and other exchangeable cations from the clay. Rinsing was repeated until the negative reaction on Cl- ions in filtrate was obtained (test with 0.1 M AgNO3) then dried at 70°C (Safa Ozcan 2004). The Na-bentonite was intercalated of DMSO or DMF into bentonite was done in a following way: 20 grams of bentonite was stirred with 200 ml of anhydrous DMSO or DMF for 9 days at 70°C. The filtered clay was washed with 25 ml of dioxane and 25 ml of ethanol, and then dried at 110°C (J. Tunney 1996, R.L. Frost 1999).

2.2. Characterization of modified clays

Modified bentonites were analyzed using thermal analysis (TGA), modifications of clays were confirmed by FTIR spectra obtained a spectrophotometer (Spectrum One FTIR spectrometer of Perkin Elmer) and Structural modifications of clays were characterised by X-ray powder diffraction (XRD).

3. Results and discussion

3.1. Thermogravimetric analyses

Thermal modification of bentonite, DMSO-bentonite and DMF-bentonite are illustrated by curves given in fig.1. The TGA record of the bentonite is show in fig.1.a. The mass loss of 8.7% observed at the mean temperature of 80.7°C corresponds to the dehydration of the clay.

In the case of the TGA of DMSO-bentonite, fig.1.b, the two stages reaction was observed. The first mass loss of 1.9% corresponding to the release of the adsorbed water was followed by the second one of 6.2% observed at 207.06°C. 6.2% of evaporated DMSO corresponds to the solvent adsorbed/absorbed by the clay.

The more complex TGA thermal curve, fig.1.c, was observed with DMF-bentonite. The four stages of the mass loss were observed in this case. The water loss was of 1.6% atteined the maximum desorption rate at 52.3°C. Two following mass losses occur at 193.9°C (4.0%) and 320.6°C (2.5%), respectively and correspond to evaporation of absorbed and chemisorbed DMF. The last one observed at 532.9°C (2.3%) corresponds to decomposition of adsorbed species. Consequently the adsorbed and absorbed DMF constituted 8.8% of the mass of this organoclay.
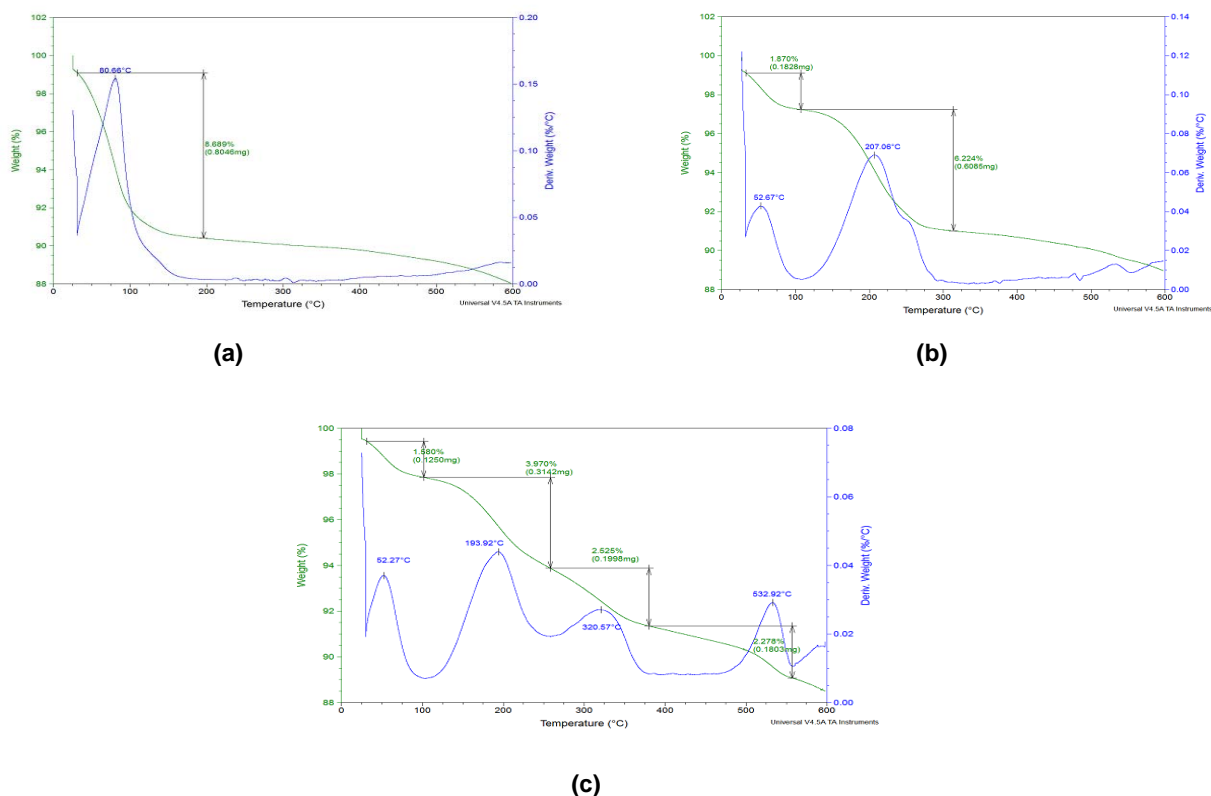

