



Adsorption of Benalaxyl and Atrazine in Natural Clays Brari (Tirana) and Dardha (Korça)

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Abstract

In this abstract we are presenting the study of adsorption of benalaxyl and atrazine in natural Brary clays (Tirana) 41 ° 21'14.49 " N; 19 ° 50'17.74 " E and Dardha (Korça) 40 ° 31'16.59 " N; 20 ° 49'33.69 " E, from aqueous solutions with a concentration of 5 mg / ml. For the study we took the fractions ≤ 0.600 mm of natural brary and pear clays, The ratio of clay / H₂O (distilled) is 1: 5, so 1g of clay for every 5 ml of working solution or 5 g of clay for 25 ml of working solution of benalaxyl and atrazine . We carried out the study at T = 25 ° C, volume V = 25 ml and as a starting point for the calculations we took the white test values after 2 hours at 25 ° C, where the amount found in V = 25 ml is 2.3325 mg (from 5 mg occurred in 25 ml). The responsible factor calculated according to the method mentioned above in the working conditions in GC / MS was found and has a value FP = 0.2738 (for brary clay) and we checked it with the standard solution for each set of measurements. Based on the obtained results it turns out that Dardha clay has weaker properties in terms of adsorption of benalaxyl and atrazine compared to Brary clay. Under the same conditions we found the factor responsible for Dardha clay and it has this value FP = 0.250, calculated according to standard solutions and working conditions in GC / MS. KR is calculated from the ratio of the amount found in the water sample to the theoretical amount of 5 mg added to the 25 ml sample. Experimental data show that Brary clay has better adsorption properties of benalaxyl and atrazine compared to Dardha clay. As for benalaxyl and atrazine compared their adsorbents in both clays, it turns out that benalaxyl adsorbs better in both clays. Benalaxyl compared to atrazine is better adsorbed in Brari clay compared to Dardha clay.

Keywords: Benalaxyl, atrazine, clay, adsorption.



1. Hyrje

1.1. Clay

Clay is a type of fine-grained natural soil material containing clay minerals.¹ Clays develop plasticity when wet, due to a molecular film of water surrounding the clay particles, but become hard, brittle and non-plastic upon drying or firing.^{2,3,4} Most pure clay minerals are white or light-coloured, but natural clays show a variety of colours from impurities, such as a reddish or brownish colour from small amounts of iron oxide.^{5,6} Clay is the oldest known ceramic material. Prehistoric humans discovered the useful properties of clay and used it for making pottery. Some of the earliest pottery shards have been dated to around 14,000 BC,⁷ and clay tablets were the first known writing medium.⁸ Clay is used in many modern industrial processes, such as paper making, cement production, and chemical filtering. Between one-half and two-thirds of the world's population still live or work in buildings made with clay, often baked into brick, as an essential part of its load-bearing structure. Clay is a very common substance. Shale, formed largely from clay, is the most common sedimentary rock.⁹ Although many naturally occurring deposits include both silts and clay, clays are distinguished from other fine-grained soils by differences in size and mineralogy. Silts, which are fine-grained soils that do not include clay minerals, tend to have larger particle sizes than clays. Mixtures of sand, silt and less than 40% clay are called loam. Soils high in swelling clays, which are clay minerals that readily expand in volume when they absorb water, are a major challenge in civil engineering.¹⁰

1.1.1. Properties

The defining mechanical property of clay is its plasticity when wet and its ability to harden when dried or fired. Clays show a broad range of water content within which they are highly plastic, from a minimum water content (called the plasticity limit) where the clay is just moist enough to mould, to a maximum water content (called the liquid limit) where the moulded clay is just dry enough to hold its shape.¹¹ The plastic limit of kaolinite clay ranges from about 36% to 40% and its liquid limit ranges from about 58% to 72%.¹² High-quality clay is also tough, as measured by the amount of mechanical work required to roll a sample of clay flat. Its toughness reflects a high degree of internal cohesion.¹³

¹ Olive et al. 1989.

² Guggenheim & Martin 1995, pp. 255–256.

³ Science Learning Hub 2010.

⁴ Breuer 2012.

⁵ Klein & Hurlbut 1993, pp. 512-514

⁶ Nesse 2000, pp. 252-257.

⁷ Scarre 2005, p. 238.

⁸ Ebert 2011, p. 64.

⁹ Boggs 2006, p. 140.

