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PREFACE

Many medicinal and aromatic plants are produced in Turkey to be used as inputs for herbal medicine, plant chemicals, food/food additives, cosmetics and perfumery sectors.

The use of organic fertilizers in crop production is necessary to ensure sustainable development, achieve agricultural policy objectives and optimize food supply in line with the needs of organic agriculture.

Organic fertilizer is a carbon-containing product that is naturally obtained from animal and plant wastes and biosolids by appropriate methods (such as compost) and contains minerals necessary for the nutrition and growth of plants. Organic fertilization enriches the organic matter content of the soil, increases the water capacity, facilitates the nutrient uptake of the plant, in short, improves the chemical and physiological structure of the soil. In this context, concise information on the advantages of using organic fertilizers in the production of quality and healthy medicinal and aromatic plants is given.

Again, nuclear energy is a clean energy source that can minimize greenhouse gases and, most importantly, generate electricity 24 hours a day

Radioactive waste from industry, pharmaceuticals and nuclear research is often generated during nuclear power generation. Whatever the source, radioactive waste needs to be managed safely and economically

Based on this idea, in the study conducted using sepiolite-based clay from Denizli region of Turkey as adsorbent, it was found that it can be a promising insulation material in radioactive waste storage systems because it can effectively adsorb radioactive cesium and prevent its leakage into the environment.

In addition, Cypermethrin (CYP) is one of the most widely used pesticides and chemicals in the world because it is a broad-spectrum pyrethroid and is used extensively in agricultural applications. Although the pesticide is banned, it is widely detected in water. CYP and its by-products from industrial, domestic and agricultural activities enter water resources through different routes (groundwater, drainage, runoff, forest spraying practices, evaporation, rainwater, accidental overspray) and non-target aquatic animals are adversely affected.

The aim of this study was to obtain comprehensive data by investigating the changes caused by CYP on the quality and oxidative stress indices in sperm of mullet (S. Oriantalis).

Naturally, the topics covered in this book are presented to the readers as a basic resource containing up-to-date information that can be used by those working in all departments related to environmental sciences and engineering.

Editor

Prof. Dr. Ali BİLGİLİ

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CHAPTER I

Organic Fertilizer in Medicinal and Aromatic Plant Production

Elanur ADAR YAZAR[1]

Introduction

Medicinal and aromatic plants (MAPs) have been used for various purposes (such as food, medicine, cosmetics, and spices) since the beginning of human history. Figure 1 shows the usage areas of MAPs.

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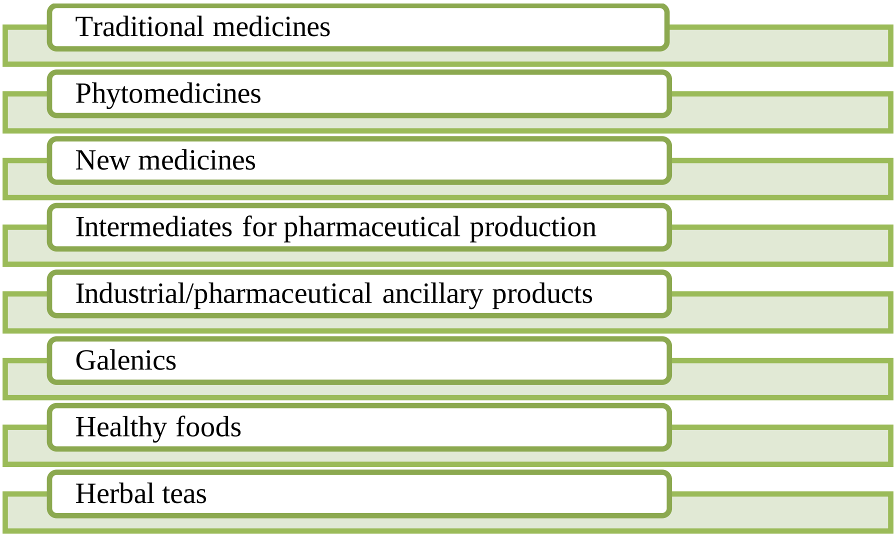

Figure 1. Uses of medicinal and aromatic plants (Pakdemirli, 2020)

Some of the MAPs are collected from nature and some are grown and produced under suitable conditions. With the emergence of new uses of MAPs after the 1990s, the demand for natural products increased.

Turkiye is an important country for the MAP market in terms of its geographical location, climate and plant diversity. Many herbal products are produced in Turkiye to be used as input in the herbal medicine, plant chemicals, food/food additives, cosmetics, and perfumery sectors. There are MAPs in every region of Turkiye, and the production of MAPs is mainly in the Aegean, Marmara, Mediterranean, Eastern Black Sea and Southeastern Anatolia regions. The largest production of organic medicinal, aromatic and recreational (tobacco, tea, hops, poppy, hemp, anise, etc.) plants, including products collected from nature, is carried out in Rize (Tıraşçı et al., 2020).

While the products collected from nature must be in the desired quantity, the produced products must be of the desired quality. The plant produced must respond to consumer and/or industry demands. In this regard, it is important to develop the species grown, determine appropriate ecological conditions, harvest natural plants on time without harming nature, and determine post-harvest processes and technologies to increase production and market opportunities in MAP (Pakdemirli, 2020). In MAP production, not only efficiency but also quality criteria should be taken into consideration. When quality is mentioned, secondary metabolite content comes to mind. Choosing plant(s) compatible with the ecosystem is important in terms of both sustainability and secondary metabolites (Sharifi et al., 2002). In addition to the secondary metabolite, the quality criterion in MAP production is determined according to the correct botanical name of the plant, source country or region, harvest time, sensory tests (organoleptic tests of color and smell), macroscopic (determining the shape, size, surface character, texture, refraction, etc. with the naked eye or authentic sample), microscopic (comparing of parenchyma, collenchyma, fungus, leaf epidermis, calcium oxalate, starch, protein, fat or samples with authentic substances), chemical (investigation for the presence of secondary metabolites such as alkaloids, cardiac glycosides) and its chromatographic properties (especially thin layer chromatography) (Bayram et al., 2010; Yaldız et al., 2019a).