(a)

(b)

(c)

Figure 1 TGA/DTG analysis of bentonite (a), DMSO-bentonite (b), DMF-bentonite (c).

3.2. FT-IR analysis

Figure.2.a displays the typical spectrum of bentonite with the intense band at 982 cm^{-1} from stretching vibration of Si-O, the other bands correspond to the presence of sorbed water in the sample: the $\upsilon 2$ H-O-H bending vibration spectral range at 1600-1700 cm^{-1}; $\upsilon 1$ H-bonding to Si-O-Al is located at 3370-3480 cm^{-1} and the Hydrogen bond to Si-O-Si linkage is located at 3613 cm^{-1}.

For the DMF-bentonite, the band corresponding to the υOH is drastically reduced proving the insertion of DMF in the bentonite structure. The chemical function of the DMF is present in the infrared spectra by assigned the well defined band at 1660cm^{-1} to the $\upsilon C=O + \upsilon C-N$ vibration. The band at 1387 cm-1 corresponds to the $\upsilon C-N + \delta CH3$ and the bands between 1400 and 1500 cm^{-1} is attributed to $\delta CH3$.
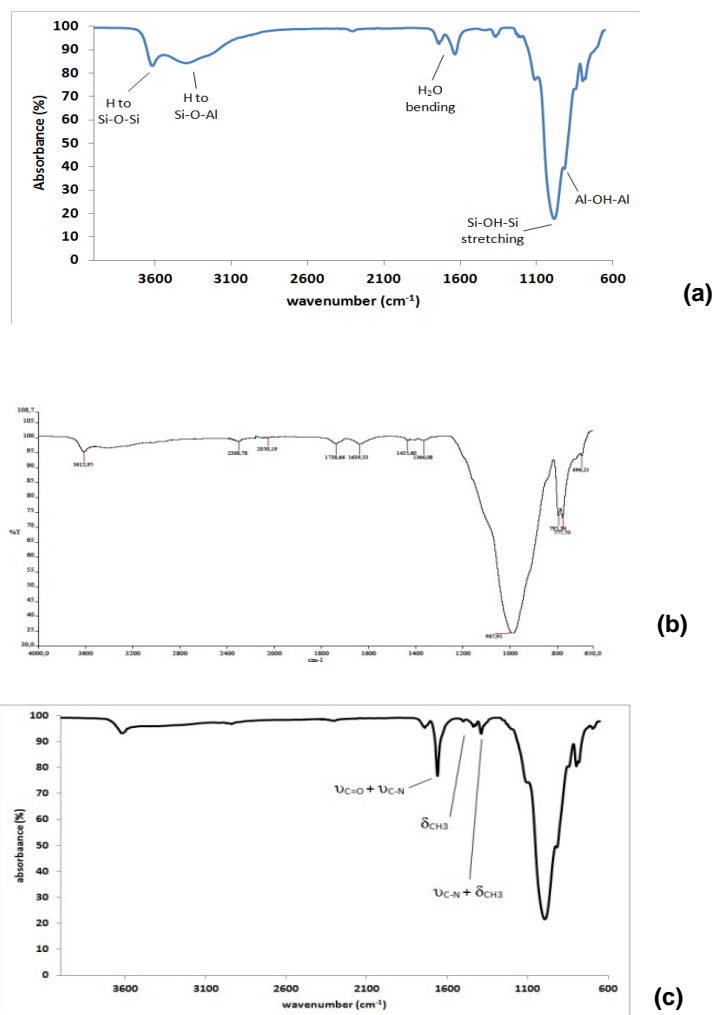