¹⁰ Moreno-Maroto & Alonso-Azcárate 2018.

¹¹ Moreno-Maroto & Alonso-Azcárate 2018.

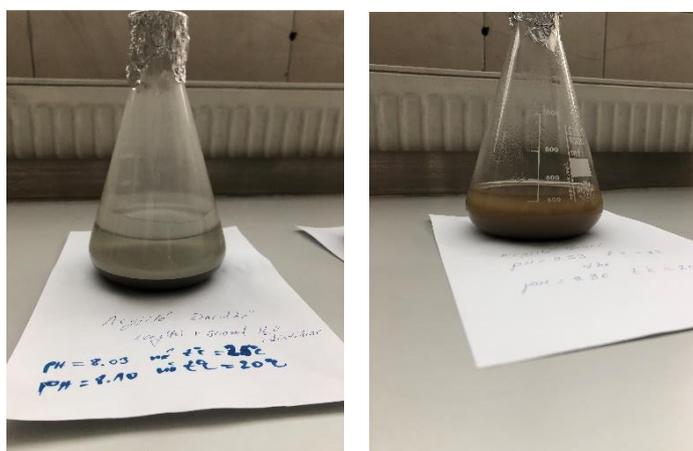
¹² White 1949

¹³ Moreno-Maroto & Alonso-Azcárate 2018.



Table 1. Chemical composition (%) of natural clays originating from two regions of Albania (DOI: 10.1002/rem.21648)

Region	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O + K ₂ O	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
Dardha	44.72	12.54	6.67	11.68	6.24	–	–	–



a)

b)

Photo.1. a) Dardha clay: 100 g clay +500 ml distilled H₂O and b) Brari clay: 100 g clay +500 ml distilled H₂O.

Clay has a high content of clay minerals that give it its plasticity. Clay minerals are hydrous aluminium phyllosilicate minerals, composed of aluminium and silicon ions bonded into tiny, thin plates by interconnecting oxygen and hydroxyl ions. These plates are tough but flexible, and in moist clay, they adhere to each other. The resulting aggregates give clay the cohesion that makes it plastic.¹⁴ In kaolinite clay, the bonding between plates is provided by a film of water molecules that hydrogen bond the plates together. The bonds are weak enough to allow the plates to slip past each other when the clay is being moulded, but strong enough to hold the plates in place and allow the moulded clay to retain its shape after it is moulded. When the clay is dried, most of the water molecules are removed, and the plates hydrogen bond directly to each other, so that the dried clay is rigid but still fragile. If the clay is moistened again, it will once more become plastic. When the clay is fired to the earthenware stage, a dehydration reaction removes additional water from the clay, causing clay plates to irreversibly adhere to each other via stronger covalent bonding, which strengthens the material. The clay mineral, kaolin, is transformed into a non-clay material, metakaolin, which remains rigid and hard if

¹⁴ Bergaya & Lagaly 2006, pp. 1-18.



moistened again. Further firing through the stoneware and porcelain stages further recrystallizes the metakaolin into yet stronger minerals such as mullite.¹⁵ The tiny size and plate form of clay particles gives clay minerals a high surface area. In some clay minerals, the plates carry a negative electrical charge that is balanced by a surrounding layer of positive ions (cations), such as sodium, potassium, or calcium. If the clay is mixed with a solution containing other cations, these can swap places with the cations in the layer around the clay particles, which gives clays a high capacity for ion exchange.¹⁶ The chemistry of clay minerals, including their capacity to retain nutrient cations such as potassium and ammonium, is important to soil fertility.¹⁷ Clay is a common component of sedimentary rock. Shale is formed largely from clay and is the most common of sedimentary rocks.¹⁸ However, most clay deposits are impure. Many naturally occurring deposits include both silts and clay. Clays are distinguished from other fine-grained soils by differences in size and mineralogy. Silts, which are fine-grained soils that do not include clay minerals, tend to have larger particle sizes than clays. There is, however, some overlap in particle size and other physical properties. The distinction between silt and clay varies by discipline. Geologists and soil scientists usually consider the separation to occur at a particle size of 2 μm (clays being finer than silts), sedimentologists often use 4–5 μm , and colloid chemists use 1 μm .¹⁹ Geotechnical engineers distinguish between silts and clays based on the plasticity properties of the soil, as measured by the soils' Atterberg limits. ISO 14688 grades clay particles as being smaller than 2 μm and silt particles as being larger. Mixtures of sand, silt and less than 40% clay are called loam.

