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Clays as Adsorbents of Tartrazine: A Sustainable Application

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Abstract—**The adsorption of tartrazine (T) by montmorillonite (M) and sepiolite (S) is studied in this work. Results show a strong interaction between clays and the colorants because of the cationic exchange and the realignments of the organic molecule when the adsorption takes place. Ultrasound technique (US) improves the colorant adsorption by the clays.**

Keywords- Adsorption, clays, ultrasound technique, tartrazine.

I. INTRODUCTION

Drinking water is an increasingly scarce commodity, especially in the countries with the lowest human development index, where millions of people do not have any access to sources of clean water to meet their basic needs and often becomes vehicle diseases. That is why water pollution is an issue of vital importance to be solved. Removal of dyes effluent is one of the most significant and difficult to treat environmental problems since many of the dyes are of synthetic origin and a complex molecular structure, making them more stable and difficult to biodegrade. Sorption techniques produce high quality treated effluent and sorption processes have been investigated as a method of removing dyes wastewater [1, 2]. Tartrazine is a typical synthetic, watersoluble anionic dye. This substance appears to cause the most allergic and intolerances reactions of all the azo dyes, particulary among asthmatics and those with aspirins intolerance. Consequently, the wastewater containing tartrazine with various concentrations should be treated before [3].

There have been several studies on the adsorption clays of organic contaminants in wastewater, in order to develop effective treatments for the removal of these substances, also using the ultrasound technique.

This means that we see already well known materials, such as clays, through a more powerful conceptual lens that we derive a richer knowledge of their properties will lead us to a world of applications where the limit is your imagination.

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The process in which the molecules are concentrated in an interfacial layer is known as adsorption. If the molecules penetrate into the solid phase, the process is called absorption. The term sorption is generally used when the processes of absorption and adsorption occur simultaneously and are indistinguishable from each other, while if the adsorption of one or more ionic species is accompanied by the simultaneous desorption of an amount of ionic species, the process it is called ion exchange [4].
The use of wastewater cleanup methods using adsorbents inexpensive and biodegradable combined with ultrasound, it could be a good tool to minimize the environmental impact caused by the bleaching use in the textile industry. [5, 6].

II. MATERIALS AND METHODS

A. Montmorillonite

It is a phyllosilicate of the smectite group having a crystal lattice of the type called three layers: two of silica tetrahedrons and one layer consisting of octahedrally coordinated with oxygen atoms or aluminum hydroxyl groups.

It is often found as a result of altered igneous rocks of acid (pegmatites , granulites , diorites) type, although you can also find sedimentary montmorillonite . The most important deposits of this are found in Wyoming (USA), Camp Berteaux (Morocco) and Marnia (Algeria) [7].

B. Sepiolite

Sepiolite (S) belongs to the group of clays called phyllosilicates. It is a magnesium hydrosilicate, clay aspect which is associated with the coil, a secondary mineral .[8] Its name derives from the Greek " sepia " , name of the fish that is so light and porous as the mineral in question. It is deposited in basic media, high in magnesium and seems that forms during sedimentation processes. The most important deposits are in Vallecas (Spain), Eski- seir (Asia Minor), Utah and Colorado (USA).

C. Dye

They can be classified into two groups according to their origin is natural or synthetic. Tartrazine (T) is an anionic azoic dye from the thiazines family. Its chemical formula is

$C_{16}H_9O_9N_4S_2Na_3$. Tartrazine is unstable in alkaline media because the solution becomes red. [9] The dye used in food industry since 1916 in bakery products, derivates meat, prepared soups, canned vegetables, sauces, ice creams, desserts, candies and it is used to color drinks. It is used in more than sixty countries inckluding USA and European Union.[10]

All materials used in this assay were from commercial sources. Among the different methods commonly used in the study of organic complexes interacting with clays, are adsorption isotherms, X-ray diffraction and infrared spectroscopy. Techniques of differential thermal analysis, thermogravimetric analysis and others are also used.

D. Adsorption

Adsorption is defined as the transfer of a chemical from a liquid or gas to the surface of a solid phase without suffering changes in the composition of the latter phase.
The adsorption isotherms for determining the amounts of adsorbed organic compound by adding increasing concentrations of the compound to a given amount of clay. Adsorbed amount corresponds to the loss of the organic compound solution [11].

According to Giles et al. [12], the adsorption isotherms provide information about the mechanism of interaction in terms of the types of isotherms obtained.

The experimental adsorption isotherms can be adjusted to the equations of Langmuir or Freundlinch. These equations, while originally were described and used to describe the adsorption of a gas on the solid surface, [13], however used generally to describe the adsorption of organic compounds in soils and its components, being the equation of Freundlinch the most used.

E. Equations

Freundlinch equation is expressed by next

$$C_s=K_fC_e^{n}{}_f \qquad (1)$$

Where,

C_s is the amount of organic compound adsorbed per unit weight of adsorbent (g/g),

C_e is the equilibrium concentration of the organic compound in the solution in contact with the adsorbent (mg/mL),

Kf is the amount adsorbed to an equilibrium concentration equal to unity; constant characteristic of the organic compound by adsorption of the adsorbent, is used as an indicator of the adsorption capacity of the adsorbents,

nf is measured intensity adsorption reflecting the degree to which the adsorption depends on the concentration ; constant characteristic of the organic compound by adsorption of the adsorbent , is used as an indicator of the adsorption capacity of the adsorbents .

Langmuir equation is expressed by next:

$$C_s=K_1K_2C_e/(1+K_2C_e) \qquad (2)$$

Where,

Cs is the amount of organic compound adsorbed per unit weight of adsorbent (g/g) ,

Ce is the equilibrium concentration of the organic compound in the solution in contact with the adsorbent (mg/mL)

K_1 is a constant representing the maximum adsorption capacity (mg/g or mmol/g), consistent feature of organic compound adsorption by the adsorbent,
K_2 is an indicator of the intensity of adsorption and represents the value of the initial slope of the isotherm, constant characteristic of the organic compound by adsorption of the adsorbent.