(a)

(b)

(c)

Figure 2 Shows the infrared spectra of bentonite (a), DMSO-bentonite (b) and DMF-bentonite (c).

3.3. XRD analysis

The XRD spectra of bentonite, DMSO-bentonite and DMF-bentonite are presented in fig.3 (a), (b) and (c) respectively. Accordingly, the d001 reflection occurs at 2-theta= 6.6 for bentonite, 6.3 for DMF-bentonite and 6.3 for DMSO-bentonite.

This indicates that that the geometry of the interlayer space was modified. The interlayer distance depends on the surface electrical charge and on the arrangement and the nature of molecules filling the interlayer space. The interlayer distance observed in the case of bentonite 13.5 A°. Natural bentonite surface is negatively charged due to the isomorphous substitutions within the layers of Al^{3}+ for Si^{4+} in the tetrahedral sheet and and Mg^{2+} for Al^{3+} in the octahedral sheet. For modified bentonite the X-ray peak shifted to lower angles indicating increasing basal spacing. The interlayer distance observed in the case of DMSO-bentonite and DMF-bentonite was of 14.1 A° and 13.9 A° respectively. These polar solvents intercalate bentonite and form probably bilayer structure in the interlayer space. The interlayer distance is slightly higher comparing to water bilayer.
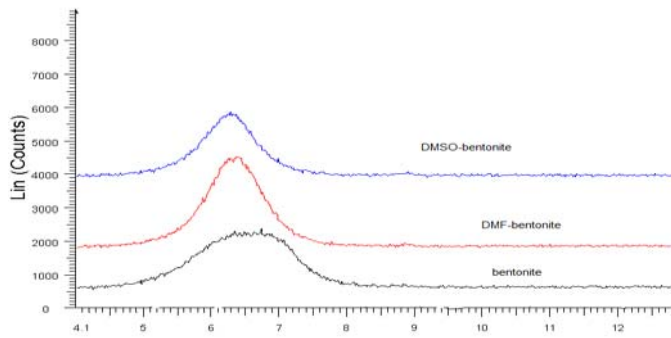
Figure 3 XRD pattern of bentonite, DMF-bentonite and DMSO-bentonite.

3.4. Adsorption kinetics studies

Kinetic experiments were carried out in erlen-meyer flasks containing saturated aqueous solutions of humic acid (100 ml) with 40 mg of the natural bentonite or modified bentonite at 25°C. Solutions were stirred at 300 rpm during a selected lapse of time. Then, the solution was centrifuged to removing the clay dispersion and analysed using the UV-vis spectrometry. The solution concentration allowed to calculating the quantity qt (mg/g) of the humic acid adsorb by one gram of adsorbent.

$$q_t = (C_0 - C_e) \times \frac{v}{m} \tag{1}$$

Where qt is the adsorption capacity of the adsorbent, C_0 and C_e (mg/L) are the initial and equilibrium concentrations, respectively, of the adsorbate in the solution. V (L) the volume of the solution and m (g) is the mass of adsorbent used. This experiment was repeated for laps of time going up to 270 min.

