DIMETHOATE ADSORPTION/REMOVAL FROM AQUEOUS SOLUTIONS BY SOME ALBANIAN CLAYS

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ABSTRACT
The present paper evaluates the adsorptive properties of some natural clays in Albania to technical dimethoate from its aqueous solutions. Consequently, these clays could be used to remove the various insecticides from aquatic environments. A new sample pretreatment method was developed for the gas chromatographic determination of dimethoate in its aqueous solutions. The representative samples of clays mineral originate from Brari, Currila, Dardha and Prrenjas regions in Albania. The initial dimethoate for the concentration are 0,200g/L and 0, 300 g/L, 0,400g/L and 0,500 g/L. Adsorption of dimethoate for the concentration of 0,200g/L was studied for a period of time from 6 to 144 hours (6 days), while the other concentrations are studied within the adsorption interval of 48-hours. The clay from Brari region exhibited better adsorptive properties compared to the others, followed by the Dardha, Currila and Prrenjasi' s clays. The results obtained show that the four clays could be used for the purification of groundwater from dimethoate residues in Agriculture.

1. INTRODUCTION

The organophosphate pesticides have been extensively used in agriculture and show considerably toxicity for humans (Colovic *et al*., 2013; **Lazarevic-Pašti** *et al*., 2019). They are persistent polluters which cause the contamination of drinking water in the agricultural areas where are used (Ali *et al*., 2017; Triassi *et al*., 2017). Removal of dimethoate from aqueous solutions has been investigated, among different techniques, by means of adsorption as well (Maria *et al*., 2010; Vagia**,** *et al*., 2010)

Dimethoate is produced and marketed by many countries around the world, with many trade names and labels. The market products usually contain about 40% active ingredient (pure dimethoate), the rest consists of emulsifiers, fillers, dyes, etc. It is commercially known as Dimethoate, Rogor, Bromthion, Perfection, Phosphamide etc. In Albania it is commonly known as

Rogor and is the most widely used organophosphate insecticide for plant protection.

On the other hand, clays are found in big quantities in Albania, widely spread on the surface of plain and hilly regions. Over 90 clay deposits have been discovered in Albania (Dede 1980; IGEWE; Kola. 1986). Nowadays, clays are used for many purposes. Currently, there are 25 deposits exploited for various application purposes in Albania. Information about the use of clays in Albania as could be found in (Kola 1986; Malaj 2006; Xhaxhiu, 2013; Xhaxhiu, 2013; Tako 2015; Xhaxhiu 2020). Here, the application areas are: i) wine clearing, ii) rehabilitation of oil removal from turbines and transformers, iii) improve the physical and chemical properties of vegetable oils, iv) removal of heavy metals from waters and, iv) organophilic surface treatment.

Recent studies are focused on the use of clays for the purification of groundwater from pesticide residues from the agriculture sector.

The present investigation aims to exploit the adsorption abilities of four Albanian clays as natural adsorbents. The clays were not chemically pretreated, but were in activated form by specific treatments.

2| MATERIALS AND METHODS

2.1 Materials:

2.1.1 Chemicals

Dimethoate Pestanal-Analitical Standart-99% - MERCK (Darmstadt, Germany)

Technical Dimethoate

The technical dimethoate is provided by the Greek company "K & N-Efthyamiadis s.a" and has an active substance content of 40%. In addition, it is accompanied by the relevant certificates and approved by the Institute of Food Safety and Veterinary (IFSV), Tirana, Albania.

Dibutyl phthalate (DBP)

Analytical standard is provided by the FLUKA, Buchs, Germany, and employed as an internal standard for the laboratory analyses (99. 5%).

Methylene chloride

High pressure liquid chromatography grade (> 99, 9%), and ethyl acetate (99, 8%) is provided by the Sigma-Aldrich, Seelze, fc Germany.

The inorganic salts used: KCl (99,999%) and Na_2SO_4 anhydrous, (for synthesis grade) is provided by the MERCK, Darmstadt, Germany.

2.1.2 Clay samples

The Table 1 below summarizes the regions where sampling occurred.