The use of organic fertilizers in plant production is necessary to achieve sustainable development, achieve agricultural policy goals and optimize food supply in line with organic farming needs. Increasing environmental and health awareness and global pollution also grow the interest in organic agriculture day by day. Since MAPs are widely used in areas that concern human health, such as the food, cosmetics and pharmaceutical industries, their production must be carried out in a healthy way. For this reason, organic or good agricultural practices should be preferred in their production. Interest in MAPs grown with organic certification is increasing and they provide many advantages in national and/or international marketing. In order to ensure sustainable use of soils, reduce environmental pollution, and produce high-quality MAPs, emphasis should be placed on the use of organic fertilizers instead of commercial chemical fertilizers.

Organic fertilizer is a carbon-containing product obtained naturally by appropriate methods (such as compost) from animal and plant-derived wastes and biosolids, which contain the minerals necessary for the nutrition and growth of plants (Anonymous1, 2023; Anonymous2, 2023). Organic fertilization enriches the organic matter content of the soil, increases water capacity, and facilitates nutrient uptake by the plant, in short, it improves the chemical and physiological structure of the soil (Bachman and Metzger, 2008).

More than 75% of Turkiye's soils contain little or no organic matter and nitrogen. It contains around 6% sufficient and excess organic matter. In terms of phosphorus, 75% of it has very little or little phosphorus available to plants. 14% contains a high amount of phosphorus available to plants. 80% of soil in Turkiye has too much or too much potassium available to plants. Potassium is insufficient in 1.3%. Soil organic matter and nutrient deficiencies can be addressed economically and environmentally by using both farmyard manure (FYM) and other organic fertilizers. As a plant food source, organic fertilizers consist of residues or wastes of plant, animal and human origin. They contain nitrogen (N), phosphorus (P), potassium (K) and other nutritional elements in different amounts depending on the source of the organic matter. Organic fertilizers are important as a source of plant nutrients; barn (farm) manure, poultry manure, green manures, urban waste manures, composts, meat combine wastes, guanas, commercial organic fertilizers (Anonymous3, 2010).

According to the statistics published by the Ministry of Agriculture and Forestry, the amount of organic plant production in Turkiye is 1101236.97 tons. 216863.10 ha of this production is produced by production and 24334.03 ha by nature. Organic production is carried out by 38748 farmers. There are approximately 30 MAPs in Turkiye country that carry out organic production. Carob, rosehip, chamomile, mint, blueberry, laurel, melissa, centaury and nettle are mainly collected from nature. Organic productions of carob (3724 tons), laurel (1227 tons), rose (902 tons), poppy (514 tons), capers (438 tons), black cumin (321 tons), fennel (277 tons), cumin (268 tons), blueberries (241 tons), lavender (155 tons), anise (113 tons), gilaburu (78.5 tons), tarragon (72 tons), marjoram (22 tons), melissa (17 tons), cress (14.5 tons), mint (8.3 tons), centaury (7 tons), basil (6.25 tons), lemon grass (4.5 tons), goji berry (4.5 tons), coriander (4.5 tons), sorrel (3.5 tons), chamomile (3.5 tons), echinacea (1 ton), and thyme (0.5 tons) are carried out (TOB, 2023). Antalya, Aydın, Izmir, Mersin and Kocaeli provinces rank first in terms of plant diversity (Kırıcı, 2015). In fourty two provinces selected for rural development, MAPs were included in the scope of support by the "Agriculture and Rural Development Support Institution" and approximately 2357 enterprises benefited from the support provided for MAP cultivation (Kırıcı, 2015; Yaldız et al., 2019a).

Interest and demand for good agricultural practices as well as organic agriculture are increasing day by day. Good agricultural practices were implemented in 18 provinces in 2007 and in 63 provinces in 2021. The production amount increased 110 times and reached 6612544 tons (TOB, 2023).

In this study, information is given about different organic fertilizer applications in MAP cultivation. For this purpose, detailed information about organic fertilizer is given first. Then, the use of different organic fertilizers in MAP production was mentioned. Studies in the literature are included.

Organic Fertilizer

Organic fertilizers, which have various benefits for soil and plant production, are especially preferred in organic farming and/or good agricultural practices. Of course, in good agricultural practices, minimum levels of pesticides and chemical fertilizers are allowed. Organic fertilizers can divide into 4 groups: barn-poultry manure, compost, vermicompost, biological fertilization (mycorrhizal fungi and bacterial application). Within the scope of organic fertilizer, peat (peat soil), green manuring and humic acid etc can also be taken into account.

Barn-Poultry Manure

Barn manure is the waste of cattle (cattle, buffalo, etc.) and small cattle (sheep, goats, etc.). The manure properties of the same animal vary from farm to farm and breeding techniques. Barn manure contains 0.5-1.0% N, 0.15-0.20% phosphorus (P_2O_5), 0.5-0.6% potassium (K_2O). In addition to macro elements, 50-100 g ton^{-1} manganese (Mn), 20-40 g ton^{-1} zinc (Zn), 10-15 g ton^{-1} boron (B), 10-12 g ton^{-1} copper (Cu). It contains 0.4-0.7 g per ton^{-1} molybdenum (Mo) and 0.8-1.2 g per ton^{-1} cobalt (Co) microelements. Most of these elements are soluble in water (Yaldız et al., 2019a).

