Article

The Process and Kinetics of Pesticide Desorption from Clay as a Function of Cleaning Polluted Waters

Esad Behrami [1] and Vahid Avdiu [2,*]

1   Department of Chemistry, Faculty of Natural and Mathematics Sciences, University of Prishtina, 10000 Prishtina, Kosovo
2   Faculty of Agriculture and Veterinary, University of Prishtina, 10000 Prishtina, Kosovo
*   Correspondence: vahidavdiu6@gmail.com; Tel.: +383-44-156-505

Abstract: This study presents an investigation into the desorption process of pesticides, namely benalaxyl, atrazine, dimethoate, and methomyl, from aqueous solutions in natural Brari clay (Tirana) located at 41°21′14.49″ N and 19° 50′17.74″ E and Dardha clay (Korça) located at 40°31′16.59″ N and 20°49′33.69″ E. The desorption process was fast, where in the first 2 hours of contact, 99.1% of atrazine was desorbed from Brari clay, and 90.1% of atrazine was desorbed from Dardha clay. In addition, in the first 2 hours of contact, 80.3% of benalaxyl was desorbed from pear clay and 79.2% of benalaxyl from Brari clay; 96.2% of methomyl and 81.2% of dimethoate were desorbed. According to the acquired curves, the desorption process began with the dominance of methomyl from Brari clay, followed by dimethoate from Brari clay, dimethoate from Dardha clay, atrazine from Brari clay, benalaxyl from Brari clay, benalaxyl from Dardha clay, and lastly atrazine from Dardha clay. Hence, compared to Dardha clay, less pesticide underwent desorption with Brari clay. Researchers immediately wondered how long (time) these pesticides would remain in the corresponding clays following the adsorption process, so the study of the kinetics of the desorption of pesticides from clay is of special interest. The kinetics of the pesticides atrazine, benalaxyl, dimethoate, and methomyl (all at a concentration of 25 mg/L) desorbing from natural Brari and Dardha clays are presented here.

Keywords: benalaxyl; atrazine; dimethoate; methomyl; clay; desorption

1. Introduction

In order to reduce insect populations and increase the production yield of all agricultural crops, agriculture has greatly benefited from the use of organochlorine pesticides (OCPs) and other agrochemicals. However, because of their persistence, bioaccumulation, and toxicity, their use has created a variety of environmental issues [1]. Although pesticides are often used in agriculture, there is real concern that their residues can contaminate aquatic and terrestrial ecosystems [2]. Atrazine has been widely used in agriculture, which has seriously polluted the environment. Through adsorption-desorption processes, the addition of biochar can decrease the bioavailability and mobility of atrazine in soil [3]. The widespread use of these chemicals in agricultural and urban areas has influenced a reduction in biodiversity [4]. Pesticide migration away from the application site is affected by several pesticide properties, including binding capacity, vapor pressure, water solubility, and degradation [5]. Absorption mechanisms and desorption regulate the transport of pesticides in soil; therefore, these processes should be viewed with more interest [6]. Pesticides can persist for a very long time in exposed environments; hence, land disposal and removal/carry-over by processes such as leaching should be carefully studied [7]. Herbicide and clay properties both affect the amount of adsorption [8]. The reduced desorption capacity reported with farmyard manure soil may be due to hydrogen bonding predominating over hydrophobic interactions. Discharge of atrazine into rivers and soil and runoff into drinking water sources can be reduced by greater hydrogen bonding [9]. Adsorption

describes the accumulation of a material without developing a three-dimensional crystal structure at the boundary between two phases. Desorption, the opposite process, is material loss from the interface, usually by diffusion into the bulk of an adjacent phase. Surfaces separating the liquid-gas, solid-gas, and solid-liquid interfaces are where the process of adsorption occurs. Figure 1 shows the structural properties, surface coatings and porosity of geosorbents that affect the kinetics of absorption limited by transport.
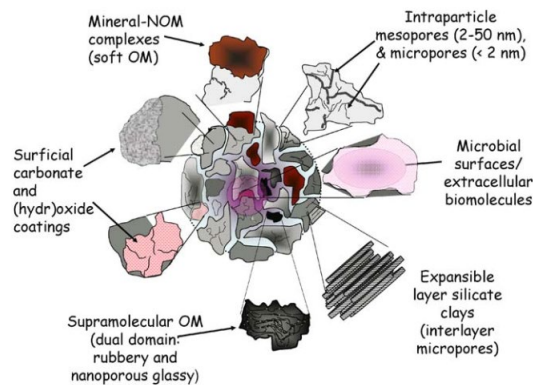

Figure 1. Structural properties, surface coatings, and porosity of geosorbents affecting transport-limited sorption kinetics (Jon Chorover and Mark L. Brusseau) [10].

Aggregate size has been reported to influence pesticide retention and behavior in soil. The aggregate and particle sizes used in this study ranged from <0.11 to >1.7 mm, and atrazine concentrations ranged from 0.65 to 39.2 μmol L^{-1}. In Barnes loam, Kf values were strongly positively correlated with aggregate size, particle size, and organic carbon (OC) content ($p = 0.01$ for each parameter), whereas in Brandt silty clay loam, Kf values were less correlated with size and OC content ($p \geq 0.1$) but better correlated with clay content and estimated specific surface area ($p = 0.05$ for each parameter). Approximately 18% more atrazine was desorbed from the smallest size fractions than from the largest during hysteretic desorption [11]. Atrazine and simazine have been identified by the United States Environmental Protection Agency (EPA) as potentially cancer-causing herbicides. The presence of these herbicides in water is of concern to the general public and regulatory bodies because of their propensity to cause cancer. Atrazine and simazine have been linked to leukemia, lymphoma, breast, ovarian, and uterine malignancies, tumors, and other cancers [12]. Atrazine is a disruptive endocrine substance that interferes with regular hormone activity, leading to weight loss, reproductive cancers, and birth abnormalities in both frogs and humans [13]. Herbicides can go through various processes once they are in the soil. Examples of sorption and desorption are used to describe how much herbicide is present in the soil solution. Plants can absorb herbicides in the soil solution, aiding in weed control. Nevertheless, when there has been a lot of rain, herbicides can leak and contaminate water supplies [14]. The Drinking Water Directive 98/83/EC of the European Commission, which regulates the quality of water meant for human consumption, states that the maximum concentration of any one pesticide in drinking water is 0.1 g/L, and the maximum concentration of all pesticides combined is 0.5 g/L [15]. In order to reduce leaching losses and manage waste disposal on land, it is necessary to be able to forecast the mobility of dissolved chemicals in soil [16]. At typical ambient pressures, all kinetic tests were conducted at a temperature of 25 °C [17]. The first 10 min saw rapid desorption in all soil samples, followed by gradual adsorption in the loam size fractions and no discernible adsorption or desorption in the decomposed granitic soil (DG) size fractions [18]. In addition to degradation rates, the degree of sorption/desorption dynamics of the herbicide in soils determines the potential for groundwater contamination [19]. While Lo and Merkle showed a larger association with particular clay minerals, such as montmorillonite and vermiculite, rather than overall clay content, other authors discovered a substantial link between soil pH and cation exchange capacity or clay content [20]. Desorption is often