Table 1. Sampling areas

Brari -Tirana:	41° 21' 14.49'' N 19° 50' 17.74 ''E
Currila- Durrës:	41° 19' 16.29 " N 19° 25' 51.92 " E
Dardha –Korçë:	40° 31' 16.59" N 20° 49' 33.69" E
Përrenjasi – Librazhd:	41° 4' 3.88" N 20° 33' 2.33'' E

Samples were selected based on a registered database from the Institute of Geological Research, at University of Tirana. In each case a sample quantity of 25-30g of clay was drawn as a representative average amount from an initial quantity of 5 kg ground natural clay. The representative clay samples were dried in a thermostat for 4 hours at a temperature of 150°C and sieved using a 74-mesh sieve (fraction: 0-0.250 mm). The chemical composition and physico-chemical properties of the clays were determined and reported in (Kola 1986), and are in the table 2 and 3 reported. Moreover, numerous literatures are focused on their physico-chemical properties, some of which we considered in our study (Nutting 1943; Kanazawa 1989; Xhaxhiu et al.,. 2013; HAL 2019; USGS Pub. Rep (n.d); Wikipedia;).

A high sodium and kalium content was found in the Brari and Currila's clays, while a high $CaCO_3$ content wad found in the Dardha's clay (22,6-26,3%), Currila's clays (19, 3-23, 9 %) and Brari's clay (21, 8-23, 2%).

Table 2. Chemical composition (%) of natural clays

Region	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O+K_2O	HK
Brari	43,4-53,9	11-15,8	5,4-7,7	7,7-11	4-7,9	-	3,03-3,93	10-14,9
Currila	42,21	12,47	5,26	13,69	5,94	-	3,35	-
Dardha	44,72	12,54	6,67	11,68	6,24	-	-	-
Prrenjasi	46,5-52,9	6,4-9,2	2,8-18	0,1-3,5	5-16	0,3-0,7	0,3-0,8	16-20

Table 3. Physico chemical parameters of natural clays

Region	pH	Density (g/cm^3)	Porosity (%)	Surface area (m^2/g)
Brari	7,5	2,77	0,490	42
Currila	9,3	2,79	0,568	45
Dardha	7,6	2,78	0,564	89
Prrenjasi	7,4	2,78	0,558	175

Traces of titan (Ti) are found in the clay of Prrenjas. It could be noted from the Table 2 that the Currila's clay has the highest pH level. Brari's clay shows the lowest density, porosity and lower surface area.

Powder XRD measurements and characterizations of the clays samples are detailed in (Xhaxhiu 2020).

2.2 Equipment

The Hewlett Packard (GC) equipped with a flame ionization detector (FID), and a nonpolar capillary column with a diameter of 0.32 mm and 30 m long, SE 30 was used for the gas-chromatographic measurements. Its working conditions are: the column working temperature was 160-280^{o}C and rate 20^{o}C/min. The detector temperature was 300^{o}C. The injection temperature was 250^{o}C. All the experiment was carried out in a splitless mode.

Centrifuge

The sample was centrifuged in an Eppendorf Centrifuge, model 5403 (Leipzig, Germany), with a rotation speed of 5000 rpm.

Sieve

The clay samples were sieved via Fritsch Analysette [Type 03502] Idar-Oberstein- Germany.

2.3 Adsorption procedure

The concentrations of the market product dimethoate with 40% active substance content are calculated after the conversion to pure substance to determine dimethoate adsorption for the four clays.

The initial concentrations of dimethoate were 0,200g/L, 0,300g/L, 0,400g/L and 0,500 g/L.

Once the work started, the solutions were prepared. The clay suspension of dimethoate aqueous solutions are prepared under the ratio: 1 gram of clay for every 5ml of solution.

Suspensions are kept under continuous stirring and, at specified time intervals samples are taken for the determination of dimethoate content in the water.

The suspension sample with a volume of 30-40 ml is centrifuged for 15 minutes at 5000 rpm, 25 ml of clear solution taken and passed through a special cork test tube. A 2,5 g of KCl is subsequently added and dissolved. Dimethoate is further extracted by adding 5-6 ml solvent (Ethyl Acetate-dichloromethane 3:1 vol/vol) and shaking on mechanical device for about 20 minutes. Once shaken, the phases are allowed to separate for 5 minutes and the organic phase gets collected. The extraction procedure is repeated three times, and the organic phases are mixed together.