Some clay minerals (such as smectite) are described as swelling clay minerals, because they have a great capacity to take up water, and they increase greatly in volume when they do so. When dried, they shrink back to their original volume. This produces distinctive textures, such as mudcracks or "popcorn" texture, in clay deposits. Soils containing swelling clay minerals (such as bentonite) pose a considerable challenge for civil engineering, because swelling clay can break foundations of buildings and ruin road beds.²⁰

1.1.2. Formation

Clay minerals most commonly form by prolonged chemical weathering of silicate-bearing rocks. They can also form locally from hydrothermal activity.²¹ Chemical weathering takes place largely by acid hydrolysis due to low concentrations of carbonic acid, dissolved in rainwater or released by plant roots. The acid breaks bonds between aluminium and

¹⁵ Breuer 2012.

¹⁶ Bergaya & Lagaly 2006, pp. 1-18.

¹⁷ Hodges 2010.

¹⁸ Boggs 2006, p. 140

¹⁹ Guggenheim & Martin 1995, pp. 255–256.

²⁰ Olive et al. 1989.

²¹ Foley 1999.



oxygen, releasing other metal ions and silica (as a gel of orthosilicic acid).²² The clay minerals formed depend on the composition of the source rock and the climate. Acid weathering of feldspar-rich rock, such as granite, in warm climates tends to produce kaolin. Weathering of the same kind of rock under alkaline conditions produces illite. Smectite forms by weathering of igneous rock under alkaline conditions, while gibbsite forms by intense weathering of other clay minerals.²³ There are two types of clay deposits: primary and secondary. Primary clays form as residual deposits in soil and remain at the site of formation. Secondary clays are clays that have been transported from their original location by water erosion and deposited in a new sedimentary deposit.²⁴ Secondary clay deposits are typically associated with very low energy depositional environments such as large lakes and marine basins.²⁵

1.1.3. Varieties

The main groups of clays include kaolinite, montmorillonite-smectite, and illite. Chlorite, vermiculite,²⁶ talc, and pyrophyllite²⁷ are sometimes also classified as clay minerals. There are approximately 30 different types of "pure" clays in these categories, but most "natural" clay deposits are mixtures of these different types, along with other weathered minerals.²⁸ Clay minerals in clays are most easily identified using X-ray diffraction rather than chemical or physical tests.²⁹ Varve (or varved clay) is clay with visible annual layers that are formed by seasonal deposition of those layers and are marked by differences in erosion and organic content. This type of deposit is common in former glacial lakes. When fine sediments are delivered into the calm waters of these glacial lake basins away from the shoreline, they settle to the lake bed. The resulting seasonal layering is preserved in an even distribution of clay sediment banding.³⁰ Quick clay is a unique type of marine clay indigenous to the glaciated terrains of Norway, Canada, Northern Ireland, and Sweden.³¹ It is a highly sensitive clay, prone to liquefaction, and has been involved in several deadly landslides.³²

1.1.4. Historical and modern uses

Clays are used for making pottery, both utilitarian and decorative, and construction products, such as bricks, walls, and floor tiles. Different types of clay, when used with different minerals and firing conditions, are used to produce earthenware, stoneware, and

²² Leeder 2011, pp. 5-11.

²³ Leeder 2011, pp. 10-11.

²⁴ Murray 2002.

²⁵ Foley 1999.

²⁶ Nesse 2000, p. 253.

²⁷ Klein & Hurlbut 1993, pp. 514-515

²⁸ Klein & Hurlbut 1993, p. 512.

²⁹ Nesse 2000, p. 256.

³⁰ Foley 1999.

³¹ Rankka et al. 2004.