F. Ultrasound Technique

Ultrasound technique (US) is defined as the sound of a frequency that is above the limit at which the human ear can not answer. The normal hearing range is between 16 Hz and 18 Hz (Hz = Hertz = cycle per second) is generally considered that ultrasound is at frequencies ranging from 20 Hz to 100Hz beyond. Sonochemistry uses frequencies typically between 20 and 40 kHz and this is the range used in ordinary laboratory equipment [14].

Ultrasound is propagated through a series of compression and rarefaction waves (expansion) induced in molecules of the medium through which it passes. With sufficient power, the rarefaction cycle may exceed the forces of attraction of the molecules of liquid and the cavitation bubbles are formed. These bubbles grow after a few cycles taking some steam or gas medium (rectified diffusion) to a size of balance that matches the resonance frequency of the bubble with the applied sound frequency, as a result, suffer some bubbles sudden expansion to reach an unstable size and collapse violently.

G. FT-IR Spectroscopy

FT-IR spectroscopy is used to determine the energies corresponding to interatomic vibrations in the sample under study that lead to changes in the dipole moment on the appropriate link.

IR interferometer consists of the following modules: Optical module, where the source is located. This module can be divided in turn interferometric area, display area and detection area. The source is a ceramic thermally stabilized to 1127 ° C. The interferometric area consists of a Michelson interferometer beam scanning monkey rotary scanning and bidirectional data collection.

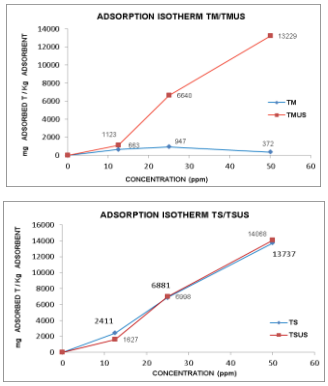

Figure 1. Adsorption isotherm: Systems Tartrazine-natural montmorillonite, natural sepiolite and ultrasounds systems

The principle of operation of this instrument is based on the Michelson interferometer. The radiation from the source is split into two beams by the beam splitter. Part of the radiation is transmitted to a fixed mirror, while the other part is reflected to a movable mirror that is connected to a motor. Thus, the path followed by these rays can be varied by adjusting the movable mirror. The current resulting from the combined rays will result in a constructive or destructive interference according to the path difference between the two beams whether or not an integral multiple of the wavelength. This radiation passes through then or converging lens system, striking the sample and the detector goes there. [13]

III. Results and Dicussion

The results in the adsorption of Tartrazine using natural sepiolite and montmorillonite and with ultrasound technique are shown in **Figure 1** [15-17].

TABLE I. FREUNDLINCH AND LANGMUIR CONSTANTS

System	Constant				
	Freundlinch			*Langmuir*	
	Ln K_f	K_f	n_f	K_1	K_2
TM	7.8	2407	1.65	149.3	0.0003
TMUS	4.45	85.36	1.49	9.61	0.012
TS	1.97	7.09	1.83	2.68	0.047
TSUS	4.11	60.95	1.34	3.76	0.04

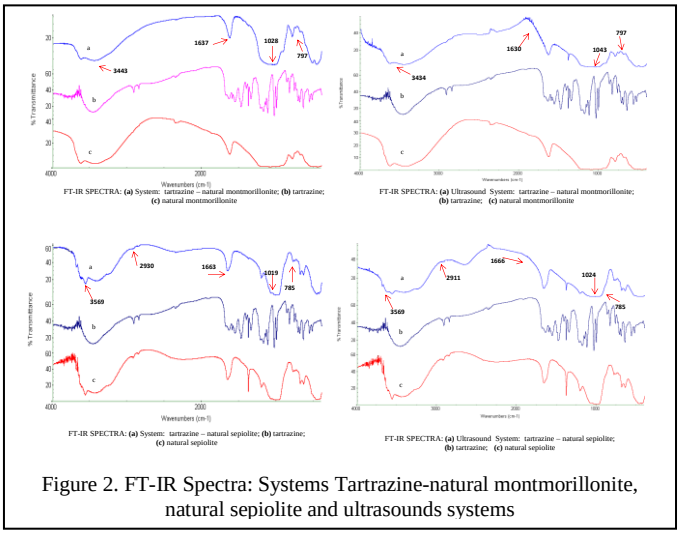

Figure 2. FT-IR Spectra: Systems Tartrazine-natural montmorillonite, natural sepiolite and ultrasounds systems

Figure 2 include the FT-IR spectra of the obtained adsorption systems. The interaction mechanism is showed in the last figure

TABLE II. FT-IR BANDS FREQUENCY

SYSTEMS		FT-IR FREQUENCY (cm^{-1})			
		TM	***TMUS***	***TS***	***TSUS***
$M_{\nu OH}$ $M_{\delta OH}$	3437 1634	3442 1637	3434 1630	-	-
$S_{\nu OH}$	3567	-	-	3569	3569
T_{NC-H}	2927	-	-	2930	2911
$S_{\delta OH}$	1664	-	-	1663	1666
$T_{\nu S=O}$	1036	1028	1043	-	-
$S_{\nu Si-O}$ $S_{\delta Si-O}$	1016 786	-	-	1019 785	1024 785

IV. CONCLUSIONS

The adsorption of Tartrazine by natural montmorillonite and sepiolite is improved using the ultrasound technique without any decomposition. This process can be used for environmental applications for textile and food industries because they are using this kind of additives for their work.

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