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Full Length Research Paper

Adsorption kinetics of 2-chloroacétophénone and 4-bromoacétophénone thiosemicarbazone on Oueme Valley clays (R. Benin)

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2-chloroacetophenone-thiosemicarbazone and 4-bromoacétophénone-thiosemicarbazone are compounds endowed with numerous pharmacological properties. In order to produce therapeutic agents using clay as excipient, this paper deals with the absorption kinetics of a clay originating from Oueme valley in Benin. A prospection in this area gave rise to the collection of 4 samples classified according to their color (yellow, white, black, and red). Toxicity studies performed on larvae gave no evidence of toxicity. These clays are highly hydrophilic and can accept a high load of organic material. The white clay, which is the least acidic, shows the best adsorption capacity. Additional experiments were carried out with this clay in ethanol. Best adsorption was obtained after 2 h. Absorption isotherms indicate low affinity between the clay and the thiosemicarbazones and can be modelized using Langmuir and Freundlich's models.

Key words: Clay, thiosemicarbazones, kinetic, absorption, larval toxicity, desorption.

INTRODUCTION

2-chloroacetophenone thiosemicarbazone and 4-bromoacetophenone thiosemicarbazone are interesting pharmacomolecules whose usefulnes has been proved in microbiology (Fatondji 2011). On the other hand, clay is a

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Tabe 1. Physicochemical characteristics of synthesized 2-CAT and 4-BAT. Eluent CH_2Cl_2 / EtOAc 2/1 (Fatondji, 2011).

Adsorbats	2-CAT	4-BAT
Molecular formula	$C_9H_{10}ClN_3S$	$C_9H_{10}BrN_3S$
Molecular weight (g/mol)	227.72	272.16
Melting point	157-158	198-199
Front report	0.88	0.80

natural material with various therapeutic applications (antibacterial, antiseptic).

In Benin, this natural resource still awaiting exploitation is available in the Oueme valley and is scarcely used by local population to cure ulcers, muscular lesions, and persistent diarrhea. In order to incorporate these thiosemicarbazones into clays as excipients to improve their therapeutic efficacy, the clay must be endowed with good capacities of sorption and desorption of these organic compounds. The aim of this paper is to follow up the evolution of the clay adsorption of 2-chloroacetophenone thiosemicarbazone (2-CAT) and 4-bromoacetophénone thiosemicarbazone (4-BAT) in ethanol.

EXPERIMENTAL

Materials

Young shrimp larvae (*Artemia salina*) were used as biological material. 2-chloroacetophenone-thiosemicarbazone (2-CAT) and 4-bromoacetophenone-thiosemicarbazone (4-BAT) used as adsorbates were previously synthesized, purified and characterized in the Laboratory of Organic Chemistry and Physical Synthesis (LACOPS / UAC). Their physicochemical characteristics are summarized in Table 1.

White, yellow, black and red consumables clay, were taken from the Oueme valley, in the township Dangbo and Aguegues (southern of Benin). A portion of each sample was dried in an oven at 105 ± 2°C, powdered, sieved to 180 µm and stored for the sorption study. The second parts were kept in plastic boxes at room temperature for toxicity studies, because freezing may reduce their sensitivity (Caquet., 1994).

Characterization of clays

Water and organic material content, acid-base nature, specific surface area and cation exchange capacity of each sample of clays were determined.

Water content

Water content was determined by Audigié et al. (1978) method.

Organic material content

Clay's organic material content is measured according to NF EN 12879 norm.

pH measurements

The pH was measured following the method proposed by Aïssata (2009).

Cation-exchange capacity (C.E.C.)

Cation-exchange capacity (CEC) is the maximum quantity of total cations, of any class, that a soil is capable of holding, at a given pH value, available for exchange with the soil solution. It is expressed as milliequivalent of hydrogen per 100 g of dry soil (m_{eq}/100 g), C.E.C was assessed according to Metson (1956) for clays below 180 µm and following the AFNOR NF X 31-130 norm.

Specific surface

The specific area in m^2 /g is assessed by methylene blue colorimetry according to Hicham El (2006).

Cytotoxicity test on shrimp larvae

The test is performed against *Artemia salina* Leach by the method of Michael et al. (1956) resumed by Vanhaecke et al. (1981) and Sleet and Brendel (1983) and proposed in the literature as a simple bio - assay method for assessment of preliminary toxicity of natural active products (Solis et al., 2001). The eggs of *A. salina* were incubated in sea water until hatching of young larvae (48 h). Then, series of solutions of each tested clay sample at varying and progressive concentrations were prepared. A defined number of larvae, (sixteen) were introduced into each solution. All solutions and control solution containing no active substance were left under stirring for 24 h. Counting under a microscope the number of dead larvae in each solution was used to evaluate the toxicity of the solution. In the case where there was death in the control medium, the data was corrected by Abbott's formula:

% death = [(test - control) / control)] × 100 **(**Abbott, 1925).