³² Natural Resources Canada 2005



porcelain. Prehistoric humans discovered the useful properties of clay. Some of the earliest pottery shards recovered are from central Honshu, Japan. They are associated with the Jōmon culture, and recovered deposits have been dated to around 14,000 BC.³³Cooking pots, art objects, dishware, smoking pipes, and even musical instruments such as the ocarina can all be shaped from clay before being fired. Clay tablets were the first known writing medium.³⁴Scribes wrote by inscribing them with cuneiform script using a blunt reed called a stylus. Purpose-made clay balls were used as sling ammunition.³⁵Clay is used in many industrial processes, such as paper making, cement production, and chemical filtering.³⁶Bentonite clay is widely used as a mold binder in the manufacture of sand castings.³⁷³⁸Clay, being relatively impermeable to water, is also used where natural seals are needed, such as in the cores of dams, or as a barrier in landfills against toxic seepage (lining the landfill, preferably in combination with geotextiles).³⁹Studies in the early 21st century have investigated clay's absorption capacities in various applications, such as the removal of heavy metals from waste water and air purification.⁴⁰⁴¹

1.2. Atrazine is an organochlorine herbicide from the triazine family and is used as a selective pre- and post-emergent herbicide to control weeds and as a non-selective herbicide in non-cultivated regions ⁴². Being one of the most widely used herbicides in the world, particularly for energetic biomass crops such as maize and sugar cane⁴³, its annual global production is between 70,000 and 90,000 tons ⁴⁴⁴⁵⁴⁶. Due to its high water solubility, extensive use and persistence in soil, atrazine presents a high risk of leaching, resulting in the pollution of soils and underground and surface water sources ⁴⁷, which presents a potential threat to human health due to its association with endocrine disruption and possible teratogenic and carcinogenic effects⁴⁸⁴⁹⁵⁰. Authors such as Graymore 2001⁵¹ indicate that atrazine has been found in concentrations of up to 1000 µg/L in waters

³³ Scarre 2005, p. 238.

³⁴ Ebert 2011, p. 64.

³⁵ Forouzan et al. 2012.

³⁶ Nesse 2000, p. 257.

³⁷ Boylu 2011.

³⁸ Eisenhour & Brown 2009.

³⁹ Koçkar, Akgün & Aktürk 2005.

⁴⁰ García-Sánchez, Alvarez-Ayuso & Rodríguez-Martin 2002.

⁴¹ Churchman et al. 2006.

⁴² Mendas, G 2012

⁴³ Jablonowski, N 2010

⁴⁴ Sharma, R 2008

⁴⁵ Udikoviç, N 2012

⁴⁶ Hou, X 2017

⁴⁷ Papadakis, E 2015

⁴⁸ Udikoviç, N 2012

⁴⁹ Copeland, C 2012

⁵⁰ Lesmes, C 2013

⁵¹ Graymore, M 2001



adjacent to treated fields and up to 80 µg/L in drinking water (DW). In the production of DW, the conventional or complete treatment technology (coagulation, flocculation, sedimentation and conventional filtration), is most often used; however, most of these processes were not designed to remove organic compounds such as pesticides, which due to their heterogeneity are difficult to reduce^{52,53}. In contrast, one of the most used and efficient techniques for the removal of organic compounds in water is adsorption⁵⁴. Given that production and regeneration costs are its main limitation, different adsorbent media have been implemented, derived from low-cost materials such as tires, wood, bone, fruit peels and agricultural waste, with low inorganic content and high carbon content^{55,56}.

1.2.1 Benalaxyl is a chemical compound from the group of acetylalanines . Benalaxyl occurs as a racemic mixture of the (R) - and the (S) - enantiomer . (R) -Benalaxyl is the more potent compound (the eutomer) and is also known as Benalaxyl-M . Benalaxyl was launched as a systemic fungicide in 1983 ; it works by inhibiting RNA polymerase I. Benalaxyl can be obtained by esterifying (RS) -2-chloropropionic acid [(±) -2-chloropropionic acid] with methanol , subsequent aminolysis of the methyl ester with 2,6-dimethylaniline and amidation with phenylacetyl chloride.⁵⁷ Benalaxyl is used in potato cultivation against late blight , alternaria and downy mildew of the grapevine . There is a partial effect against botrytis and red burn . In 2004, the EU Commission decided to include benalaxyl for use as a fungicide in the list of substances permitted as active ingredients in pesticides.⁵⁸ The active ingredient Benalaxyl-M was added to the list of permitted active ingredients in 2013.⁵⁹ In Germany, Switzerland and Austria pesticides with the active ingredient Benalaxyl-M are approved, in Austria also pesticides with Benalaxyl.⁶⁰

2. Material and Methods

The study was conducted using the material possibilities available to the laboratories of FSHN, FMNS and other institutions. For our purpose were made available: Various glasses for analytical purposes: balloons, berets, pipettes and various funnels, and others. Reagents and solvents: Dichloromethane, acetone, Ethyl acetate, ethanol, Benzene and others of AR quality.