characterized by an initial quick pace, followed by a significantly slower approach to an apparent equilibrium. Desorption was slower than sorption [21]. The availability of organic pollutants for plant absorption and microbial breakdown is affected by sorption mechanisms, which also restrict pesticide movement in soils by lowering their concentration in the soil [22]. Knowing these processes is crucial to correctly estimating the mobility and destiny of these compounds in the subsurface, since adsorption-desorption events greatly influence pesticide behavior in soil (Bailey and White, 1970; Barriuso and Calvet, 1991; Coquet, 2003) [23]. In comparison with neutral pH, desorption was more pronounced in both acidic and alkaline pH levels [24]. Failure to attain equilibrium during desorption may be the cause of the appearance of irreversibility or hysteresis [25]. To prevent unacceptably severe crop damage, additional information is required to forecast soil adsorption and desorption, bioavailability, and permanence [26]. Adsorption and desorption mechanisms regulate the interactions between soil and pesticides and are also important in understanding the results of the regulated or uncontrolled application of pesticides to soil (Shariff, 2009) [27]. Recent excellent reviews have analyzed the interactions between organic chemicals and clay minerals, intending to create formulations for controlled-release herbicides and water purification [28]. Depending on the structure of the mineral sorbents and the composition of the aqueous medium, diffusion may take days, weeks, months, years, or even decades to achieve the equilibrium state for sorption or desorption (Evans et al., 1983; Di Toro et al., 1986; De Preter, 1990; Comans et al.,1991) [29]. Eluent composition (often the mobile phase) and flow rate affect dynamic desorption efficiency. Dynamic desorption might not be able to completely desorb all the analytes in an acceptable length of time due to the sluggish kinetics of the desorption process. This means that static desorption for a predetermined period of time is frequently utilized to sweep the desorbed analytes into the analytical column, followed by a quick dynamic desorption phase [30]. The temperature dependency of water adsorption and desorption rates was compared based on the calculated activation energies. According to our estimates, the mechanism of water desorption on the MMT surface differs from that of water adsorption because of surface factors that promote the stability of water conformers throughout the desorption process [31].

Properties

Clay minerals are generally categorized into the following groups: montmorillonite, smectite, kaolinite, illite, and chlorite. Montmorillonite, kaolinite, and illite are widely used because of their high specific surface area, chemical and mechanical stability, variety of surface and structural properties, and low cost. [32] The distinct two-dimensional (2D) layer structure and unique physicochemical properties of clays and clay minerals, including swelling and ion exchange capacity, enable them to adsorb various organic and inorganic water pollutants (Chen et al., 2016; Ewis and Hameed, 2021) [33]. Clay plays a key role in environmental protection from pollutants through ion exchange and/or adsorption [34]. Since filtration is the main procedure in water purification, clay composites, which have been demonstrated to be very good adsorbents, have become natural candidates for materials to fill the filters. It turned out that the powdered composites had to be mixed with granulated materials, such as sand, in order to enable flow in the filter. Consequently, efficient filtration was required to develop granulation procedures for the clay composites [35]. Clay minerals form excellent natural barriers due to their small grain size, specific surface area, high efficiency with high uptake capacity, and their diagenetic processes (which cause high natural density). In addition, they have the ability to close fissures and cracks, which may form paths for leachates. Moreover, their chemical reactivity enables the immobilization of important contaminants [36]. The characteristics that determine the configuration of a mineral come from its chemical structure and geometrical arrangements of molecules and ions, along with the electrical forces that bind the molecules in the structure. The eight main elements, O^{2+}, Si^{4+}, Al^{3+}, Fe^{2+}, Mg^{2+}, Ca^{2+}, Na^{2+}, and K^+, are the major constituents of 99% of the earth's crust. The majority of clay minerals consist of Si and Al_2O_3 sheets that directly belong to the phyllosilicate family [37].

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 mold, to a maximum water content (called the liquid limit), where the molded clay is just dry enough to hold its shape [38]. Clay has a high content of clay minerals, which gives it its plasticity. Clay minerals are hydrous aluminum phyllosilicate minerals composed of aluminum 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 [39]. Clay comes from the ground, usually in areas where streams or rivers once flowed. It is made from minerals, plant life, and animals—all the ingredients of soil. Over time, water pressure breaks up the remains of flora, fauna, and minerals, pulverizing them into fine particles. Larger particles are filtered out through rocks and sand, leaving silt to settle into beds of clay. How far silt travels from its source and how pure the silt is determines the type of clay it becomes [40].

2. Materials and Methods

Hexane, dichloromethane, absolute ethanol, dibutyl phthalate, technical ethanol, sodium chloride, and sodium sulfurate were among the reactants and solvents used. Instruments: Electromagnetic mixer, ISOLAB, VELP SCIENTIFIKA (Milan, Italy), and DIAB; electronic centrifuge, Hermle, Z 206A, 6000 rpm (Wehingen, Germany); analytical scales: JS-110, Chyo, max 110 g, d = 0.0001 g (Milan, Italy) [41].