Data (dose-response) are transformed by logarithm and the LC_{50} were determined by linear regression (Hafner et al., 1977). Tests were carried out in triplicate.

Adsorption kinetics of 2-CAT and 4-BAT in ethanol

Sorption technique

The initial concentrations of thiosemicarbazone were: 0.0625, 0.125, 0.25 and 0.5 mg/ml. 0.02 g of clay (< 180 µm) is mixed with 2 ml of an ethanolic solution of thiosemicarbazone. The suspensions are stirred for 10 h at room temperature. The supernatant is assayed by high performance thin layer chromatography (HPTLC) after centrifugation to determine the

Table 2. Physicochemical characteristics of consumables clays.

Variables		Yellow clay	Black clay	Red clay	White clay
Te(%)		36.70	54.73	33.38	59.95
M. O. (%)		14.34	23.84	18.12	13.76
C E C (m_{eq} /100 g)		23.79	20.13	22.21	16.01
S.S. (m^2/g)		3.32	2.29	2.46	4.82
pH medium	KCl	3.54±0.01	3.29±0.01	4.18±0.03	5.02±0.03
à 25°C	H_2O	4.65±0.00	4.17±0.01	5.12±0.01	6.04±0.02

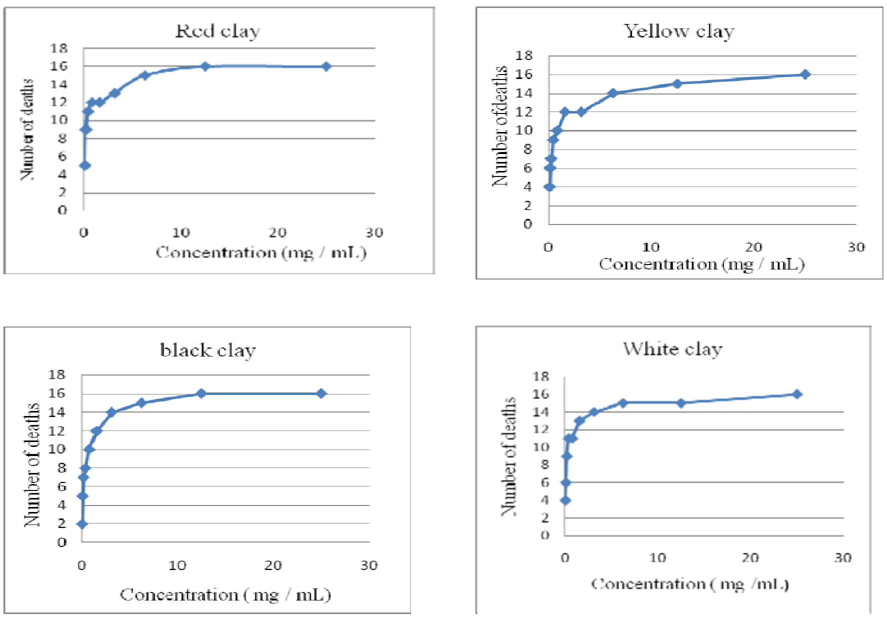

Figure 1. Dose-response curves illustrating the sensitivity of shrimp larvae to clay species.

residual thiosemicarbazone concentration.

Analyses of the thiosemicarbazones

Thiosemicarbazones are analyzed by CCMHP densitometer (Camag TLC Scanner III) at 300 nm. A mother solution (1 $mg.mL^{-1}$) is prepared in ethanol and further diluted to get concentrations of 0.0625, 0.125, 0.25 and 0.5 mg/ml used for standardization. HPTLC plates (Silica gel 60 F254S Merck®) are developed using a toluene: acetonitrile mixture (6 : 7, v/v).

RESULTS AND DISCUSSION

Physicochemical parameters of the clays

As can be seen in Table 2, the studied clays are rather hydrophilic with a content of water ranging between 33.38 and 59.95%. The white (59.95%) and black clays (54.73%) are notably more hydrophilic than the red (33.38%) and yellow clays (36.70). Clay's CEC values are found in the range 16.01 and 23.79 m_{eq} / 100 g. These figures are satisfactory since Morel (1996) found for kaolinite values between 5 and 15 m_{eq} /100 g, for illite and chlorite values between 10 and 40 m_{eq} /100 g. These clays exhibit a weak adsorption capacity in accordance with their low specific area (2.29 – 4.82 $m^2.g^{-1}$). The white clay exhibits the highest specific surface. Clay's pH figures are all below 7, attesting to their acidic character. Yellow, red and black clays are found clearly more acidic ($3.5 \leq pH \leq 5$), than the white one (6.04).