Table 1. Properties of barnyard animal manures (Yaldız et al., 2019a, Anonymous3 2010)

Genus	**H_2O (%)**	**Dry Matter (%)**	**N (%)**	**P_2O_5 (%)**	**K_2O (%)**	**CaO (%)**
Cattle	83.2	16.2	0.29	0.17	0.10	0.34
Horse	75.7	24.3	0.44	0.35	0.35	0.15
Sheep	65.5	34.8	0.55	0.31	0.15	0.46
Goose, Duck	75.0	25.0	0.80	1.00	0.80	1.30
Pigeon, Chicken	62.0	38.0	1.70	1.60	0.90	2.00

The amounts in the tables vary depending on the animal's age, function and nutritional status. Annual fresh manure production per animal varies between 12-15 tons, 0.5-0.7 tons and 8-16 tons for cattle, sheep-goats and horses, respectively (Anonymous3, 2010).

Poultry manure (chicken, rooster, goose, turkey etc.) is the waste of animals living in the poultry house. Chicken manure contains 3.9% N, 2.1% P, and 1.8% K as dry matter (Soyergin, 2003; Yaldız et al., 2019a).

According to 2022 TUIK data, the number of cattle, buffalo, sheep and goats is approximately 17 million, 172 thousand, 45 million, and 12 thousand, respectively. Again, according to 2022 TUIK data, the numbers of chicken, turkey, duck and goose coops are approximately 361 thousand, 4 thousand, 432, and 1400, respectively. In Turkiye, cattle and sheep are among the barn animals, and chicken from poultry animals is grown in large quantities. Therefore, many studies have been realized with the animal manures. Poultry manure has less water content. Because of this feature, it is not preferred to use it directly as fertilizer. If chicken manure is to be used, composting should be done beforehand to avoid burning the plant. To minimize this disadvantage of chicken manure, it can be mixed with different organic wastes such as stalk, and straw, which generally have low nutritional element content (Khalid et al. 2007; Yaldız et al. 2019a). In other words, necessary preliminary processes (mixing with different waste/material, composting, etc.) should be carried out for the fertilizer to be used according to the soil type and the needs of the plant to be grown.

By using barn manure:

- Soil properties (physical, chemical and biological) are improved,
- Organic matter source is created,
- Microorganism activity is accelerated,
- Water retention capacity is increased,
- Ventilation feature is increased,
- It ensures retention of plant nutrients,
- It contributes to salinity and pH regulation,
- It prevents soil compaction,

- It enables the roots to develop more easily.

Compost Fertilization

Compost is the decomposition of organic matter by microorganisms under certain operating conditions (temperature, humidity, etc.). Composting is actually a process that occurs everywhere in nature and is a nutrient recycling in the ecosystem.

Composting can be done with materials such as food waste (fruit and vegetable residues, egg shells, coffee grounds, etc.), animal manure, cardboard-paper residues, fallen, dried, rotten leaves, branches, other plant residues, mowed grass pieces, indoor plants, stalks and straw, sawdust and wood splinters, cotton and wool pieces, wood ashes, organic material operating wastes (pistachios, olive oil (except black water), tea, fruit juice, etc.). In short, all organic wastes, except inorganic (plastic, glass, metal, etc.) and organics containing harmful and dangerous substances (coal ash, drugs, medical waste, pesticide plants, etc.), can be composted and used in plant production. To obtain good compost, the amount of organic matter should be high, it should be in the ideal concentration of trace nutrients that plants can benefit from, it should be free from all harmful substances and there should be little useless ballast substances (Anonymous4, 2023).

Table 2. C/N ratios of organic materials

High Carbon Content Material	**C/N (Carbon/Nitrogen)**
Leaves	30-80:1
Straw	40-100:1
Wood chips and sawdust	100-500:1
Mixed paper	150-200:1
Newspaper or corrugated cardboard	560:1
High Nitrogen Content Material	
Vegetable pieces	15-20:1

Coffee residue	20:1
Grass	15-25:1
Animal manure	5-25:1

Utilizing non-hazardous/harmless organic waste, including food that cannot be used for human and animal consumption, as compost will provide many benefits. By making compost, a material with soil regulator properties and fertilizer value is obtained. It improves the structure of the soil physically, chemically and biologically; and ensures the moisture balance of the soil.

Plant nutrients that are difficult to be used by plants in the soil become available. Well-decomposed, mature compost is a constant source of humus, carbon, nitrogen, phosphorus, potassium and many trace elements (Anonymous4, 2023). Since compost mainly provides the structural order of the soil, it is possible to obtain superior quality fertilizer by adding nitrogen, phosphorus and potassium in certain proportions. To provide the desired properties in compost, wastes with different compositions can be composted together or the desired elements can be added. The high temperature generated during the hot composting process destroys disease-causing pathogens and weed seeds. Recycling of waste is also achieved through composting. Leaks that occur as a result of uncontrolled storage of waste due to insufficient storage and transformation facilities in enterprises, deteriorate the surface and groundwater quality and make them unusable over time. In addition, due to the fact that these wastes are kept in large uncontrolled piles in open, empty lands, they cause serious environmental and health problems, as well as bad odor and unpleasant appearance. In this respect, composting is a very useful application for solving the waste problem in businesses and eliminating the environmental and health problems caused by waste to some extent. It protects soil, surface water and groundwater quality. It reduces carbon footprint and reduces methane emissions from garbage. It reduces waste costs and helps reduce the need for landfills. Composts are used in all kinds of plant production. Composts can also be used as mulch to retain water in the soil. Mulching reduces water loss from the surface and water consumption of plants, it can also prevent some plant diseases. It promotes the production of beneficial bacteria and fungi that break down organic matter in the soil to create humus with rich plant nutrients content (Anonymous5, 2023).

