INTRODUCTION

Many physical and chemical characteristics, as well as the soil’s nutritional status, can be impacted by composition and relative content. The parent material, climate, and micro-topography all impact clay minerals’ composition and relative concentration. Moreover, the mineral make-up of clay varies according to pedogenesis (Ouyang et al. 2021). It has been suggested that the aforementioned characteristics serve as the cornerstone for the socioeconomic growth and sustainability of small-scale and artisanal clay mining industries in emerging nations (Diko-Makia and Ligege 2020). Clays are widely distributed in practically every nation (Singh 2022). Clay minerals rank among the world’s most significant and practical industrial minerals. Clay minerals play a significant role in the building since they are a key component of brick and tile. Clay minerals are used in process industries depending on their physical and chemical characteristics (Aboudi Mana, Hanafiah, and Chowdhury 2017). These minerals have a platy morphology due to the arrangement of their atoms in their structure. Clay minerals may be divided into three groups according to their sheet arrangements: 1:1, 2:1, and 2:1:1 (Massaro et al. 2018). The most researched clays are kaolin and bentonite, which have 2:1 and 1:1 structural ratios, respectively. These clays’ structures and their chemical composition, granulometric distribution, swelling capacity, morphology, plasticity, resistance, and cation-exchange capacity may all be used to characterize the engineering features being sought. In this sense, the clay’s purity level is a crucial characteristic for various applications. On the other hand, clay’s mineralogical standard makes it more useful for a certain purpose (Silva-Valenzuela et al. 2013). Chin C L used a field emission scanning electron microscope to do a chemical analysis utilizing a multi-dispersive X-ray fluorescence approach as well as more in-depth analyses employing grain size distribution, dilatometry, and microstructure study of clay shape before and after burning.
(FESEM Zeiss, Supra TM 350 VP). Using SEM, the morphology of the burned samples was investigated (Hitachi TM3000) (Yanti and Pratiwi 2018). Natural occurring minerals like clay and clay minerals serve crucial roles in preserving the ecosystem. Clay is made of unprocessed minerals and has various morphologies and geometries. These clay minerals have been utilized for cleaning up contaminated water as well as for the storage and disposal of dangerous compounds. Clay is employed as a nano-adsorbent in numerous adsorption procedures due to its distinct characteristics and high removal effectiveness. Nano-clays have been proven to be a very effective and efficient property enhancer for water purification. The solubility of the substance in water is crucial, and the word “solubility” refers to the chemical interaction or activity of the solute and water. The adsorption of compounds from water depends on two types of mechanisms: hydrophobic and hydrophilic. It implies that a material with high hydrophilicity reduces adsorption and vice versa. The key component of this process is the driving force that lowers the surface tension between the matrix and the solid adsorbed (Awasthi, Jadhao, and Kumari 2019). Water treatment has grown to be a significant global business. Wastewater treatment, industrial process water treatment, and potable water treatment are this sector’s three main application categories (Beall 2003). Although hazardous waste is still being released by industrial sectors, the issue is getting worse (Ewis et al. 2022). Pesticides, heavy metals, and pathogens are just a few of the contaminants constantly contaminating our environment’s water. The fast rise of industrial and agricultural operations, as well as artificial and human activities that led to increased pollution and contamination of water resources, have posed serious difficulties to the availability of clean water for drinking and planting in recent years (Soliman, Hassan, and Farid 2021). Due to their tiny particle size, specific surface area, high efficiency, high adsorption capacity, and diagenetic processes, clay minerals provide good natural barriers (which cause high natural density). They can also seal cracks and fissures (which may form paths for leachates). Moreover, because of their chemical reactivity, significant pollutants can be immobilized (ElBastamy et al. 2021). Nanomaterials with high surface-to-volume ratios and high aspect ratios have also been investigated for their possible use in water treatment technologies, in addition to clay ceramics. Due to their special features, nanomaterials are useful as antibacterial agents, adsorbents, and photocatalysts. TiO$_2$, carbon nanotubes, halloysite nano clays, Fe$_3$O$_4$, and other nanomaterials may improve the effectiveness of currently used water treatment systems in cleaning up contaminated water bodies. According to a recent study, Halloysite nanotubes may have a future in water treatment technology Aluminosilicate clay minerals called halloysite nanocatalysts have tubular shapes and distinctive surface charge properties, making them promising adsorbents for water contaminants (Annan et al. 2018). It is anticipated that the cost of production will be minimal, making membrane purifiers accessible, provided easily available natural materials and a straightforward manufacturing process are used to create the purification membranes. Natural raw materials with porous microstructures and adsorption capabilities, such as clay minerals, natural zeolites, volcanic glasses, diatomite, and other plentiful silicate minerals, present an opportunity to produce low-cost, low-tech, effective products as compared to alternative beginning materials (Ajenifuja et al. 2012; Hnamte and Pulikkal 2022). Chemical and biological pollutants are the two different types of water contaminants. Inorganic and organic pollutants are subcategories of chemical pollutants. Due to their extensive usage in contemporary agriculture, pesticide levels in water have skyrocketed. The kind of pesticide and the effectiveness of the treatment procedure determine the best water treatment technique for removing pesticides. Adsorption is a well-known, inexpensive water filtration technique that has shown to be quite successful in removing some of the ecologically harmful and socially upsetting impurities. Due to their extensive usage in contemporary agriculture, pesticide levels in water have skyrocketed. The kind of pesticide and the effectiveness of the treatment procedure determine the best water treatment technique for removing pesticides. Adsorption is a well-known, inexpensive water filtration technique that has shown to be quite successful in removing some of the ecologically harmful and socially upsetting impurities (Undabeytia et al. 2021). Clays significantly impact the environment because they operate as natural scavengers of contaminants by absorbing cations and anions through ion exchange,
adsorption, or a combination of the two. Consequently, exchangeable cations and anions held to the surface are always present in clays. Clay surfaces include the following notable cations and anions: Ca$^{2+}$, Mg$^{2+}$, H$^+$, K$^+$, Na$^+$, Cl$^-$, and NO$_3^-$ (Srinivasan 2011). Many organochlorine insecticides and their metabolites are extremely toxic. They have been linked to a variety of harmful health outcomes, including cancer, neurological damage, abnormalities of the reproductive system, congenital disabilities, and immune system damage. They are difficult to degrade in the environment because of their resistance to chemical, physical, microbiological, and biological processes, which increases their environmental significance. Some areas have water that is unsafe to drink because of the high levels of pesticides present. Clay-based adsorbents’ surface charges affect how pesticides are absorbed by them (Fosu-Mensah et al. 2016; Srivastava et al., n.d.; Saleh, Zouari, and Al-Ghouti 2020). Because it uses inexpensive components, including biomaterials, aluminum, iron oxides, oxyhydroxides, zeolites, and clay minerals, adsorption is one of the most effective approaches for preventing or removing pesticide contamination (Masini and Abate 2021; M. Wang and Phillips 2019). These chlorophenol substances are persistent in nature and are frequently found in soils, ponds, and rivers. Hexachlorocyclohexanes like lindane are frequently used to treat pediculosis and scabies. It tends to bioaccumulate in the food chain since it is durable and inert.