The organic phase is dried over 1g anhydrous Na_2SO_4. Once dried over, a solution of an internal standard (Dibutyl phthalate in absolute ethyl alcohol – 2,5 mg/ml) is added to obtain the concentration of the standard of 50 micrograms / ml.

Only sample volume of 1-2 ml is analyzed. The gas chromatographic analysis of the dimethoate is based on the aforementioned method with an heating rate of 20^{o}C / min and the splitless injection method x 1 microliter. The resulted retention time for dimethoate is 6, 30 minutes. For the internal standard DBP, it is 7, 90 minutes.

The amount of dimethoate in solution is calculated according to the corresponding factor on the basis of the chromatograms of the standard and of samples. The results are in the table 4 and 5 reported. In addition, the hydrolysis of dimethoate is determined and appears to be on average 4%. This value is used to correct all the obtained results for the adsorbed amount of dimethoate on clays.

The technical dimethoate recovery is in average 46.65%, due to the influence of emulsifiers and other accompanying substances of the technical product.

This sample preparation method for the gas chromatographic analysis of dimethoate is based on a range of experiments and (Amandola 1967; Melluso *et al.* 1994; **Othmer** 2000; **Othmer** 2000; Al Kuisi 2002; HAL. 2019; Xin *et al*, 2021**)**

3. RESULTS AND DISCUSSIONS

The adsorption of technical (market) dimethoate from its aqueous solutions was investigated applying the aforementioned experimental procedure and the results on the concentration of 0.200g / L and for adsorption times from 6 hours to 144 hours (6 days) are in the Table 4 reported.

Table 4. The influence of clay type and contact time on dimethoate adsorption initial concentration C=0.200 g/L, T=25 ºC)

Time / Region	6	24	48	72	96	120	144
Brari	0,0875	0,1250	0,1905	0,2691	0,2812	0,3570	0,3818
Currila	0,0823	0,1155	0,1605	0,2116	0,2553	0,3205	0,3387
Dardha	0,1127	0,1494	0,1884	0,2384	0,3282	0,3554	0,3568
Prrenjasi	0,0550	0,0961	0, 1252	0,1765	0,2287	0,3065	0,3294

Brari's clay followed by Dardha's clay exhibit better the adsorptive properties to dimethoate in aqueous solutions, for the concentration C 0,200 g / L. The samples collected from Currila and Perrenjas have a mean adsorptive ability.

The results in the Table 4 reported are graphically depicted in the Figure 1. The variation of the adsorbed amount of dimethoate with the contact time for the four clay samples has similar pattern. The amount of dimethoate adsorbed increases steadily in any case for 140 hours at the initial concentration of 0.200 g/L, i.e. basically the same adsorption ability towards dimethoate, regadless the specific adsorption values of each clay. Consequently, they have the same potential to be used for the purification of water contaminated with this insecticide.

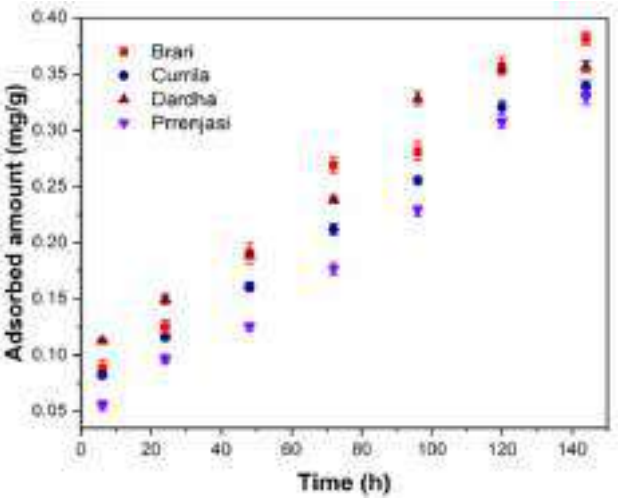

Fig. 1: Adsorbed amount of dimethoate as function of its initial concentration from its aqueous solutions at 25°C on one gram of clays of Brari, Currila, Dardha and Prrenjasi.

The investigation of dimethoate adsorption at higher concentrations and, specifically with concentrations of 0.300g / L, 0.400g / L and 0.500 g / L, was carried out in the same way.