Vermicompost Fertilization

Vermicompost is produced by the digestion of organic wastes (animal manure, stalks, straw, fruit and vegetable wastes, garden wastes, sawdust, waste paper, etc.) by some worms. It is a product used as organic fertilizer and soil conditioner in the agricultural sector. Although there are literally thousands of species of worms, only a few species of worms can be used in vermicompost production. Vermicomposting is done by organically growing the earthworm species *Lumbricus rubellus* and *Eisenia fetida*. It is also known by another name as “Red Worm”. For vermicompost production in the temperate climate zone, it would be more beneficial to select *Eisenia fetida, Eisenia andrei and Dendrobaena veneta* species, which are more common in the temperate climate zone. *Lumbricus rubellus and Perionyx excavatus* species are better adapted to vermicompost production in a region with a hot tropical climate (Şimşek-Erşahin, 2007). If you aim to produce vermicompost for commercial purposes, the most preferred ones in commercial areas are *Eisenia spp*. (Bansal and Kapoor, 2000) and *Lumbricus spp.* (Dickerson, 2004) taxa. Sharma (2003) compared these two species in a study and found that the vermicompost obtained from the *Eisenia fetida* species was superior in terms of total organic matter, C:N ratio, total nitrogen, phosphorusl, and potassium amounts. It has been stated that it has features. It has also been stated that the salinity rate (electrical conductivity) is lower in vermicompost products obtained with this species (Abacıoğlu et al., 2020).

The reasons why red worms are preferred commercially in the use of vermicompost are; this worm has a voracious feeding habit, can move easily through the food pile thanks to its thin body, and has the capacity to produce fertilizer as much as its own weight. These worms, which can live in many climates, can reproduce rapidly when climatic conditions are provided (Abacıoğlu et al., 2020).

Worm droppings are richer in nutrients and microbials, and are therefore considered a high-value product. It is an excellent soil additive. When the chemical analysis of vermicompost was carried out, it was determined that it contained 5 times more usable nitrogen, 7 times more usable potassium and 1.5 times more calcium than that found in a 15 cm thick good soil layer. Additionally, it has been determined that the nutrient lifespan is 6 times longer compared to other soils, and also, as phosphorus passes through the digestive system of the worm, it turns into phosphorus form that the plant can absorb. The changes it creates in soil properties improve the air and water intake of the soil and trigger seed sprouting and root development. Vermicompost contains on average 1.5% – 2.2% N, 1.8% – 2.2% P and 1.0% – 1.5% K. Organic carbon varies between 9.15 and 17.98 and it contains some micronutrients such as sodium (Na), calcium (Ca), zinc (Zn), sulfur (S), magnesium (Mg) and iron (Fe). Vermicompost contains a high amount of humus. It creates channels for soil particles that enable air passage and increases water retention capacity. The presence of earthworms makes it possible to reshape compacted soil and increase the penetration of water into such soils by more than 50% (Anonymous6, 2023).

Compost application also has other agricultural benefits such as suppressing soil-borne diseases and eliminating soil salinity. According to a study, it was determined that as a result of applying compost to the soil, the average root disease rate decreased from 82% to 18% in tomatoes and from 98% to 26% in red pepper. The microbial activities of beneficial microorganisms in vermicompost are 10 to 20 times higher than those in soil or other organic substances. Beneficial soil microbes include "nitrogen-fixing and phosphate-solubilizing bacteria", "actinomycetes" and "mycorrhizal fungi". Worm feces contain slow-release nutrients that the plant can absorb immediately, and the nutrients it contains are covered with the mucus membrane secreted by the worms. Thus, the food is not washed away quickly, but instead dissolves slowly. Worm feces can hold 2-3 times more water than its weight in soil. It does not burn the root system of the plant. It insulates plant roots from extreme temperatures, prevents erosion and can reduce weeds. It is 100% odorless and made of recycled material. Vermicompost also has much more “high porosity”, “aeration”, “drainage” and “water retention capacity” than traditional compost, due to its humus content. It does not burn even your most sensitive plants, and all the nutrients it contains are in water-soluble form, making it immediately available to plants. In addition, it provides plant growth regulator effect, ability to develop biological resistance in plants, ability to reduce pest attacks and ability to suppress plant diseases (Yaldız et al., 2019a).

Biological Fertilization

Mycorrhizal fungi

Mycorrhizal fungi are beneficial microorganisms and are known as biological fertilizers. Mycorrhiza is the mutual life form between plant roots and certain fungal species. In this cooperation, mycorrhiza provides carbon from the plant, and the plant provides nutrients and water through mycorrhiza. In other words, plant nutrients in the soil are taken up not only by plant roots but also by mycorrhizae and delivered to the plant (Atiyeh, 2000). Greenhouse studies have revealed that mycorrhizae increase phosphorus uptake by 3-4 times. Mycorrhizae become a part of the environment with the hyphae released into the plant root, and these hyphae release P to the plant and C to the outside from the plant. Mycorrhizae are infected in the roots of many plants and maintain their symbiotic life in a widespread manner. Mycorrhizal fungi contribute to the plants' uptake of fixed elements such as phosphorus, zinc and copper. Due to the effects of mycorrhizal fungi in the production of plant hormones, they have resistance to biotic and abiotic stress (Yaldız et al., 2019a).