The environment of the soil and pesticides

The problem of soil accumulation is made worse by the frequent and indiscriminate use of pesticides. Spray-applied pesticides must undergo several steps of degradation, transport, and adsorption/desorption before they may be used. Many factors, including microflora and soil properties, affect each of these phases (Hussain, Hussain, and Ahmed 2009; Weber 2004). The bioavailability, degradation, and effects of pesticides on soil microorganisms are all influenced by a number of environmental factors in addition to the timing, concentration, and toxicity of the pesticides used (Murage et al. 2011). The texture of the soil, the presence of organic materials, the presence of plants, and cultural practices are a few examples.

Pesticides in water

Pesticides containing organophosphorus (OP) are extensively utilized around the world and are crucial to the advancement of agricultural goods. Nonetheless, the environment has been significantly impacted by the direct or indirect release of agricultural effluent and wastewater from the manufacture of pesticides. Dimethoate, one of the typical OPs, is often found in groundwater and surface water in China at concentrations ranging from ng/L to mg/L (Gao et al. 2009; Beasley et al. 2002). Dimethoate inhibits acetylcholinesterase in humans, which can result in mutagenic, teratogenic, and carcinogenic effects as well as problems with the nervous system (M.-C. Wang et al. 2006; Lu et al. 2020). Thus, research on removing dimethoate from water bodies is urgently needed. Producers and researchers are developing novel pesticide formulations to address the demand for these chemicals internationally. The pesticides used should, in theory, be reasonably biodegradable, environmentally safe, and solely detrimental to the creatures they are intended to affect (Rosell et al. 2008). Studies have shown that although the pesticide concentrations in the Spanish Llobregat River basin were below the EU’s environmental quality criteria, they nevertheless posed a low to high ecotoxicological risk to aquatic life, particularly algae and macro-invertebrates (Köck-Schulmeyer et al. 2012; Satyavani et al. 2011). Pesticides in natural water can have adverse effects even in acceptable quantities. Expired pesticides should be properly disposed of to prevent harming aquatic life when released into rivers. This is due to the possibility that expired pesticides might change the pH of the water and cause severe fish poisoning.