These concentrations are not met in agricultural practices, but considered as extreme possibilities that could appear by chance, or due to indiscriminate use of insecticides by unprofessionals.

As the maximum concentration of C = 0,500g / L (or otherwise 1,250 g / L gross technical product with active substance content 40%) is inappropriate to be used due to the high content of surfactants and other accompanying substances of the product, it is not used. The concentration 0.400g /L is less problematic to the experiment process.

An average interval of 24 hours, 48 hours, and 72 hours were chosen as the clay-dimethoate aqueous solution contact time.

The contact time of 48 hours was chosen as the average time for the comparison of the adsorption results for the different clays.

In this time interval the adsorption phenomena are stabilized and comparisons could be made among the clays. No result is expected for the extension of time beyond 72 hours. As time extends, the counter-slowing down adsorption, reducing the adsorption capacity of clays, saturation and finally desorption appears.

All the results obtained experimentally for concentrations mentioned above are presented in Table 5.

The data of table 5, are presented graphically in Figures 2, 3, 4 and 5 (adsorbed amount mg/g from concentration) graphically depicted.

Table 5. The Influence of clay type, contact time and initial concentration on the adsorption of dimethoate on four different clays from its aqueous solutions at 25°C.

C, g/L	0,200			0,300			0,400			0,500		
Time, h / Region	24	48	72	24	48	72	24	48	72	24	48	72
Brari	0,125	0,250	0,269	0,215	0,542	0,634	0,281	0,672	0,751	0,635	0,822	0,910
Currila	0,115	0,130	0,212	0,118	0,260	0,301	0,123	0,265	0,441	0,132	0,251	0,175
Dardha	0,149	0,188	0,238	0,099	0,207	0,255	0,190	0,250	0,330	0,191	0,193	0,204
Prrenjasi	0,096	0,125	0,176	0,103	0,289	0,384	0,122	0,233	0,318	0,154	0,389	0,376

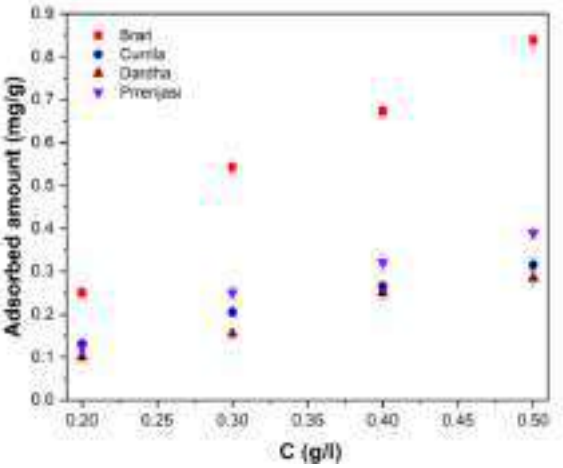

Fig. 2: Adsorbed amount of dimethoate as function of its initial concentration from its aqueous solutions at 25°C on one gram of clays of Brari, Currila, Dardha and Prrenjasi.

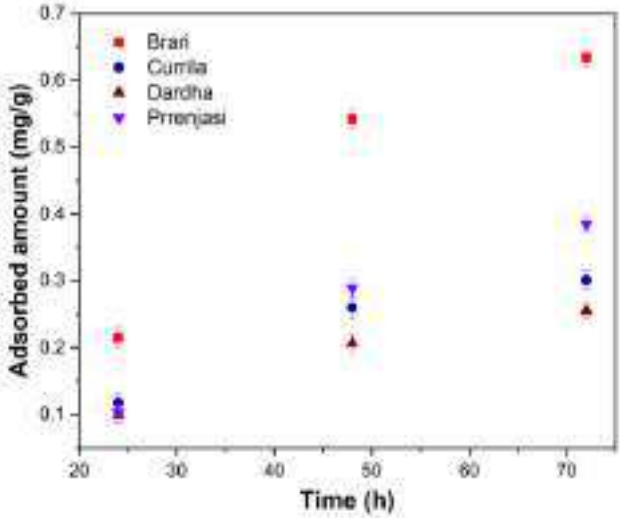

Fig. 3: Adsorbed amount of dimethoate as function of the contact time from its aqueous solution with the initial concentration of 0.300 g/L at 25°C on one gram of clays of Brari, Currila, Dardha and Prrenjasi.