Bacterial application

Some researchers reported that in soil inoculation with a bacterial mixture, plants are fed more balancedly and that there is a main mechanical interaction between phosphate solubility and nitrogen uptake and that nitrogen and phosphorus uptake improves the root (Belimov et al., 1995; Sharma, 2002; Abou-Aly et al., 2006). Ratti et al. (2001) stated that the height and biome of the lemongrass plant increased in different varieties of phosphate-soluble bacteria. In Iran, Putida 41, Azotobacterchroococcum 5 and Azosprillumlipoferum, which promote plant growth, were used for basil roots, and the highest fresh weight (3.96 g plant^{-1}), N content (4.72%) and essential oil rate (0.82%) had observed in Pseudomonas+Azotobacter+Azosprillum treatment. It was stated that higher data were obtained in the Pseudomonas + Azotobacter + Azosprillum and Azotobacter + Azosprillum treatments in terms of all parameters (Ordookhani et al., 2011; Yaldız et al., 2019a).

Green Fertilization

Green fertilization is the use of certain plants as fertilizer during a certain period of their development, i.e. while they are still green. Plants used as green manure are green fertilizer plants (GFP). As GFP; legumes (clover, meadow clover, stone clover, soybean, forage pea, forage cowpea, red clover, hairy vetch, Hungarian vetch, hairy fruit vetch, big vetch, common vetch, pea, damson, lupine, Alexandria clover, white clover), grasses (rye, oats, barley, millet, wheat, grass, sudan grass, silage corn) and plants from other families (mustard, rapeseed, radish, poppy, safflower, turnip) are used alone or as a mixture.

The primary and most important benefit of green fertilization, which helps to obtain more and higher quality products by increasing the fertility of the soil, is the enriching the soil with organic matter. Where barnyard manure is scarce, the organic matter content of the soil is increased, especially by green manuring. Organic matter is one of the most important factors affecting the physical, chemical and biological properties of soils. Organic matter directly increases soil fertility by improving the physical properties of soils such as improving their structural structure, aggregate durability, water retention capacity and aeration. Organic matter is the source of all nutrients, especially nitrogen, which is constantly present in the soil and is not easily washed away. For this reason, soil organic matter is used as the most important indicator of nitrogen in the soil. At the same time, a significant amount of nitrogen is given to the soil with green fertilization, depending on the nitrogen content of the plant used. This amount is much higher when green fertilizer is used, especially if legume plants are used. Studies have shown that legume forage plants planted for green fertilization purposes provide approximately 10-30 kg N per decare (Anonymous7, 1975, Anonymous8, 1996). Soil biological activity is one of the indicators of soil fertility. It improves some basic physical properties such as soil structure, pore size and distribution, and infiltration; and creates suitable conditions for plant development. In particular, climate has an impact on organic matter by affecting microorganism activity. While the rate of decomposition of soil organic matter increases and the organic matter content decreases due to the increase in temperature, the increase in vegetation cover due to the increase in precipitation and humidity also potentially increases the organic matter content. Especially, in arid regions, the rapid loss of soil temper creates a major problem in plowing. Since GFP cover the upper surface of the soil and increase the bacterial activity in the upper layer thanks to the shade they create, the structure of the soil becomes suitable for plant development and soil cultivation becomes extremely easy. In green fertilization, it is possible to control most harmful insects, nematodes and fungi by using GFP, especially plants that kill diseases and pests and secrete substances that retard harmful activities (for example; mustard, rapeseed and other brassicas). By choosing a GFP that does not have a host, disease or pest density is reduced. With high biological activity, soil diseases are eliminated or reduced. It is also possible to benefit from green fertilization in weed control, which increases soil fertility by having a positive effect on the physical, chemical and biological properties of the soil. GFP are mixed into the soil when weeds are to be controlled, while the weeds are mixed into the soil together. These will be completely eliminated with the next version. If green fertilizer is left as a thick mulch layer on the soil surface, the germination of weeds will be prevented. Thus, the weeds buried in the soil along with the GFP are used both as mulch and are used as shelter for soil organisms, plant nutrients and, by decaying, as soil organic matter (Karakurt, 2009). Its most important negative aspect is that it causes the pH of the soil to decrease with long years of use (Anonymous3, 2010).

Advantages-Disadvantages of Organic Fertilizer

The utilization rate of inorganic (chemical, mineral) fertilizer is about 50-60% even under the most favorable conditions. Almost half of chemical fertilizers are either fixed in the soil or enter surface/underground water sources or the atmosphere in gaseous form. Organic materials applied together with inorganic fertilizers increase the efficiency and reduce the use of inorganic fertilizers (Anonymous5, 2023).

Advantages of organic fertilizers;

- It greatly reduces the use of inorganic fertilizers.
- It is a more environmentally friendly and sustainable alternative compared to inorganic fertilizers.

- Organic residues/wastes (city wastes, animal manures, harvest residues) are evaluated and recycled for this purpose.
- It greatly reduces the garbage collection costs of municipalities by reducing the amount of waste.
- It reduces air pollution and greenhouse gas emissions as a result of the municipality making fewer trips.
- If people apply these simple processes at home, they can sell or use the fertilizers they obtain, thus benefiting the country's economy.
- Thanks to the organic substances they contain, they provide an increase in beneficial microorganisms (bacteria, fungi, etc.) in the soil.
- The compost produced can be used to make agricultural lands that have become infertile due to excessive erosion productive again.
- It riches the organic matter content of soil and improves the all properties of the soil (structure, aeration, water retention capacity, etc.).
- Since organic fertilizer darkens the color of the soil, soil rich in organic matter absorbs more sunlight.
- It also provides macronutrients such as nitrogen, phosphorus and potassium
- It ensures that nitrogen in the soil is evenly distributed to plants
- Organic fertilizer increases cell division in the plant, enabling the plant to grow faster and provide earlier product intake.
- By creating a fibrous dense structure on the soil surface, it prevents water from flowing and evaporating independently from the soil surface, so plants and soil need less water. Thus, soil resistance against drought increases. The soil becomes more resistant to the danger of erosion.