MATERIAL AND METHODS

Participants in this study included the Food and Veterinary Agency (FVA), the Agricultural Institute of Kosovo, the Faculty of Natural Sciences at the University of Tirana (FSHN-UT), the Faculty of Agriculture and Veterinary at the University of Pristina (“HASAN PRISHTINA”), and the Faculty of Mathematical Sciences at the University of Tetovo (“FMNS-UT”). The substances and solvents employed in the experiment were ethyl acetate, dichloromethane, absolute ethanol, dibutyl phthalate, technical ethanol, sodium chloride,
and sodium sulfuric acid. An electronic centrifuge from Hermle, model Z 206A, an electromagnetic mixer from ISOLAB, VELP SCIENTIFIC, and DIAB, as well as analytical scales from Chyo, model JS-110, with a maximum weight of 110 g and a d = 0.0001 g, are among the tools used. The clay samples were gathered from Dardh (Korca) and Brari, two different areas in Albania (Tirana). Clays were ground, sieved, and powdered. In each case, 1.5 µm was the chosen fraction. The recovered fractions were dried at 150 °C for four hours before being put in plastic bottles that were securely sealed. The working technique was verified using the following examples after doing multiple experiments to arrive at the final method: In order to extract dimethoate from its aqueous solutions, a mixture of ethyl acetate and dichloromethane (1: 3, vw) was used as the extraction solvent. Dimethoate extraction was made in each case using solvent extraction from 5 mL. Due to the clay’s planar structure, dibutyl phthalate (DBF), which was initially introduced to the solution at the beginning of the extraction procedure as an internal standard, was concurrently adsorbed with dimethoate, changing the adsorption results. To avoid competing with dimethoate for adsorption, it was added later in the process, after the clay had been centrifuged. However, even in these cases, we observed considerable variances in the results. The best outcomes were ultimately obtained by isolating the organic extract from the dimethoate aqueous solution and then adding the internal standard (DBF). Sodium chloride (NaCl) was used as an anti-emulsifier throughout the extraction process to avoid the production of emulsions. Standard solutions of the dimethoate (96%) and internal standard DBF (99.5%) were used in the GC-FID analysis up until the creation of the optimal operating conditions. According to the study, neither clay exhibited any sign of dimethoate adsorption between hours 2 and 24. As a result, more research was done at extended time points between 24 and 72 hours. (Behrami, Xhaxhiu, Dragusha, Berisha, et al. 2021; Behrami, Xhaxhiu, Dragusha, Reka, et al. 2021b) The detector and injection temperatures were adjusted to 290.1°C, the column operating temperature was 277.1°C, and the head pressure was 214.7 kPa.

**RESULTS AND DISCUSSION**

**Brari and Dardha clay X-ray (XRF) analysis**

The compositions of both clays are noticeably different, as shown by the Fluorescence Spectrometer X-Ray (XRF) measurements shown in Table 1. SiO₂, Al₂O₃, and CaO are present in greater quantities in Dardha clay than in Brari clay. When compared to Brari clay, the higher montmorillonite content of Dardha clay is negatively correlated with the bigger number of these binary compounds.

**SEM-EDX method elemental analysis of Brari clay**

The Brari clay (Tirana), which I used for this experiment, was originally subjected to
SEM-EDX analysis to understand the topography of the clay and its composition. The natural clay from Brari (Tirana) is seen in the SEM-EDX images that are presented below. Basic details on the percentage composition of the clay in Brari are shown in Table 2 and Figure 1 (Spectrum 1), where it is evident that this clay is predominantly made up of oxygen (52.16%), silicon (17.55%), aluminum (11.16%), potassium (9.75%), and iron (5.35%), with lower quantities of other elements. Brari clay is seen in this SEM picture with resolutions of 10 µm. The SEM pictures of Brari clay in Figure 2 show changes in particle size and shape. SEM images with a resolution of 10 µm show that Brari clay is composed of particles with an elongated morphology. The clay is thought to be a great adsorbent and has a large specific surface area, according to past studies. (Xhaxhiu et al. 2020; Behrami et al. 2021b).