Methods for Characterization

Before researching the capacity of Brari and pear clays for the adsorption and desorption of pesticides, we analyzed the clays in relation to the composition and morphology of the clays. Analyses were conducted using the XRF and SEM methods; the XRF analysis results are shown in Table 1, while the SEM analysis results are presented in Figures 2 and 3. Pesticides were determined using the GC-MS method. The analyses were performed with the XRF method, which is a technique suitable for very fast qualitative elemental analysis, where typically all elements from sodium to uranium can be detected simultaneously, with good-quality spectra obtained in a few seconds/minutes. The XRF method is also used as a quantitative determination technique, where the height of the maximum for each element is directly related to the concentration of that element within the sampling volume. The scanning electron microscope (SEM) method, which is a type of microscope that uses a focused beam of electrons to scan the surface of a sample and create a high-resolution image, can provide information on the surface composition of a material and its topography.

An x-ray fluorescence spectrometer (XRF) ARL 900 model with a measuring capacity of Ppm-100%, a measurement precision of +0.10%, and an x-ray tube of 40 kV–80 mA was used to conduct the spectrometric fluorescence analyses. A gas chromatograph (GC) with mass spectrometry was used to perform the gas chromatographic studies (MS). The carrier gas, helium, had a flow rate of 1.71 mL/min. The detector and injection temperatures were set at 290.1 °C and 277.1 °C, respectively. Conventional GC capillary columns (SLB®-5 ms capillary GC column; L × I.D. 30 m × 0.32 mm, df 0.25 μm; parameter −60–340 °C temperature (isothermal), −60–360 °C temperature (programmed); beta value 320; df = 0.25 μm; technique(s) GC/MS: suitable gas chromatography (GC); L × I.D. 30 m × 0.32 mm; matrix active group bonded and highly crosslinked; and silphenylene polymer virtually equivalent in polarity to poly(5% diphenyl/95% dimethyl siloxane) phase) with a head pressure of 214.7 kPa were used. The VEGA3 LMU paired with energy dispersive underwent SEM investigation. The INCA Energy 250 Microanalysis System's x-ray spectroscopy was used to analyze the substance quantitatively. The SE detector's accelerating voltage was set to 20 kV.

3. Results and Discussion

Below are the results obtained during the desorption of benalaxyl, atrazine, dimethoate, and methomyl in natural Brari and Dardha clays from aqueous solutions at a concentration of 25 mg/L. We took the 0–0.250 mm fractions of natural Brari and Dardha clays. The ratios were: 1 g of clay for every 5 mL of working solution or 5 g of clay for every 25 mL of working solution of benalaxyl, atrazine, dimethoate, and methomyl tested (T = 35 °C; volume of the aliquot amount V = 25 mL). Each clay was subjected to fluorescence spectrometer x-ray (XRF) analyses of chronologically sedimented sample fractions. The initial sample fractions (1-B and 1-D) corresponded to the fractions that settled out of the Brari and Dardha clay suspensions after the first 10 min. The collection of all other fractions took place at intervals of 10 min. Table 1 summarizes the findings from each clay's first 10 parts of sediment.

Table 1. Brari and Dardha clay composition data.

23 December 2020 PANalytical Results quantitative—Selected archive: Number of results Selected:	20								
Seq.	Sample name (1–20)	Fe	SiO_2	MgO	Al_2O_3	Ni	Co	CaO	Cr_2O_3
		Fe	Si	Mg	Al	Ni	Co	Ca	Cr
		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
1	1-B	5.96	46.31	6.13	5.91	0.07	0.01	8.50	0.44
2	2-B	6.17	46.55	6.36	5.98	0.08	0.00	8.58	0.44
3	3-B	6.60	44.53	6.45	6.34	0.08	0.00	8.51	0.45
4	4-B	6.53	44.25	6.28	6.59	0.08	0.01	8.58	0.45
5	5-B	6.38	44.50	6.28	6.52	0.07	0.01	8.60	0.44
6	6-B	6.55	43.80	6.28	6.48	0.07	0.00	8.75	0.44
7	7-B	4.36	30.51	4.01	3.76	0.07	0.01	5.28	0.43
8	8-B	6.79	43.95	6.43	6.39	0.08	0.01	8.91	0.45
9	9-B	6.66	43.48	6.49	6.63	0.08	0.00	8.87	0.45
10	10-B	6.76	43.92	7.06	6.81	0.07	0.01	8.59	0.44
11	1-D	5.38	48.68	6.09	5.02	0.07	0.01	9.86	0.47
12	2-D	5.45	48.88	5.82	5.26	0.07	0.01	9.15	0.46
13	3-D	5.49	48.67	5.81	5.15	0.07	0.00	9.73	0.46
14	4-D	5.42	48.86	6.49	5.00	0.07	0.01	10.00	0.46
15	5-D	5.53	48.87	5.82	4.98	0.08	0.01	9.75	0.46
16	6-D	5.39	47.25	5.73	4.84	0.07	0.00	10.28	0.47
17	7-D	5.33	48.91	6.01	5.00	0.07	0.01	10.59	0.47
18	8-D	5.64	49.00	5.75	5.22	0.08	0.00	8.81	0.45
19	9-D	5.63	48.85	5.98	5.45	0.07	0.00	9.19	0.45
20	10-D	5.49	49.03	6.10	5.21	0.07	0.00	9.65	0.45

According to the fluorescence spectrometer x-ray (XRF) data presented in Table 1 for both clays, the clays' compositions are noticeably different. SiO_2, Al_2O_3, and CaO were found in greater concentrations in Dardha clay than in Brari clay. The higher montmorillonite concentration in Dardha clay compared to Brari clay correlated proportionately

with the higher content of these binary compounds. This conclusion fully supports the information presented by (Kola, 1986) [41].