Larval toxicity

The shrimp larvae are sensitive to clays. We noticed a gradual increase in the number of dead larvae gradually as the extract concentration increased (Figure 1). The LC50 (Table 3) compared to the values of table drawn by

Table 3. LC50 value of the various supplies clays.

	Yellow clay	Black clay	Red clay	White clay
CL_{50} value (mg/mL)	0.17	0.10	0.17	0.29

Table 4. Correspondence between LC50 and toxicity.

CL_{50}	Toxicity
CL_{50} > 100 μg /mL ou 0.1 mg /mL	-
100 μg /mL > CL_{50} ≥ 50 ou 0.05 mg /mL	++
50 μg /mL > CL_{50} ≥ 10 g /mL ou 0.01 mg /mL	++
CL_{50} < 10 μg /mL	+++

- No toxic, + Low toxicity,++ : Moderate toxicity, +++ : High toxicity.

Table 5. Isotherm parameters studied 2-CAT and 4-BAT for white clay.

Models		Settings			
		q_m	b	R_L	R^2
Langmuir	2-CAT	$-1.35.10^{-5}$	-17.386	0.999 – 0.996	0.99
	4-BAT	$-2.03.10^{-5}$	-3.640	0. 556 – 0.843	0.97
Freundlich	2-CAT	$1/n$ = 4.20		k_f = 4.426	0.96
	4-BAT	$1/n$ = 1.86		$k_f = 5.14.10^{-2}$	0.88

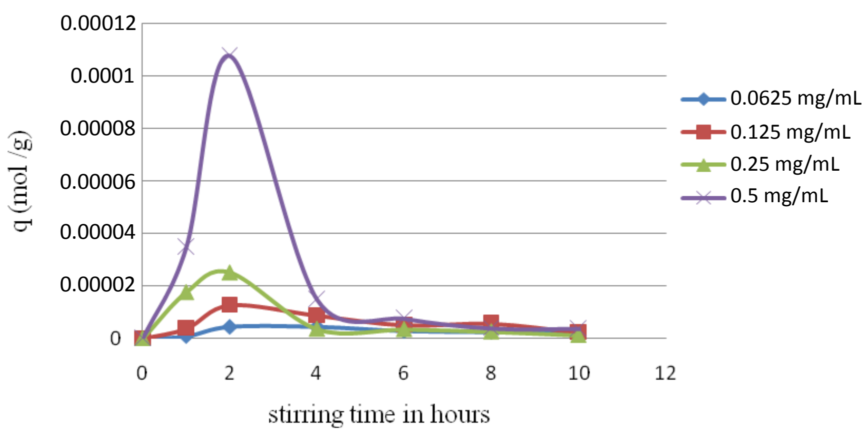

Figure 2. Kinetics test of adsorption 4-BAT on the white clay in ethanol medium.

Mireille (1995) sparkling (Table 4) shows that these clays are not toxic. Thus, consumables clays of the valley can be used without toxicological risk.
In view of these results of LC_{50} figures (Table 5) compared with those established by Mireille (1995) demonstrate the lack of toxicity of these clays.

Adsorption kinetics of 2-CAT and 4-BAT in ethanol

According to Figures 2 and 3, adsorption kinetics of 2-CAT and 4-BAT on white clay shows that there is no apparent equilibration time for adsorption of thiosemicarbazones by this clay and that adsorption is

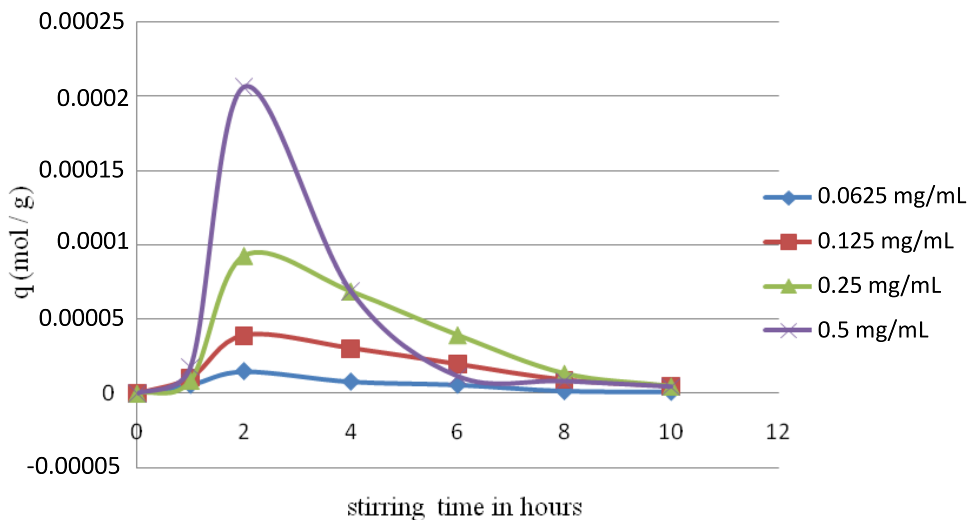

Figure 3. Kinetics test of adsorption 2-CAT on the white clay in ethanol medium.