To understand the composition and topography of the clay, which I used for this study, and to describe the particle size of Dardha (Korça) clay, I first did the SEM-EDX Analysis. Table 3 and Figure 3 (Spectrum 1) provide basic information on the percentage composition of Dardha clay, showing that it is primarily made up of oxygen (62.63%), carbon (15.12%), calcium (8.99%), magnesium (7.31%), silica (3.49%), aluminum (1.41%), and sodium (1.05%), with other elements making up a minor portion of the clay. The images of Dardha clay are then displayed using the SEM technique, with discoveries beginning at a distance of 5 µm. Images of Dardha Clay show significant differences in particle size Figure 4. Dardha clay has smaller particles than Brari clay, as can be seen by comparing SEM pictures with resolutions of 5 µm and 10 µm. Moreover, a prior study on these clays (Behrami et al. 2021) discovered that the specific surface area of Dardha clay might be up to twice as large as that of Brari clay.

<table>
<thead>
<tr>
<th>Table 1. Composition information for the Brari and Dardha clays</th>
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<tbody>
<tr>
<td>Type of clay</td>
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<tr>
<td>Brari</td>
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<td>Dardha</td>
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<th>Table 2. Basic quantitative and analytical data pertaining to Brari clay (SEM-EDX) (Spectrum 1)</th>
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<tr>
<td>Element</td>
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<tr>
<td>C</td>
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<td>O</td>
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<td>Mg</td>
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<tr>
<td>Al</td>
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<tr>
<td>Si</td>
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<tr>
<td>K</td>
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<tr>
<td>Fe</td>
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<tr>
<td>Total</td>
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</tbody>
</table>

Figure 1. Shows a typical spectrum for elementary-quantitative Brari clay identification with a resolution of 20 µm, (Spectrum 1)
Clay from Brari and Dardha studied by GC/MS

The investigation of Dardha and Brari on dimethoate adsorption in clay. An instrument called a gas chromatography-mass spectrometer was used for the studies. Figures 5 and 6 depict the results of the Dimethoate adsorption process in both natural Dardha and Brari clays, with an initial concentration of 25 mg/L. It is clear from the data in Figures 5 and 6 that different amounts of dimethoate have been absorbed into the native clays of Brari and Dardha. Figure 5 displays the quantities (mg/g) of dimethoate adsorbed on brari clay with a contact time between the two materials varying from 24 to 120 hours. As shown in Figure 5, dimethoate is adsorbed in Brari clay at a rate of 1.96 mg/g after 24 hours and 0.612 mg/g after 120 hours. As a result, the clay loses its capacity to absorb chemicals over time. As a result of the clay’s contact surface becoming saturated, dimethoate can no longer be supported, in accordance with our theory. Figure 5 depicts the temporal ratio of the amount of dimethoate adsorbed in Brari clay, which can be shown to be skewed between 24 and 120 hours. This exemplifies what was previously mentioned. As a result, less is adsorbed over time.

Dimethoate is adsorbed in levels ranging from 1.26 mg/g for 24 hours to 0.39 mg/g for 120 hours, as shown in Figure 6. These numbers demonstrate that when compared to Brari clay, Dardha clay adsors less dimethoate. Even said, Dardha clay has a greater contact surface and has demonstrated a higher potential for some other pesticides to bind to its surface.

The values of the adsorbed quantities of dimethoate in both clays are shown in Figure 2.

<table>
<thead>
<tr>
<th>Element</th>
<th>% by weight</th>
<th>% atomic</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>15.1</td>
<td>21.26</td>
</tr>
<tr>
<td>O</td>
<td>62.6</td>
<td>66.12</td>
</tr>
<tr>
<td>Na</td>
<td>1.05</td>
<td>0.77</td>
</tr>
<tr>
<td>Mg</td>
<td>7.31</td>
<td>5.08</td>
</tr>
<tr>
<td>Al</td>
<td>1.41</td>
<td>0.88</td>
</tr>
<tr>
<td>Si</td>
<td>3.49</td>
<td>2.10</td>
</tr>
<tr>
<td>Ca</td>
<td>8.99</td>
<td>3.79</td>
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<tr>
<td>Total</td>
<td>100.00</td>
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Figure 2. The results of SEM analysis using pictures of Brari clay with a resolution 10 µm

Figure 3. A typical spectrum for elementary-quantitative Dardha clay identification with a resolution of 20 µm, (Spectrum 1)
where it can be observed that the adsorbed amounts rise as the dimethoate concentration rises. Figure 7 illustrates that even these findings demonstrate that Brari clay adsorbs more dimethoate than Dardha clay.