Apparatus: electronic centrifuge 5000rrot / min, analytical scales, complete set of sieves, mechanical mill, electromagnetic mixer, complete gas chromatograph with capillary column and results calculation program. Clay raw materials: selected in 2 different areas of our country Dardha (Korcë) and Brari (Tirana). The clays were crushed and ground in

⁵² Sarkar, B 2007

⁵³ Jardim, W 2012

⁵⁴ Gupta, V 2013

⁵⁵ Gupta, V 2013

⁵⁶ Peláez, A 2012

⁵⁷ Thomas A 1996

⁵⁸ <https://eur-lex.europa.eu/legal-content/DE/TXT/PDF/?uri=uriserv:OJ.L .2004.120.01.0026.01.DEU> 2004

⁵⁹ <https://eur-lex.europa.eu/legal-content/DE/TXT/PDF/?uri=uriserv:OJ.L .2013.312.01.0018.01.DEU> 2013

⁶⁰ https://de.wikipedia.org/wiki/Generaldirektion_Gesundheit_und_Lebensmittelsicherheit 2016

a mill, sieved and the 0-0.250mm fraction was selected and dried at 150 ° C for 4 hours. Store in airtight plastic bottles. After the various variants we applied to arrive at the final scheme of the method, we are briefly mentioning facts that we specified during the work after many analytical tests.

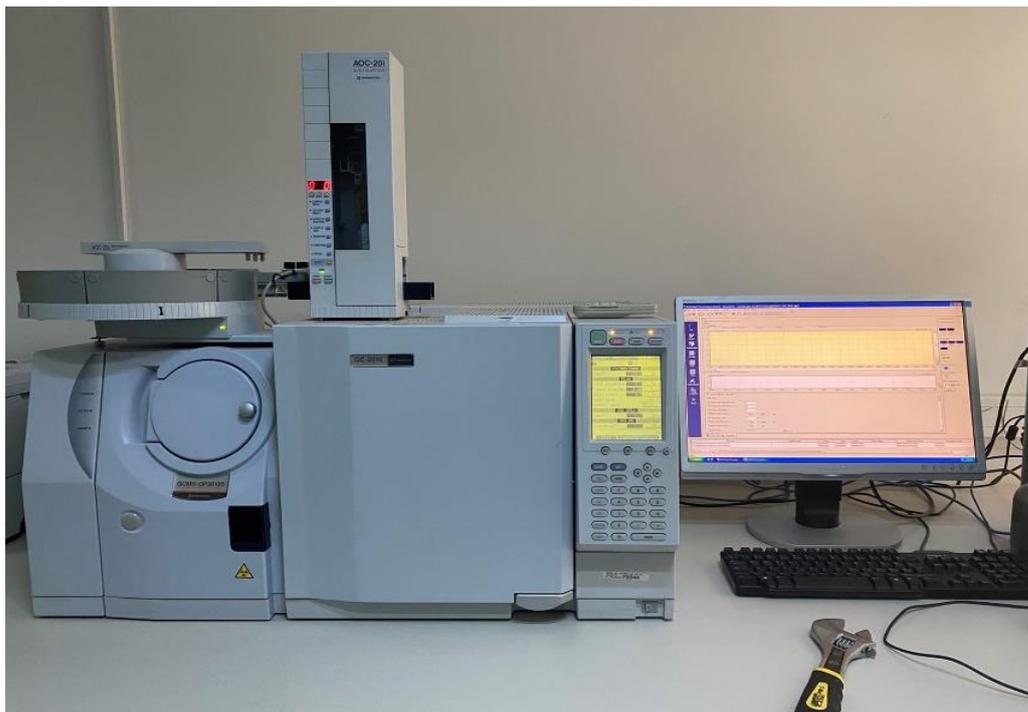


Foto.2. GC/MS

3. Results and discussion

3.1.Experiments with natural Brari and Dardha clays

The following are the results obtained during the adsorption of benalaxyl and atrazine in natural Brari and Dardha clays from aqueous solutions at a concentration of 5 mg / ml. Natural and Dardha clays have fractions of 0 - 0.250 mm. The ratios are: 1 g of clay for every 5 ml of working solution or 5 g of clay for 25 ml of working solution of Benalaxyl and Atrazine that the tests were performed. T = 35 ° C. Volume of aliquot quantity V = 25 ml.