3.1. Electron Microscope for Scanning

SEM images of natural Brari and Dardha clays were captured in order to characterize the size of the clays used for this investigation (see Figures 2 and 3).
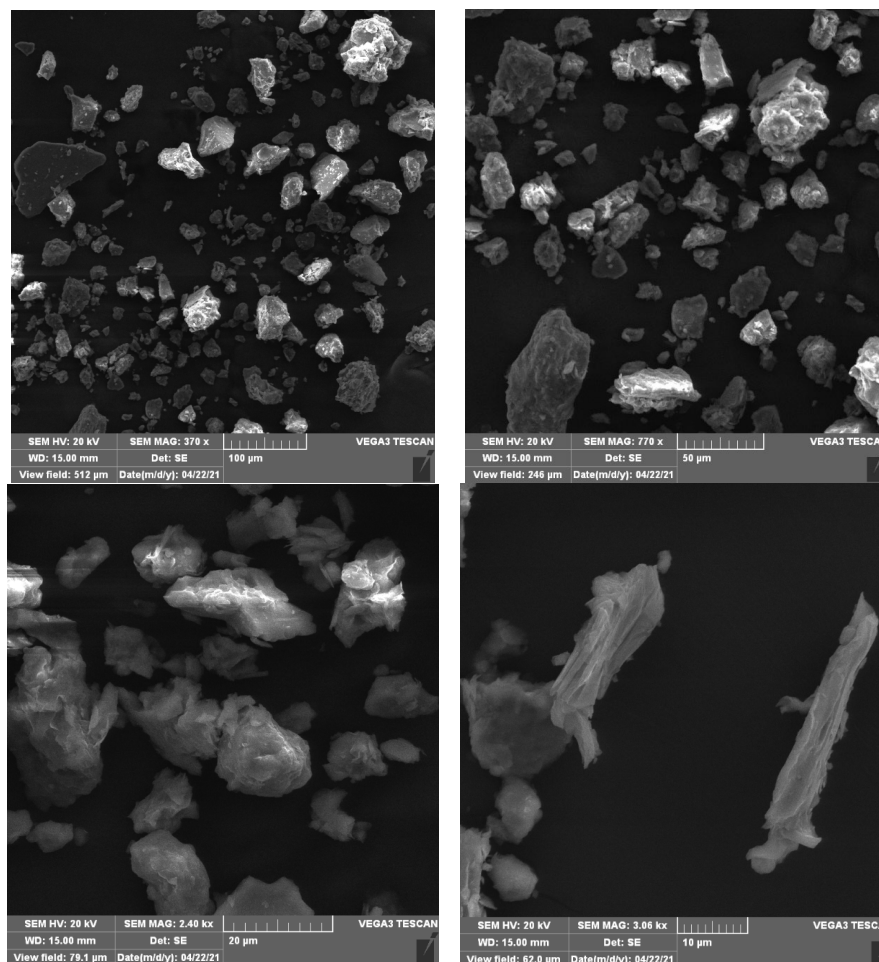

Figure 2. Brari clay images analyzed by scanning electron microscope (SEM) with resolutions of 100 μm, 50 m, 20 μm, and 10 μm.

The particle sizes of the two clays can clearly be seen to vary in the SEM images of Figures 2 and 3. Dardha clay has smaller particles than Brari clay, as seen in the SEM images of both figures, with resolutions of 100 μm, 50 μm, and 20 μm. Moreover, a prior study on these clays revealed that Dardha clay showed twice the specific surface of Brari clay. The following figures show the outcomes of the desorption process in natural Dardha and Brari clays. Benalaxyl, atrazine, dimethoate, and methomyl were all absorbed into the clay throughout the analyses, which were carried out with a gas chromatography-mass spectrometer.

The Brari clay exhibits the lowest density, surface area, and porosity (Table 2). The density and pH values are similar for the clays from Dardha and Brari, although these two clays have significant differences in surface area and porosity. This observation is consistent with the differences of the clay's respective surface areas, as shown in Table 2 (i.e., more effective adsorption for clays with higher surface areas).
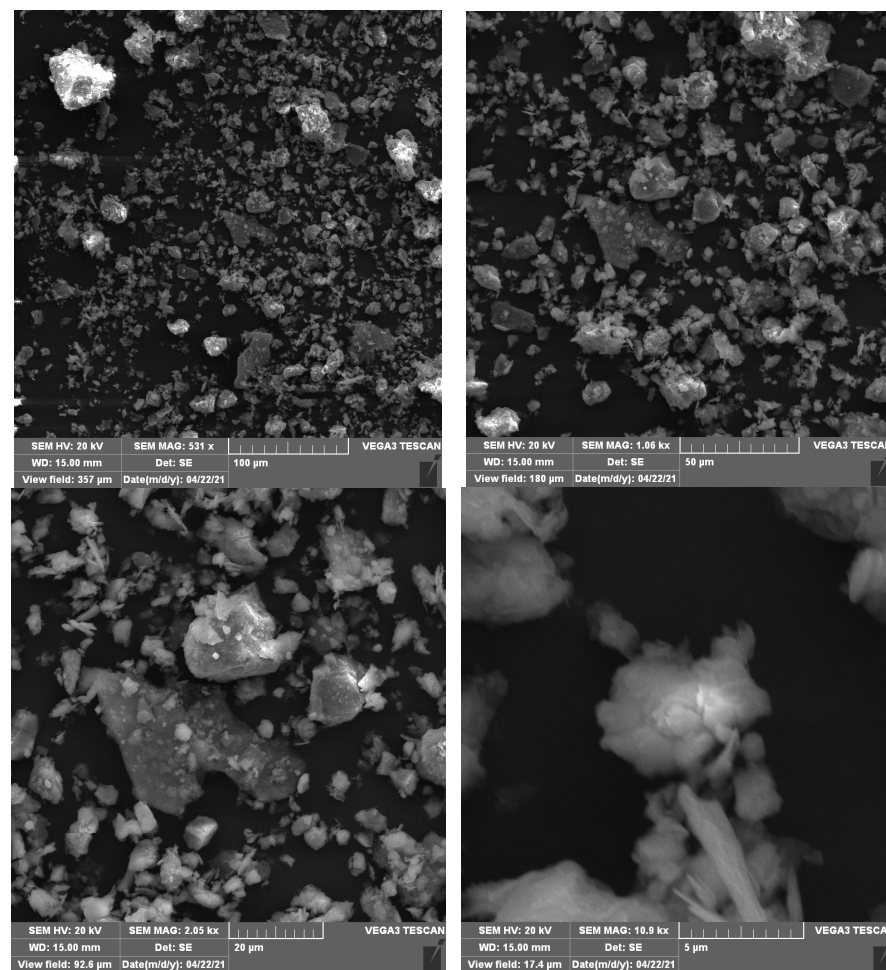
Figure 3. Dardha clay images analyzed by scanning electron microscope (SEM) with resolutions of 100 μm, 50 mm, 20 μm, and 5 μm.

Table 2. Physicochemical parameters of natural clays originating from two regions of Albania (Kledi Xhaxhiu, Erinda Prifti, and Ondřej Zitka) [42].