- It provides plant resistance against pests and insects, thus reducing the use of pesticidesThe plant gains resistance against harmful pests and insects, less pesticides are used.
- It dissolves the lime that water cannot dissolve, and the carbon dioxide resulting from melting is used in photosynthesis (applies to sulfur-fortified organic fertilizers).
- It converts iron into a form that the plant can absorb.

Disadvantages of organic fertilizers;

- The ratios of salts and elements in organic fertilizers are not constant. Salts are generally concentrated and, if used unconsciously, cause the soil to become salinized.
- It is also doubtful that the elements-salts in organic fertilizers are useful in every organic fertilizer. In other words, in order for plants to absorb the elements contained in animal feces or vegetal decay, the fertilizer must be burnt manure. Otherwise, they will only become useful in the soil after a year or two (organic fertilizers that have become useful are called burnt manure).
- The quality of animal manures is generally poor today. No matter what you do, manure from animals fed with artificial feeds, medicines, or medicated feeds may not be as beneficial as in the past.
- Fertilizers applied without plant and soil analysis cause long-term health problems, especially for soil health, humans, animals and other living things in the region. Fertilizer should be applied with appropriate methods and amounts.
- The amount of fertilizer applied, application technique and time are important (Cüre, 2022).

- Biofertilizers have the potential to harbor human pathogens, so they need to be monitored.
- It is more labor intensive for the consumer compared to commercial ready-made fertilizers, which may reduce its accessibility.
- It results in lower crop yields, which increases prices.
- More planning and efficient operations are required to implement.
- When organic fertilizers are used more and for longer periods than inorganic fertilizers, environmental problems such as salinization, heavy metal accumulation, nutrient imbalance, disruption of microorganism activity, eutrophication (increase in nitrate and phosphorus in water), release of nitrogen and sulfur-containing gases into the air, ozone depletion and greenhouse effect may occur, albeit to a lesser extent (Tunç, 2017).

Use of Organic Fertilizers in Medicinal and Aromatic Plant

Production

The studies show that different organic fertilizers are used in different MAP production studies. In these studies, not only a single type of fertilizer was used, but also combinations of different organic fertilizers and inorganic/chemical fertilizers were used.