Fig.4 presents the adsorption kinetics obtained at room temperature with the initial concentration of adsorbate being 20 mg/L solutions of humic acid.
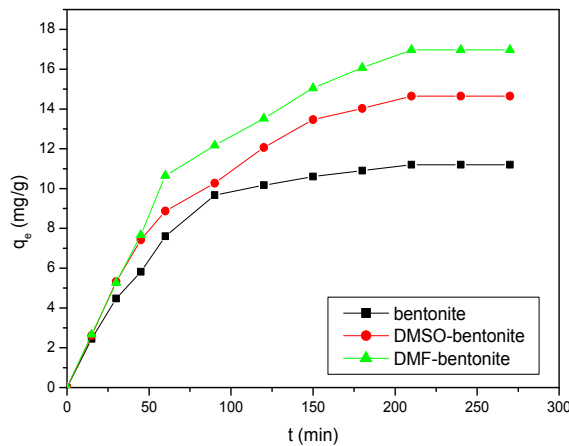

Figure 4. Kinetics of adsorption the humic acid on modified bentonites C_0 =20 mg/L.

Figure 4 shows the variation of the amount of HA adsorbed as function of time onto bentonite and modified bentonite. It may be observed from the figure that the amount of HA adsorbed onto bentonite and modified bentonite was rapid initially and then slowed down gradually until the equilibrium is reached about 210 min. this is because that a large number of vacant surface sites are available for adsorption during the initial stage, adsorption slowed down in later stages because after some time the remaining vacant surface sites are

difficult to be occupied due to repulsive forces between the adsorbate molecules in the aqueous solution and those on the adsorbent surface (D. Doulia 2009, Jianwei. Lin 2012 and H. Uslu 2009) .

Humic acid adsorbed by bentonite, DMSO-bentonite and DMF-bentonite reaches 11.2 mg/g, 14.65 mg/g and 16.97 mg/g respectively.

3.5. Adsorption isotherms

An adsorption isotherm describes the mechanism of retention of the solution components to a solid-phase at a constant temperature and pH. Batch experiments were conducted by shaking 40 mg of bentonite or modified bentonite with 100 ml aqueous solutions of HA at different concentrations (2-50 mg/L) was equilibrated during 3.5 hours at 25°C Results obtained for HA are presented at fig. 5a, 5b and 5c respectively.
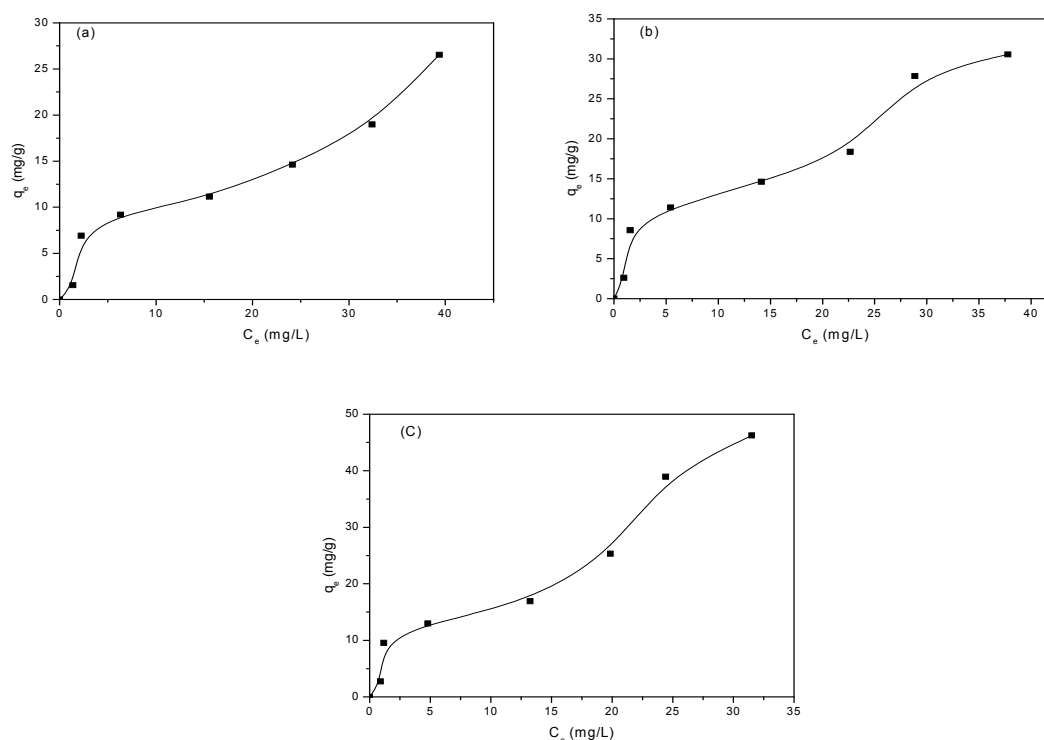