Table 2. Adsorption of benalaxyl in Dardha clay

№. Test	Time of absorption (hours)	Quantity found corrected (mg / 25ml)	Quantity absorbed in mg / 5g clay	Quantity absorbed mg / g clay	K_R (%)
1	6	1.7683	0.5637	0.1127	3.6
2	24	1.5850	0.7470	0.1494	3.7
3	48	1.3900	0.9420	0.1884	2.8
4	72	1.1400	1.1920	0.2384	2.8
5	96	0.6905	1.6415	0.3283	1.8
6	120	0.5550	1.7770	0.3554	1.1

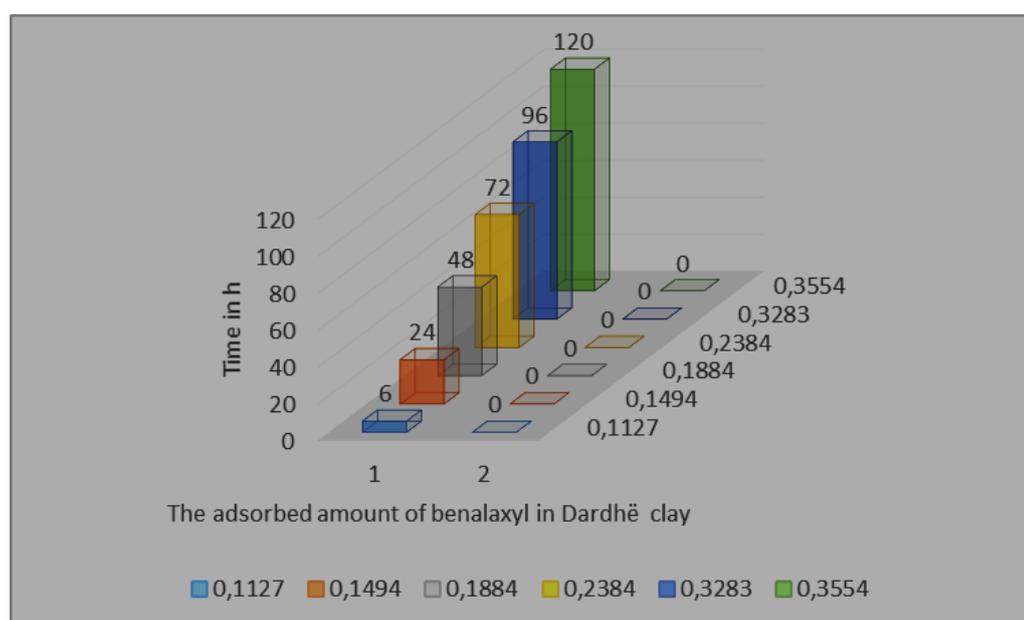


Figure 1. Dependence of the adsorbed amount of benalaxyl on dardha clay depending on time



Note: 1. Recall that as a starting point for the calculations we used the value of the white test after 2 hours at 35 ° C, where the amount found in the amount of aliquot $V = 25$ ml is 2.3325 mg (from 5 mg occurred in 25 ml) . The responsible factor calculated according to the method mentioned above in the working conditions in GC / MS is $FP = 0.2738$ and we checked it with the standard solution for each set of experiments according to each mirror.

Tabela 3. Adsorbimi e benalaxylit në argjilën e brarit $T = 35^{\circ}C$

Nr. Test	Time of absorption (hours)	Quantity found corrected (mg / 25ml)	Quantity absorbed in mg		K_R (%)
			mg/5g	mg/g	
1	6	1.857	0.5315	0.0689	32
2	24	1.9122	0.4203	0.0841	38.2
3	48	2.0799	0.2530	0.0506	41.6
4	72	1.8330	0.4990	0.0995	36.7
5	96	1.7382	0.5938	0.1187	34.7
6	120	0.7995	1.5325	0.3065	16.0