Succop and Newman (2004) grew basil in soilless agriculture using organic and inorganic fertilizers in rock wool, commercial bog moss mixed with perlite and compost media. The yield of basil grown in perlite using organic fertilizer was 22% higher in the first year and 100% higher in the second year compared to those using inorganic fertilizer. Anwar et al. (2007) grew basil (*Ocimum basilicum L. cv. Vikas Sudha*) using six different organic (FYM and vermicompost) and inorganic (N-P-K) fertilizers and observed that it performed best in terms of growth, plant, dry matter, oil content and oil yield in the combination of organic and inorganic fertilizer. Basil oil (methyl chavicol and linalool) content was also higher in vermicompost and inorganic combination. They stated that co-application of organic and inorganic fertilizers increases crop productivity and quality and helps to maintain soil fertility. In white thyme (*Origanum majorana L.*) using organic burnt sheep manure (500, 1000, 1500 kg da^{-1}) and inorganic ammonium nitrate (33%) (NH_4NO_3) (3, 6, 9 kg N da^{-1}) to determine the effects on plant yield and essential oil content, the highest plant height of 35.00 cm, fresh herb yield of 922.46 kg ha^{-1}, yield of 789.00 kg ha^{-1}, essential oil content of 5.30% and essential oil yield of 14.67 kg ha^{-1} were obtained from 1500 kg ha^{-1} sheep manure (Baştaş, 2007). Yılmaz (2007) investigated the effects of nitrogen, FYM and quail manure applied at different doses and times on plant and fruit characteristics of raspberry (*Tulameen*) variety. Nitrogen was recommended to be applied at a single dose of 112 kg ha^{-1}, quail manure at 4 tons ha^{-1} or farm manure (burnt sheep manure) at 3 tons ha^{-1}. Kocabaş (2007) studied the effect of different organic fertilizers (cattle, sheep and chicken) on the nutrient and essential oil content of sage (*Salvia fructicosa Mill*.) plant. The essential oil content increased with the addition of organic fertilizers and the highest essential oil was obtained from the mixture of chicken and sheep manures. Ateia et al. (2009) investigated the effect of organic fertilization (compost, chicken and sheep manure) on yield and active constituents of garden thyme (*Thymus vulgaris L*) in two consecutive seasons in 2003/2004 and 2004/2005 under North Sinai conditions. The highest yield was obtained from 20 m^3 compost and 10 m^3 chicken-sheep manure mixture and the highest thymol content was obtained from 30 m^3 compost and 10 m^3 sheep manure treatments. Doğramacı and Arabacı (2010) determined the effect of organic and inorganic fertilizer applications on the yield of anise (*Pimpinella anisum L.*) cultivars and ecotypes. Six different fertilizer (control, commercial fertilizer, barnyard manure, organic fertilizer, commercial fertilizer x organic fertilizer and commercial fertilizer x barnyard manure combination) were tested. Good results have obtained from organic fertilizer and organic-inorganic fertilizer mixture. Karaal (2011) reported that arugula and cress can be grown with the addition of organic fertilizers to hazelnut waste compost, the highest yield of arugula was obtained from 15% fertilizer dose with 3479.61 g m^{-2} and the highest yield of cress was obtained from 20% fertilizer dose with 2936.30 g m^{-2}. Hellal et al. (2011) determined the effect of mineral nitrogen fertilizer and biofertilizers (*1- Azotobacter chroococcum, 2- Azospirillum lipoferum, 3- Bacillus polymyxa, 4- Bacillus megatherium and 5- Pseudomonas fluorescens*) and their effects on growth, yield and chemical components of dill plant (*Anethum graveolens L.*). In the study, it was suggested that mineral nitrogen fertilizer should be used together with biofertilizer to increase the yield as well as the quality of dill plants. Tabrizi et al. (2011) investigated the effect of irrigation and organic fertilizer on Khorasan thyme (*Thymus transcaspicus Klokov*). Different amounts (10, 20 and 30 tons ha^{-1}) of four-year composted cattle manure were applied three months before planting. Under optimal conditions of soil water, lower fertilizer application (10 t ha^{-1}) was found to provide high yield. Çelik and Kan (2012) determined the yield and quality characteristics of Mary's thistle at different sheep manure doses (0, 500 and 1500 kg ha^{-1}). It varied plant height between 75.73 - 118.66 cm, number of branches between 5.06 - 21.33 pieces $plant^{-1}$, seed yield between 72.26 - 148.73 kg ha^{-1}, fixed oil yield between 20.2-27.7% and silymarin content between 1.1-3.1%. It was stated that 1500 kg da^{-1} organic fertilizer application was the optimum value. Batiray and Kan (2013) determined the yield and quality characteristics of Izmir thyme grown at different nitrogen (inorganic fertilizer) and organic fertilizer (sheep manure) doses. It was stated that it would be appropriate to grow Izmir thyme (*Origanum onites L.*) in Konya and similar ecologies by applying 10 kg da^{-1} nitrogen and 2000 kg da^{-1} sheep manure together for high yields of drog and essential oil. Yeşil and Kan (2013) determined the effects of fertilizers on some yield and essential oil characteristics of echinacea species (*Echinacea pallida and E. purpurea*) grown at different organic (0, 500, 1000, 2000 kg da^{-1}) and inorganic fertilizer (0, 2.5, 5, 10 kg da^{-1}) doses. It was explained that *Echinacea purpurea* should be grown with 5 kg da^{-1} nitrogen and 500 kg da^{-1} organic fertilizer and *Echinacea pallida* should be grown with 2.5 kg da^{-1} nitrogen and 1000 kg da^{-1} organic fertilizer for high yield of drugs and essential oil. Aboutalebi et al. (2013) compared organic nutrient solution, solid poultry manure and inorganic nutrient solution in basil cultivation in soilless farming. They reported that the highest yield was obtained from inorganic nutrient solution and the lowest yield was obtained from solid poultry manure. However, it was observed that there was no significant difference between inorganic nutrient solution and organic nutrient solution treatments. The researchers stated that organic nutrient solution can be used successfully in basil cultivation. Bufalo et al. (2015) compared organic and inorganic fertilization in basil cultivation in greenhouse soil and found that different fertilizer sources changed fresh weight, leaf micronutrient content, dry weight and nitrogen absorption but not essential oil composition. They stated that organic fertilization can be used except for essential oil production. Sezer (2015) applied two organic fertilizers in sorrel (*Rumex acetosella L.*) cultivation to four different soilless media at three different rates before planting. According to the results, it was reported that yield increased with the increase of organic fertilizer dose. Good results were obtained for quality sorrel cultivation with the addition of organic fertilizers. Gerami et al. (2016) used different irrigation intervals (1, 2 and 3 weeks) and different doses of organic cattle manure (0, 10, 20 and 30 t ha^{-1}) to evaluate its effect on thyme yield (*Origanum vulgare L.*), essential oil content, and morphological traits. They reported that increasing irrigation intervals decreased the values of all morphological traits except stem ratio, and the values of stem number, plant spread, stem diameter, leaf area, fresh and dry herbage yield increased with increasing levels of cattle manure, the highest essential oil content (2.07%) and yield (66.62 kg ha^{-1}) were obtained at the highest irrigation intervals and the highest doses of organic animal manure, while the lowest essential oil content (1.55%) was obtained at one-week irrigation interval without cattle manure. Yaldiz et al. (2017) determined the effect of different amounts of turkey manure (750, 1000, 1250 and 1500 kg da^{-1}) on basil (*Ocimum basilicum L.