Region	pH	Density (g/cm^3)	Surface (m^2/g)	Porosity (%)
Brari	7.5	2.77	42	0.490
Dardha	7.6	2.78	89	0.564

Desorption, the opposite of adsorption, occurred in this investigation under identical circumstances for all pesticides from both natural and activated clays. Thus, the desorption rate of each pesticide from natural and activated clays was investigated [43]. Here are the experimental results from each pesticide's desorption procedure in its appropriate clay. The following equation is used to represent the desorption process curves in each scenario:

$$\Gamma = \beta t^{-b} \tag{1}$$

where we have: Γ = amount desorbed (mg/g); t = time (h); β = desorption coefficient for zero time (h); and $-b$ = power with values from 0 to 1 (it has a value of 0 for small concentrations and 1 for large concentrations).

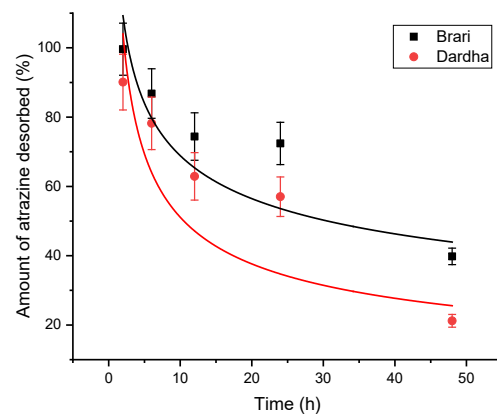Figure 4 shows the amount desorbed (%) from natural Brari and Dardha clays.

Figure 4. Desorbed amounts (%) of atrazine (25 mg/L) from Brari and Dardha clay.

The curves show that atrazine desorbed faster from Brari clay than from Dardha clay. This was expected because, as shown above, Dardha clay better adsorbed atrazine, so consequently, its desorption would be slower. As can be seen from the curve, in the first two hours of clay-water solution of atrazine contact, 99.1% of atrazine was desorbed.

The data in Figure 5 present the desorbed amounts of benalaxyl from natural Brari and Dardha clays. From the curves obtained, we can see that the desorption process of benalaxyl from Brari clay was faster than for Dardha clay. It is worth noting that the desorption process is generally faster than the adsorption process, where this process is slower.
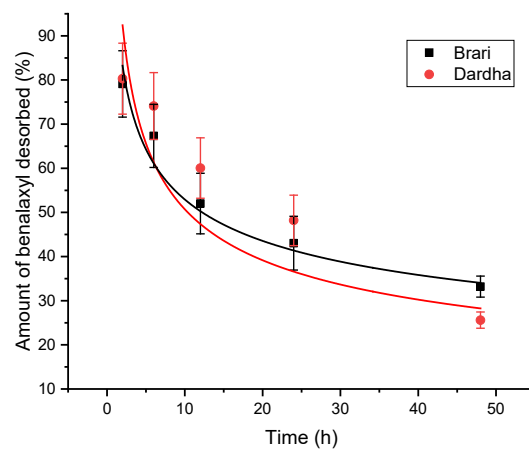

Figure 5. Desorbed amounts (%) of benalaxyl (25 mg/L) from Brari and Dardha clays.

Figure 6 graphically shows the desorption process of dimethoate and methomyl from natural Brari clay. The curves show that methomyl desorbed much faster than dimethoate from Brari clay. At the same time, the desorbed amount (in %) of methomyl was twice the amount of dimethoate desorbed from Brari clay under strictly the same conditions.

Figures 4–6 present the desorbed amounts in % of atrazine, benalaxyl, dimethoate, and methomyl from natural Brari and Dardha clays. From the curves obtained, it can be seen that in the desorption process, methomyl from Brari clay dominated, then it continued with desorption of dimethoate from Brari clay, followed by desorption of atrazine from Brari clay, desorption of benalaxyl from Brari clay, desorption of benalaxyl from Dardha clay, and finally desorption of atrazine from Dardha clay. These data comparatively reflect the desorbed amounts of all pesticides from the clays presented in the graph. Thus, Brari clay held less adsorbed pesticide than Dardha clay.
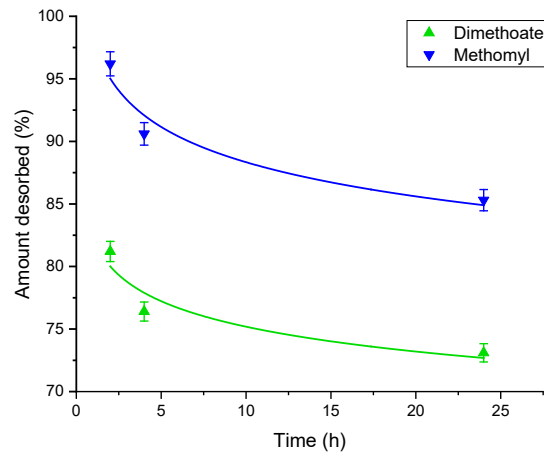
Figure 6. Desorbed amounts (%) of dimethoate and methomyl (25 mg/L) from natural Brari clay.

3.2. Kinetics of the Desorption of Pesticides from Clay

The study of the kinetics of the desorption of pesticides from clay is of particular interest because, after the adsorption process, the question immediately asked by researchers is how long (time) these pesticides will remain in the corresponding clays. The kinetics of desorption of the pesticides atrazine, benalaxyl, dimethoate, and methomyl (all at a concentration of 25 mg/L) from natural Brari and Dardha clays are presented below.