**Process of desorption**

Desorption is often characterized by an initial quick pace followed by a significantly slower approach to an apparent equilibrium. Desorption was slower than sorption (Shariff 2011). 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 (Caceres-Jensen et al. 2020). Knowing these processes is crucial to correctly estimate the mobility and destiny of these compounds in the subsurface since adsorption-desorption events greatly influence pesticide behavior in soil (Boivin, Cherrier, and Schiavon 2005). In comparison to neutral pH, desorption was more pronounced in both acidic and alkaline pH levels (Kumar and Philip 2006). Failure to attain equilibrium during desorption may be the cause of the appearance of irreversibility or hysteresis (Shariff and Hassan, n.d.). To prevent unacceptably severe crop damage, additional information is required to forecast its soil adsorption and desorption, bioavailability, and permanence (Li et al. 2019). 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 the soil (Ahmad 2018). Fantastic reviews analyzed the interactions between organic chemicals and clay minerals recently with the goal of creating formulations for controlled-release herbicides and water purification (Masini and Abate 2021). 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 (Liu et al. 2003). The eluent composition (often the mobile phase) and flow rate affect dynamic desorption efficiency. Dynamic desorption might not be able to completely desorb all of the analyte in an acceptable length of time due to the sluggish kinetics of the desorption process. This means that to sweep the desorbed analytes into the analytical column, static desorption for a predetermined period of time is frequently utilized, followed by a quick dynamic desorption phase (Kudlejova et al. 2012). Based on the calculated activation energies, the temperature dependency of the water adsorption and desorption rates was compared. 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 stability of water conformers throughout the desorption process (Zhang et al. 2016). Desorption, which is the opposite of adsorption, took place in this investigation under identical conditions (as in the adsorption process) for dimethoate from the natural clay of Brari and Dardha. Thus, the desorption rate (%) of dimethoate from natural clays was investigated (Behrami et al. 2022b). Below are the experimental results from the dimethoate desorption procedure and we have used the following equation to represent the desorption process curves.

\[ \Gamma = \beta t^{-b} \]
Desorption of dimethoate from natural clays of Brari and Dardha

Figure 8 graphically shows the desorption process of dimethoate from the natural clay of Brari and Dardhe. The curves show that dimethoate desorption was 96.2% from pear clay in the first two hours, while 81.2% from Brari clay in the same time. So, at the same time, 15% more dimethoate is desorbed from the Dardha clay compared to the Brari clay.

CONCLUSIONS

Only one extraction is sufficient, thus in the research for this study, we performed three series of extractions, i.e., we performed three extractions in each aqueous sample, and then we mixed the reaction for 20 minutes, 15 minutes, and 10 minutes, respectively. The extraction was done in a tiny volume (3.3 ml of solvent Ethyl acetate + dichloromethane) to make sure the end volume is as small as is practical and has a concentration that can be easily assessed by gas chromatography. We saw a decrease in the amount of dimethoate adsorbed between 24 and 120 hours of the clay and water interaction, which initially lasted between 24 and 120 hours. We saw a significant decrease in the amount of dimethoate adsorbed in both clays after 120 hours of contact. Due to the saturation of the clays’ active surfaces, the quantity has decreased. When the concentration of dimethoate in aqueous solutions rises, we have shown that the amount of dimethoate adsorbed on clay likewise rises.

Based on the study carried out and the concrete results obtained experimentally and elaborated theoretically, we can say that the use of natural clays as an adsorbent for the purification of water polluted by pesticides represents a good real possibility and is feasible in practice. The desorption process of dimethoate from Brari and Dardha clays was also studied, from which it turned out that this process was fast in terms of time, because in all experiments, in any case, the largest amount of dimethoate is desorbed in the first two hours of clay-water contact.

The results obtained from the study of the desorption of dimethoate in water can be used for certain information and various practical purposes, for example, to follow the fate of adsorbed pesticides, or in the use of adsorbents impregnated with pesticides in agriculture, which would simplify the control and technique of using pesticides, in many countries this way of working is applicable. The adsorbents that I have studied, the natural clays, I think can be recommended for practical use in the direction of cleaning water contaminated with different pesticides applied in agriculture, cleaning can be done in different practical ways depending on the concrete circumstances for each case, devising static or dynamic water purification schemes.
of the mass use of the studied adsorbents are low, however, for each specific case, the corresponding visibility study should be performed. I think that our study in the field of the use of the above adsorbents for the purification of waters loaded with pesticides will make a modest contribution in this field, in addition to the many studies that have been carried out and are being carried out in the direction of preserving the environment where we live. Even in the future, I will try that my intellectual and professional commitment is closely related to the many problems that require a clean and healthy environment.

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