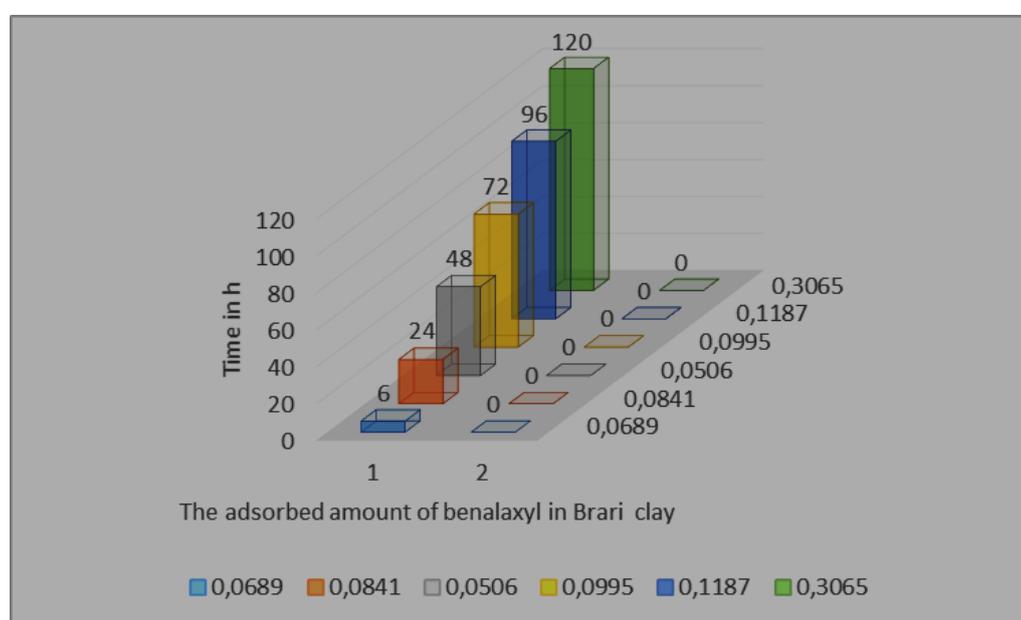


Figure 2. Adsorbed amount of benalaxyl in Brari clay depending on time

4. Adsorption of Atrazine in Brari clay



Nr. Test	Time of absorption (hours)	Quantity found corrected (mg / 25ml)	Quantity absorbed in mg		K _R (%)
			mg/5g	mg/g	
1	6	1.6683	0.5537	0.1133	33
2	24	1.7075	0.6250	0.1250	34.1
3	48	1.0799	1.2526	0.2505	21.6
4	72	0.9868	1.3457	0.2691	19.7
5	96	1.0263	1.3062	0.2612	20.5
6	120	0.5475	1.7850	0.3570	10.9

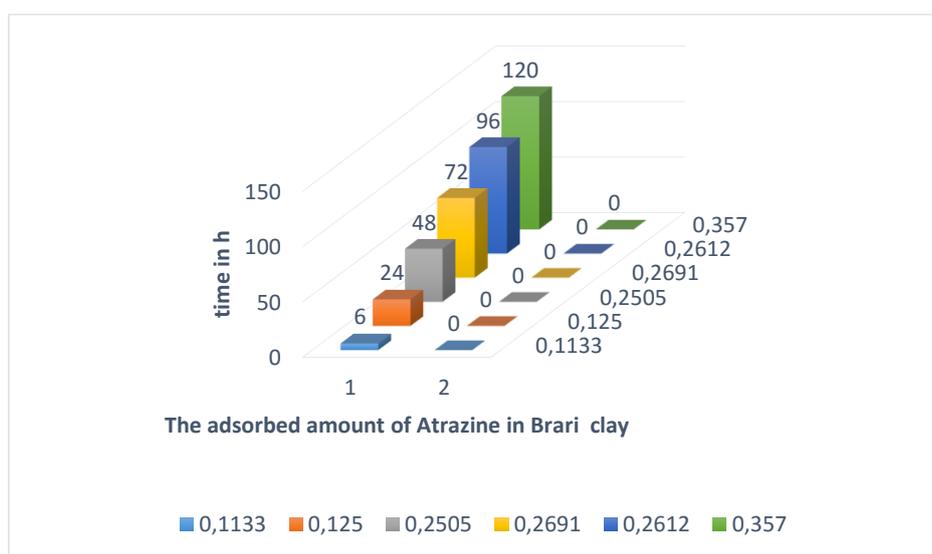


Figure 3. The adsorbed amount of atrazine in Braur clay depending on time

Table 5. Adsorption of atrazine in Dardha clay

Nr. Test	Time of absorption (hours)	Quantity found corrected (mg / 25ml)	Quantity absorbed in mg		K _R (%)
			mg/5g	mg/g	
1	6	1.6683	0.4637	0.1116	34
2	24	1.7550	0.5775	0.1155	35.1
3	48	1.6799	0.6526	0.1305	33.6
4	72	1.2743	1.0582	0.2116	25.5
5	96	1.0559	1.2766	0.2553	21.1