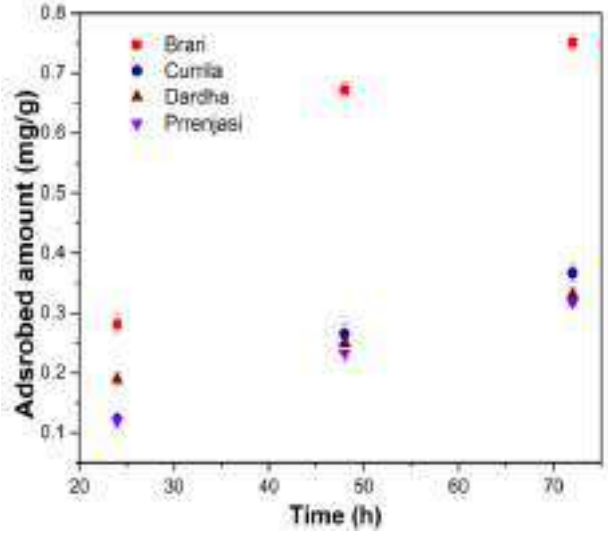

Fig. 4: Adsorbed amount of dimethoate as function of the contact time from its aqueous solution with the initial concentration of 0.400 g/L at 25°C on one gram of clays of Brari, Currila, Dardha and Prrenjasi.

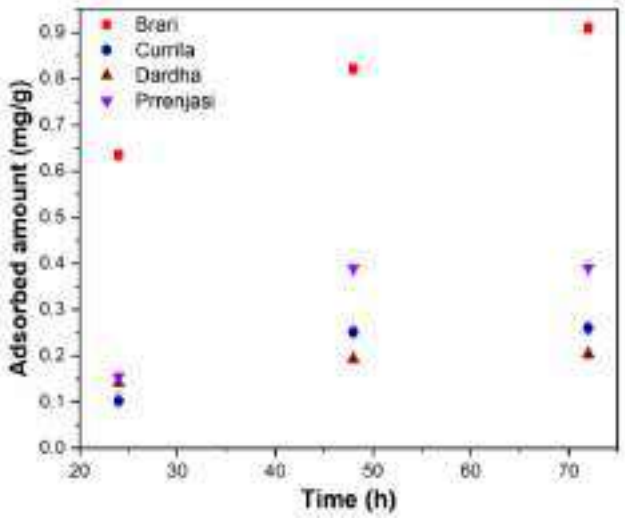

Fig. 5: Adsorbed amount of dimethoate as function of the contact time from its aqueous solution with the initial concentration of 0.500 g/L at 25°C on one gram of clays of Brari, Currila, Dardha and Prrenjasi.

4 CONCLUSIONS

The adsorption behavior of dimethoate on four different natural clay minerals of Albania from its aqueous solutions is studied for its variation with the contact time and the initial concentration of dimethoate solutions. Contact time of the clays with the dimethoate solutions ranged from 6 hours to 144 hours and the initial concentrations were 0.200 g/L, 0.300 g/L, 0.400 g/L and 0.500 g/L.

The variation of the adsorbed amount with the contact time follows a similar pattern for all the four clay samples, showing as the best adsorbent in every time interval and every initial solution's concentration the clay of Brari followed by the Prrenjas clay that displayed better properties at increased concentrations of (0.300-0,500g/ L).

Other clays have medium adsorptive properties. To make a relative comparison of clays we take Brari's clay basis, for the concentration C = 0,200g / L and in time 48 hours which we estimate 100%, then the Currila's clay represent 52% of this value, Dardha 75,2 % and Prrenjas 34,2 %. As increased of concentrations, also changes the order of adsorptive properties occur, Prrenjas's sample displayed a marked increase in concentrations: C=0,300, C= 0,400, C=0,500 g/L with respective values of 53, 3%, 47, 8% and 47, 3% compared with Brari's values of 100%. Dardha's and Currila's samples show average values, with stable increasing concentration almost all indicators show a downward trend. Finally, the study shows that the four selected natural clays, of our regions, can be successfully used to remove dimethoate from contaminated groundwater during the practice of using this insecticide in agriculture sector.

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