Figure 7a shows the desorption kinetics of atrazine (expressed %) at a concentration of 25 mg/L from natural Brari clay. The obtained curves show that we are dealing with a pseudo-second-order reaction with $R_2^2 = 0.9523$. The kinetics of pesticide desorption from clay is generally seen to be dominated by pseudo-second-order.
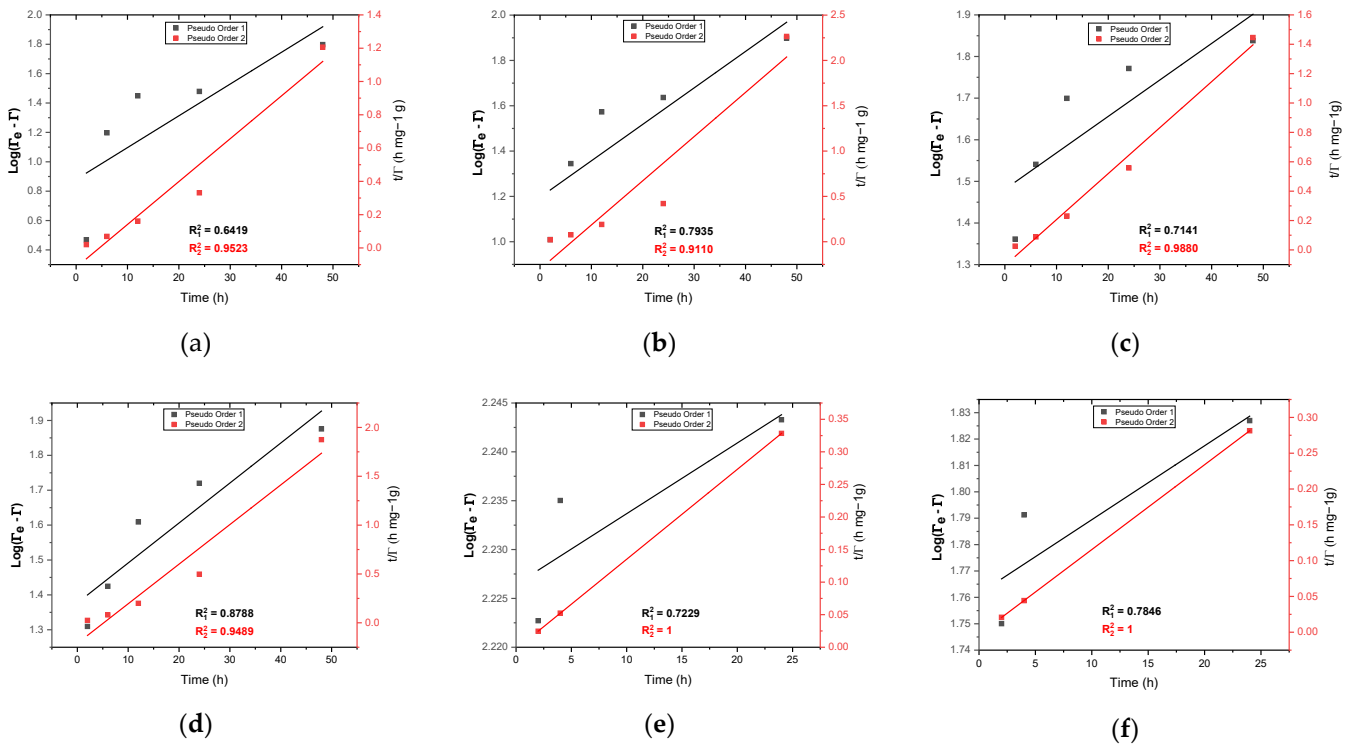

Figure 7. (**a**) Kinetics of desorption (%) of atrazine with C = 25 mg/L from natural Brari clay; (**b**) kinetics of desorption (%) of atrazine with C = 25 mg/L from natural Dardha clay; (**c**) kinetics of

desorption (%) of benalaxyl with C = 25 mg/L from natural Brari clay; (**d**) kinetics of desorption (%) of benalaxyl with C = 25 mg/L from natural Dardha clay; (**e**) kinetics of desorption (%) of dimethoate with C = 25 mg/L from natural Brari clay; and (**f**) kinetics of desorption (%) of methomyl with C = 25 mg/L from natural Brari clay. They present the kinetics of desorption (%) of atrazine, benalaxyl, dimethoate, and methomyl with C = 25 mg/L from natural Brari and Dardha clays.

The curves plotted in Figure 7b represent the desorption kinetics of atrazine at a concentration of 25 mg/L from natural Darda clay. From the data obtained and presented with the corresponding curves, it can be seen that even in this specific process, the reaction is pseudo-second order, with $R_2^2 = 0.9110$.

Below are presented the kinetics of desorption of benalaxyl at a concentration of 25 mg/L from natural Brari clay. In Figure 7c, the corresponding desorption kinetics curves are graphically presented, and it is observed that the pseudo-second-order reaction dominates, with $R_2^2 = 0.9880$.

Figure 7d shows the desorption kinetics (%) of benalaxyl at a concentration of 25 mg/L from natural Darda clay. The curves clearly show that the process obeys the pseudo-second order, with $R_2^2 = 0.9489$.

The data in Figure 7e represent the desorption kinetics (%) of dimethoate with a concentration of 25 mg/L from natural Brari clay. The curves show that the reaction is completely dominated by pseudo-second order, with, $R_2^2 = 1$.

Figure 7f shows the desorption kinetics (%) of methomyl at a concentration of 25 mg/L from natural Brari clay. It can be seen from the graph that even in this case, the reaction is pseudo-second order, with $R_2^2 = 1$.

From the data of the graphs, it can be seen that, in all cases, the desorption of all pesticides is dominated by pseudo-second-order kinetics.

4. Conclusions

The process of pesticide desorption from Brari and Dardha clays was investigated. This process was discovered to be time-efficient since, in all trials, most pesticides were desorbed during the first two hours of clay-water interaction. Based on how much the pesticides atrazine, benalaxyl, dimethoate, and methomyl were naturally desorbed from natural Brari and Dardha clays, it was discovered that atrazine was desorbed from Brari clay more quickly than from Dardha clay. In comparison to Dardha clay, even benalaxyl desorbed more quickly from Brari clay. Compared to dimethoate, methomyl desorbed more quickly from Brari clay. The results from research on the desorption of various pesticides in water may be utilized for a variety of informational and practical applications, such as tracking the destiny of adsorbed pesticides or using adsorbents impregnated with pesticides in farming. This method of operation is suitable in many nations and would ease the management and application of pesticides. While most researchers are interested in how long (in time) clays can retain adsorbed pesticides, investigating the desorption kinetics of these pesticides in natural Brari and Dardha clays is an important addition. The researched adsorbents have minimal economic costs when used in large quantities. However, conducting the related visibility analysis for each situation is still advisable. In addition to the numerous studies that have been conducted and are currently being conducted in the direction of preserving the environment where we live, we believe that our study on the topic of using the adsorbents mentioned above for the purification of waters loaded with pesticides will make a modest contribution in this field. We will continue to make an effort to ensure that our intellectual and professional dedication is intimately tied to the numerous issues that call for a clean and healthy environment.