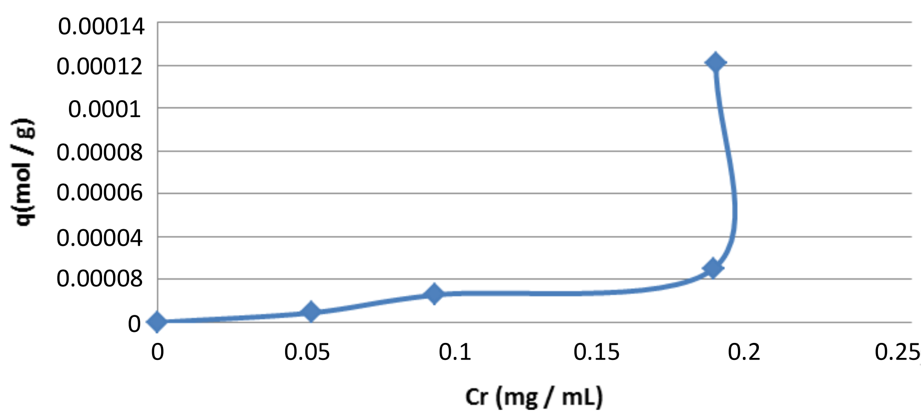

Figure 4. Adsorption isotherms of 4-BAT on white clay in ethanol medium at 25 ± 2°C.

reversible. After a fast initial phase, adsorption is maximal after 2 h. Desorption follows the same kinetic behaviour and reaches a plateau after 2 h. Thiosemicarbazone's adsorption is considerably influenced by its initial concentration in ethanol. Maximal sorption goes up to 63% for 4-BAT and 89% for 2-CAT after 2 h equilibration.

Sorption isotherm of 2-CAT and 4-BAT

A sorption isotherm (also adsorption isotherm) describes the equilibrium of the sorption of a material at a surface (more general at a surface boundary) at constant temperature. It represents the amount of material bound at the surface (called the sorbate) as a function of the material present in the solution. In this study, sorption isotherms were determined at room temperature after 2 h equilibration and were found of the concave S-shape type, suggesting a low affinity of the white clay (Figures 4 and 5 and Table 5) for thiosemicarbazone derivatives according to Giles et al. (1974). Modeling of these isotherms give intensity parameters which fit with those computed following to the models of Langmuir and Freundlich ($R^2 > 0.8$).

Conclusion

Selected clays originating from Oueme valley of Benin are not toxic. They are highly hydrophilic, rich in organic materials and are of acidic nature. They exhibit low specific area and CEC comparative analysis of their characteristics shows that the white clay, less acidic and hydrophilic shows the best adsorption capacity.
Adsorption isotherms suggest a low affinity between the white clays and thiosemicarbazones and can be

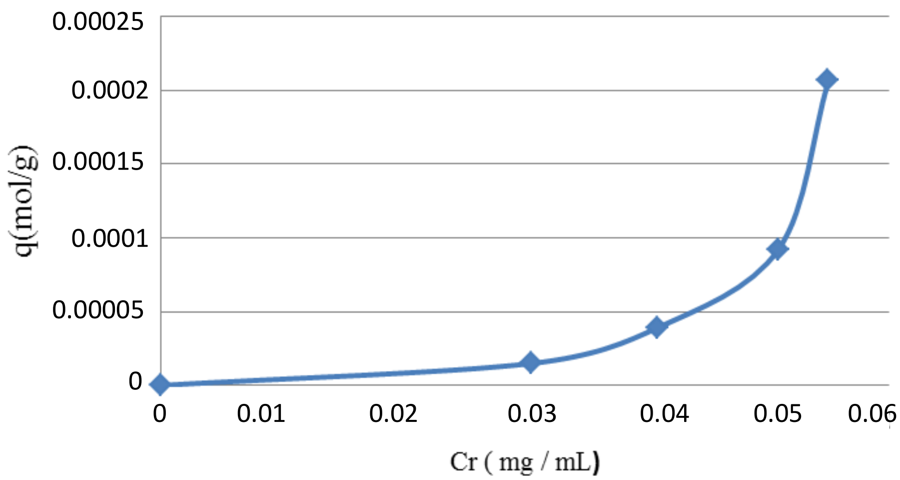

Figure 5. Adsorption isotherms of 2-CAT on the white clay in ethanol medium at 25 ± 2°C.

rationalized following the models of Freundlich and Langmuir. Adsorption kinetics demonstrates that adsorption is reversible and optimal after 2 h.

Conflict of Interest

The author(s) have not declared any conflict of interests.

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