6	120	0.7302	1.6023	0.3205	14.6
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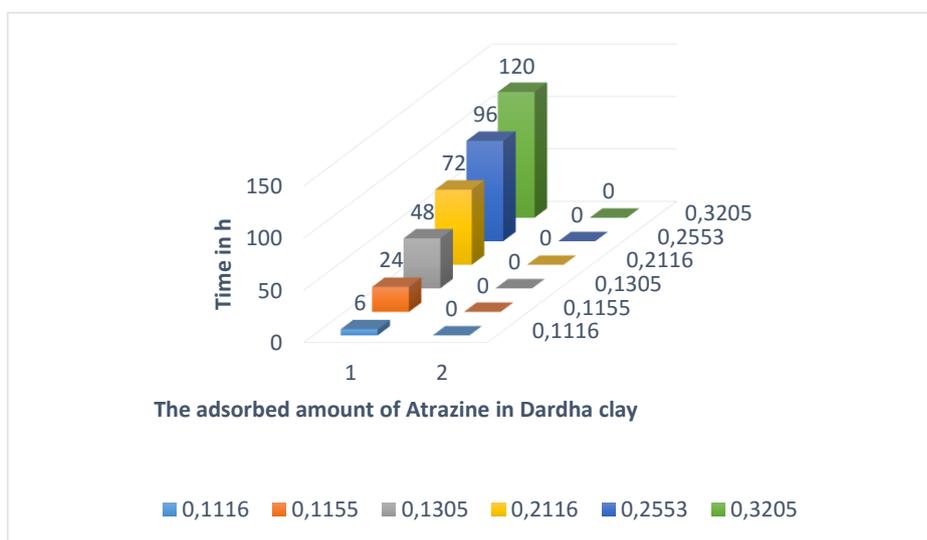


Figure 4. Adsorbed amount of atrazine in Dardha clay depending on time

4. Conclusion

1. Internal standard: Dibutylphthalate (DBF) - It is absorbed by the clay due to its planar structure and spoils the analysis results. Its addition was proved in the later stages of the procedure eg after centrifugation of the clay. Even at this moment there are numerous deviations in the results. Eventually the internal standard should be added to the organic extract separated from the water. In 10 analyzes performed we were convinced that the internal standard should be added to the organic extract separated from the aqueous solution.
2. The best extractor is the mixture: Ethyl Acetate + Dichloromethane in a ratio of 3 to 1 by volume. Single use of Dichloromethane leads to large losses due to the low boiling point of 41 ° C, despite the large amount of solvent. Ethyl acetate is soluble in water (8% volume) and does not provide good separation of Benalaxyl and Atrazine from water. This conclusion was reached after a series of trials.
3. The use of saturated solutions of NaCl and KCl in aqueous solutions of Benalaxyl and Atrazine had satisfactory results for breaking down emulsions and reducing the solubility of Benalaxyl and Atrazine in water. It was therefore switched to the use of KCl in crystalline form directly in the solution to be analyzed.
4. The extraction was performed in triplicate, i.e. in the aqueous sample the extraction is performed 3 times in times of 10min, 15min, 20 min. The extraction is done with the minimum possible volume of solvent, so that the final volume is as small as possible and we have a concentration that is normally analyzed in the Gas Chromatograph.



5. Studying the dependence of the adsorption of Benalaxyl and Atrazine from clay on aqueous solutions, from the time of contact clay + water, it is noticed that from 2 hours to 24 hours there is no visible adsorption of Benalaxyl and Atrazine on clay. Further studies were therefore extended at intervals from 24 hours to 120 hours. Longer intervals are of no interest because they increase too much due to spontaneous hydrolysis of dimethoate, which is clearly seen in chromatograms in practice, but also from the theoretical data that well explain this phenomenon.

6. To stabilize the analysis on the gas chromatograph, a series of determinations were performed with standard solutions of Benalaxyl and Atrazine (99%) and the internal standard DBF (99.5%) until the achievement of optimal operating parameters, obtaining clear chromatograms with the respective points visible and easily calculated.

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