References

1. Vaikosen, E.N.; Davidson, C.M.; Olu-Owolabi, B.I.; Gibson, L.T.; Agunbiade, F.O.; Kashimawo, A.J.; Adebowale, K.O. Kinetic and isotherm studies on the adsorption–desorption of technical-grade endosulfan in loamy soils under *Theobroma cacao* L cultivation, Southwestern Nigeria. *Environ. Sci. Adv.* **2023**, *2*, 257–277. [CrossRef]
2. Rojas, R.; Repetto, G.; Morillo, J.; Usero, J. Sorption/Desorption and Kinetics of Atrazine, Chlorfenvinphos, Endosulfan Sulfate and Trifluralin on Agro-Industrial and Composted Organic Wastes. *Toxics* **2022**, *10*, 85. [CrossRef] [PubMed]
3. Li, W.; Shan, R.; Fan, Y.; Sun, X. Effects of tall fescue biochar on the adsorption and desorption of atrazine in different types of soil. *Environ. Sci. Pollut. Res.* **2021**, *28*, 4503–4514. [CrossRef] [PubMed]
4. Lizethly, C.-J.; Rodríguez-Becerra, J.; Garrido, C.; Escudey, M.; Barrientos, L.; Parra-Rivero, J.; Domínguez-Vera, V.; Loch-Arellano, B. Study of Sorption Kinetics and Sorption–Desorption Models to Assess the Transport Mechanisms of 2,4-Dichlorophenoxyacetic Acid on Volcanic Soils. *Int. J. Environ. Res. Public. Health* **2021**, *18*, 6264.
5. Ahmad, K.S.; Rashid, N.; Azhar, S. Adsorption and desorption characteristics of chlorosulfuron in selected minerals and Pakistani soils. *EJSS* **2016**, *5*, 1. [CrossRef]
6. Srivastava, A.; Chandra, R.; Srivastava, P.C. Kinetics of sorption-desorption of benfuracarb insecticide in mollisols. *Pest Manag. Sci.* **2011**, *67*, 209–212. [CrossRef]
7. Otero, R.; Fernández, J.M.; González, M.A.; Pavlovic, I.; Ulibarri, M.A. Pesticides adsorption–desorption on Mg–Al mixed oxides. Kinetic modeling, competing factors and recyclability. *Chem. Eng. J.* **2013**, *221*, 214–221. [CrossRef]
8. Torrents, A.; Jayasundera, S. The sorption of nonionic pesticides onto clays and the influence of natural organic carbon. *Chemosphere* **1997**, *35*, 1549–1565. [CrossRef]
9. Lima, D.L.D.; Schneider, R.J.; Scherer, H.W.; Duarte, A.C.; Santos, E.B.H.; Esteves, V.I. Sorption−Desorption Behavior of Atrazine on Soils Subjected to Different Organic Long-Term Amendments. *J. Agric. Food Chem.* **2010**, *58*, 3101–3106. [CrossRef]
10. Chorover, J.; Brusseau, M.L. Kinetics of Sorption—Desorption. In *Kinetics of Water-Rock Interaction*; Brantley, S.L., Kubicki, J.D., White, A.F., Eds.; Springer: New York, NY, USA, 2008; pp. 109–149.
11. DeSutter, T.M.; Clay, S.A.; Clay, D.E. Atrazine Sorption and Desorption as Affected by Aggregate Size, Particle Size, and Soil Type. *Weed Sci.* **2003**, *51*, 456–462. [CrossRef]
12. Young, H.A.; Mills, P.K.; Riordan, D.G.; Cress, R.D. Triazine Herbicides and Epithelial Ovarian Cancer Risk in Central California. *J. Occup. Environ. Med.* **2005**, *47*, 1148–1156. [CrossRef]
13. Singh, A.K.; Cameotra, S.S. Adsorption and Desorption Behavior of Chlorotriazine Herbicides in the Agricultural Soils. *J. Pet. Environ. Biotechnol.* **2013**, *4*, 154. [CrossRef]
14. Cortez, A.O.; Das Chagas, P.S.F.; Silva, T.S.; Silva, D.V.; Freitas, C.D.M.; Pamplona, J.d.P.; De Mesquita, H.C.; Souza, M.d.F. Sorption and desorption of ametryn in different types of soils. *Biosci. J.* **2019**, *35*, 1718–1787. [CrossRef]
15. Morton, P.A.; Fennell, C.; Cassidy, R.; Doody, D.; Fenton, O.; Mellander, P.-E.; Jordan, P. A review of the pesticide MCPA in the land-water environment and emerging research needs. *WIREs Water* **2020**, *7*, e1402. [CrossRef]
16. Gupta, R.K.; Abrol, I.P.; Finkl, C.W.; Kirkham, M.B.; Arbestain, M.C.; Macías, F.; Chesworth, W.; Germida, J.J.; Loeppert, R.H.; Cook, M.G.; et al. Solute Sorption-Desorption Kinetics. In *Encyclopedia of Soil Science*; Chesworth, W., Ed.; Springer: Dordrecht, The Netherlands, 2008; pp. 739–744.
17. Yu, H.; Liu, Y.; Shu, X.; Fang, H.; Sun, X.; Pan, Y.; Ma, L. Equilibrium, kinetic and thermodynamic studies on the adsorption of atrazine in soils of the water fluctuation zone in the Three-Gorges Reservoir. *Environ. Sci. Eur.* **2020**, *32*, 27. [CrossRef]
18. Farcasanu, R.I.; Yamaguchi, T.; Moldrup, P.; Jonge, L.W.D.; Fukushima, T. Kinetics of Simazine Sorption on Soils and Soil Particle Size Fractions. *Soils Found.* **1999**, *39*, 143–149. [CrossRef]
19. Muendo, B.M.; Shikuku, V.O.; Getenga, Z.M.; Lalah, J.O.; Wandiga, S.O.; Rothballer, M. Adsorption-desorption and leaching behavior of diuron on selected Kenyan agricultural soils. *Heliyon* **2021**, *7*, e06073. [CrossRef]
20. Morillo, E.; Undabeytia, T.; Cabrera, A.; Villaverde, J.; Maqueda, C. Effect of Soil Type on Adsorption−Desorption, Mobility, and Activity of the Herbicide Norflurazon. *J. Agric. Food Chem.* **2004**, *52*, 884–890. [CrossRef]
21. Shariff, R.M. Adsorption—Desorption of Metolachlorand 2,4-D on Agricultural Soils. *Int. J. Sci. Eng. Res.* **2011**, *2*, 1–11.