Figure 5. Adsorption isotherms of humic acid onto; a) bentonite, b) DMSO-bentonite, C) DMF-bentonite

The equilibrium adsorption isotherm is one of the most important data to understand the adsorption system mechanisms. The adsorption isotherms of HA on bentonite, DMSO-bentonite and DMF-bentonite shown in Fig.5. It was shown that the HA adsorption capacity for DMF-bentonite was much higher than that for DMSO-bentonite and bentonite, indicating that surface modification of DMF-bentonite enhances the HA adsorption capacity. Adsorption isotherm showed an initial steep slop and reached a plateau at elevated equilibrium conditions, indicating a relatively high affinity type interaction of HA with modified clay surface. Although the amounts adsorbed by organo-bentonite increase compared to unmodified bentonite, this increase is not regular. The adsorption of HA onto DMF-bentonite, DMSO-bentonite and bentonite has an L-type profile of Giles et al's classification (C. H. Giles).

3.6. The effect of pH on the adsorption of humic acid

The influence of pH on the adsorption of HA onto bentonite modified was investigated in the pH range 2.3- 9. Fig.6 shows the variations in the removal of AH at various solution initial pH. It was observed that the maximum quantity removal of HA was at pH 3.2. As the pH of the solution was increased from 2.3 to 9, the quantity adsorbed of HA decreased from 46.6 mg/g to 10.87 mg/g for DMF-bentonite, 46.77 mg/g to 3.62 mg/g for DMSO-bentonite and 47.07mg/g to 4.05mg/g for bentonite. The maximum adsorption at pH 3.2 this may attribute to the HA molecules comes near organic cations on the clay surface the interaction between the positive surface and HA molecule is thermodynamically favored and this results in expulsion of an acidic

hydrogen from carboxylic acid group of HA molecule to generate a negatively charged HA, the groups –COOH of HA dissociated into HA-COO⁻.
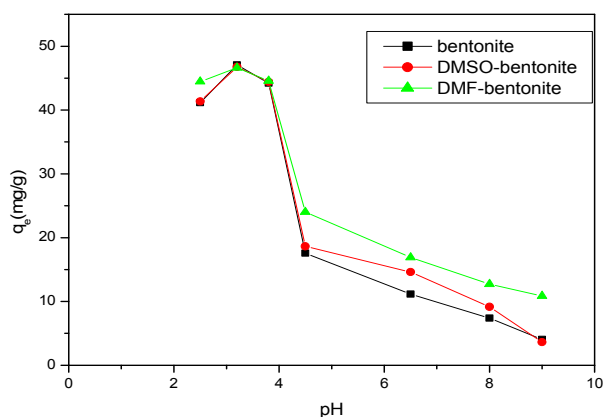

Figure 6. Effect of pH on the adsorption of humic acid on modified bentonites.

4. Conclusion

The work carried out concerns the adsorption of HA on various clay materials. From this point of view, we have developed modified clays in order to improve their adsorption properties.

The removal of humic acid by bentonite and bentonite modified with DMSO and DMF was carried as a function of the influence of various parameters such as contact time, pH of the solution and concentration of the adsorbed molecules. Results obtained confirm the utility of modified bentonites to removing humic acid from aqueous solutions. The maximum adsorption capacity of HA was found to be 16.97 mg/g, 14.65 mg/g, and 11.2 mg/g for DMF-bentonite, DMSO-bentonite and bentonite respectively.

The results obtained in this work confirm the utility of modified bentonites in removing humic acid from aqueous solutions.

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