22. Caceres-Jensen, L.; Rodriguez-Becerra, J.; Escudey, M.; Joo-Nagata, J.; Villagra, C.A.; Dominguez-Vera, V.; Neira-Albornoz, A.; Cornejo-Huentemilla, M. Nicosulfuron sorption kinetics and sorption/desorption on volcanic ash-derived soils: Proposal of sorption and transport mechanisms. *J. Hazard. Mater.* **2020**, *385*, 121576. [CrossRef]

23. Boivin, A.; Cherrier, R.; Schiavon, M. Bentazone adsorption and desorption on agricultural soils. *Agron. Sustain. Dev.* **2005**, *25*, 309–315. [CrossRef]

24. Kumar, M.; Philip, L. Adsorption and desorption characteristics of hydrophobic pesticide endosulfan in four Indian soils. *Chemosphere* **2006**, *62*, 1064–1077. [CrossRef] [PubMed]

25. Shariff, R.M.; Hassan, M.A. Kinetic Study of Adsorption-Desorption of Simazine on Agricultural Soils. *Int. J. Eng. Res. Dev.* **2012**, *4*, 1–9.

26. Li, X.; Grey, T.; Price, K.; Vencill, W.; Webster, T. Adsorption, desorption and persistence of fomesafen in soil. *Pest Manag. Sci.* **2019**, *75*, 270–278. [CrossRef]

27. Ahmad, K.S. Sorption-Desorption Characteristics of Benzimidazole Based Fungicide Benomyl on Physicochemical Properties of Selected Pakistani Soils and their Minerals: Fungicide Characteristics on Soil. *Biol. Sci. PJSIR* **2018**, *61*, 59–67. [CrossRef]

28. Masini, J.C.; Abate, G. Guidelines to Study the Adsorption of Pesticides onto Clay Minerals Aiming at a Straightforward Evaluation of Their Removal Performance. *Minerals* **2021**, *11*, 1282. [CrossRef]

29. Liu, C.; Zachara, J.M.; Smith, S.C.; McKinley, J.P.; Ainsworth, C.C. Desorption kinetics of radiocesium from subsurface sediments at Hanford Site, USA. *Geochim. Cosmochim. Acta* **2003**, *67*, 2893–2912. [CrossRef]

30. Kudlejova, L.; Risticevic, S.; Vuckovic, D. 7—Solid-Phase Microextraction Method Development. In *Handbook of Solid Phase Microextraction*; Pawliszyn, J., Ed.; Elsevier: Oxford, UK, 2012; pp. 201–249.

31. Zhang, Y.; Meng, Y.; Liu, H.; Yang, M. First-principles study of water desorption from montmorillonite surface. *J. Mol. Model* **2016**, *22*, 105. [CrossRef]

32. Srinivasan, R. Advances in Application of Natural Clay and Its Composites in Removal of Biological, Organic, and Inorganic Contaminants from Drinking Water. *Adv. Mater. Sci. Eng.* **2011**, *2011*, e872531. [CrossRef]

33. Ewis, D.; Ba-Abbad, M.M.; Benamor, A.; El-Naas, M.H. Adsorption of organic water pollutants by clays and clay minerals composites: A comprehensive review. *Appl. Clay Sci.* **2022**, *229*, 106686. [CrossRef]

34. Soliman, E.S.; Hassan, R.A.; Farid, D.S. The efficiency of natural-ecofriendly clay filters on water purification for improving performance and immunity in broiler chickens. *Open Vet. J.* **2021**, *11*, 483–499. [CrossRef]

35. Undabeytia, T.; Shuali, U.; Nir, S.; Rubin, B. Applications of Chemically Modified Clay Minerals and Clays to Water Purification and Slow Release Formulations of Herbicides. *Minerals* **2021**, *11*, 9. [CrossRef]

36. ElBastamy, E.; Ibrahim, L.A.; Ghandour, A.; Zelenakova, M.; Vranayova, Z.; Abu-Hashim, M. Efficiency of Natural Clay Mineral Adsorbent Filtration Systems in Wastewater Treatment for Potential Irrigation Purposes. *Sustainability* **2021**, *13*, 5738. [CrossRef]

37. Awasthi, A.; Jadhao, P.; Kumari, K. Clay nano-adsorbent: Structures, applications and mechanism for water treatment. *SN Appl. Sci.* **2019**, *1*, 1076. [CrossRef]

38. Moreno-Maroto, J.M.; Alonso-Azcárate, J.; O'Kelly, B.C. Review and critical examination of fine-grained soil classification systems based on plasticity. *Appl. Clay Sci.* **2021**, *200*, 105955. [CrossRef]

39. Bergaya, F.; Lagaly, G. Chapter 1 General Introduction: Clays, Clay Minerals, and Clay Science. In *Developments in Clay Science*; Elsevier: Amsterdam, The Netherlands, 2006; Volume 1, pp. 1–18.

40. Fortnum, K. Where Does Clay Come From? Available online: https://www.katherinefortnumceramics.com/post/where-does-clay-come-from (accessed on 1 April 2023).

41. Behrami, E.; Xhaxhiu, K.; Dragusha, B.; Reka, A.; Hajrulai-Musliu, Z.; Berisha, A.; Andoni, A.; Hamiti, X.; Drushku, S. Study of absorption and desorption of benalaxyl from natural and activated brari and dardha clay. *Int. J. Ecosyst. Ecol. Sci.* **2021**, *11*, 545–556. [CrossRef]

42. Xhaxhiu, K.; Prifti, E.; Zitka, O. A case study of methomyl removal from aqueous solutions by four natural Albanian clays. *Remediat. J.* **2020**, *30*, 89–100. [CrossRef]

43. Behrami, E.; Xhaxhiu, K.; Dragusha, B.; Reka, A.; Andoni, A.; Hamiti, X.; Drushku, S. The Removal of Atrazine and Benalaxyl by the Fly Ash Released from Kosovo A Power Plant. *Int. J. Anal. Chem.* **2022**, *2022*, 9945199. [CrossRef]