*) yield. As a result, 750 kg da^{-1} turkey fertilizer dose was determined as the optimum value for basil yield. Akşahin (2018) applied inorganic fertilizer with tea waste (0%, 2.5% and 5.0%) and waste mushroom compost (0%, 2.5% and 5.0%) with inorganic fertilizers (ammonium sulfate (0, 125, 250 mg N kg^{-1}), triple super phosphate (0, 50, 100 mg P_2O_5 kg^{-1}) and potassium sulfate (0, 75, 150 mg K_2O kg^{-1}) on the growth and nutrient content of fenugreek (*Trigonella foenum graecum*) plant. It was concluded that supplementing the tea waste with phosphorus and potassium, which are less in its content, and applying the waste mushroom compost after removing the salinity by washing several times due to the salts it contains, may be more effective on plant growth. Özliman (2019) investigated the biological activities and essential oil components of dill (*Anethum graveolens L.*) plants grown with different doses of nitrogen (ammonium nitrate: 3-6-9-12 kg da^{-1}) and organic fertilizers (farm manure: 750-1000-1250-1500 kg da^{-1}). In terms of essential oil components, 3 kg da^{-1} nitrogen, 1250 kg da^{-1} farm fertilizer and 1500 kg da^{-1} farm fertilizer applications were effective. Yaldiz et al. (2019b) evaluated the effects of poultry manure (7.5, 10, 12.5, 15 t ha^{-1} chicken and turkey manure) and conventional fertilization on basil plant growth, yield and inorganic matter content. The highest fresh and dry weights from plants grown were obtained in 10-12.5 t ha^{-1}turkey and chicken manure mixture. Yüksek et al. (2020) investigated the effect of vermicompost and peat applications on the growth of Cuban Thyme (*Plectranthus amboinicus Lour. Spreng*). The best result was obtained from the application of 10 grams of solid vermicompost. Matlok et al. (2020) investigated the effect of organic and inorganic fertilizer on the yield of oregano (*Origanum vulgare L.*). It was concluded that the use of organic fertilizers in thyme cultivation has higher bioactive and better organoleptic properties and contributes to the production of raw materials for direct consumption/drying. Şenyiğit et al. (2021) studied to determine the effects of different irrigation water levels (0%, 25%, 50% and 75%) and different doses of vermicompost (100 and 200 kg da^{-1}) on the water consumption level and yield of basil (*Ocinum basilicum L.*). In the study, it was concluded that 100 kg da^{-1} vermicompost level can be recommended because it reduces the amount of water consumption of the plant, increases yield and is an environmentally friendly fertilizer. The optimum water level was determined as 75%. Çiçek (2021) investigated the effect of bat manure and vermicompost on the development, quality and photosynthetic pigments of marigold (*Tagetes erecta*), which has an important sales potential in Turkiye and the world. At the end of the study, it has determined that the most suitable bat manure dose for marigold was 6%. Kara (2021) was conducted in 2019 and 2020 to investigate the effect of vermicomposting on herb yield and essential oil content of sater (*Satureja hortensis L.*). According to the producer's preference, it is recommended that liquid vermicompost can be applied alone for organic crop production, but vermicompost should be applied in combination with conventional production due to higher wet/dry herb and leaf yields. Özyazıcı (2021) determined the effects of different combinations of inorganic and organic fertilizers (vermicompost, cattle and chicken manure) on yield and essential oil ratio in coriander plant, which belongs to the Umbelliferae family of *Coriandrum sativum L.* and is one of the oldest spices used by mankind. It was recommended that chemical fertilizer and chicken manure should be applied together (50:50) in terms of seed and essential oil yield. It was stated that the use of chemical fertilizer decreased with the addition of organic fertilizer. Almasi (2021) investigated the effect of different amounts of FYM (0, 15 and 25 t ha^{-1}) on coriander yield and essential oil. He stated that the effect of fertilizer on yield was significant, while essential oil yield was not significantly affected by fertilizer. Rad and Radbakht (2021) investigated the effect of organic (cattle, vermicompost, thiobacillus bacteria, mycorrhizal fungi) and chemical (N, P, K) fertilizers on the characteristics of Ducrosia anethifolia. Inoculation with thiobacillus, micorrhiza and thiobacillus+mycorrhiza resulted in higher amounts of seed yield, essential oil yield and percentage, chlorophyll a, b and total, and carotenoid. Farrokhi et al. (2021) investigated the effects of sheep manure, chemical fertilizer (80 kg ha^{-1} super phosphate + 200 kg ha^{-1} urea), fungal fertilizer (mycorrhiza) and bacterial fertilizer (*Azotobacter, Pseudomomas and Azosprillium species*) on alovera plant yield. The combination of sheep and chemical fertilizers produced better aloe vera. In addition, as an alternative to chemical fertilizers, high quality aloe vera was obtained by applying manure and biological fertilizers together. Yılmaz (2022) investigated the effect of organic and commercial fertilizers on cress (*Lepidium sativum L.).* Conventional organic fertilizers sheep manure (300 ml pot^{-1}) and chicken manure (100 ml pot^{-1}) and commercial organic fertilizers Algaren Twin (2.5 ml/L), Casolex (2.5 ml/L), Potasmin (3 ml/L) and Plantol (5 ml/L) were used. It was observed that especially chicken manure application provided a significant increase in yield and other parameters examined in cress compared to control and other treatments. Kösem (2022) investigated the effect of liquid vermicompost application (25, 50, 75 and 100%) on some agronomic traits and phenolic compounds of basil plants exposed to drought stress. Vermicompost treatments also significantly positively affected all other parameters except leaf length. Çelik (2022) determined the effects of organic (vermicompost and chicken manure) and inorganic (15:15:15 N-P-K) fertilizer applications on yield and quality factors in Izmir thyme (*Origanum onites L.).* In the study, the average plant height values were 29.06-32.5 cm and the highest value was obtained from NPK application, the average green herb yield was 105.27-164.99 kg da^{-1} and the highest value was taken from vermicompost application, the average herb yield was 51.94-81.11 kg da^{-1}, the average leaf yield was 34. 58-58.33 kg ha^{-1}, the average ratio of culm leaves was 66.46-71.8 kg ha^{-1}, the highest essential oil yield was obtained from chicken manure application with an average of 38.52-64.2 L ha^{-1}, and the highest essential oil ratio was achieved from vermicompost application with an average of 3.6-3.4%. The highest rate of carvacrol was found among the essential oil components and the carvacrol rate varied between 74.12-81.68%. The highest herb yield and leaf yield were achieved from the chicken manure application, while the lowest was obtained from the control treatment. Çelik-Kart (2022) cultivated two varieties (Heritage and Rubin) of raspberry (*Rubus idaeus L.),* which are known to contain bioactive compounds that are very beneficial for human health, in open and uncontrolled greenhouse conditions using organic fertilizers, one of the sustainable agricultural techniques, within the scope of good agricultural practices and compared the results with the data obtained from conventional fertilization. Organic farm manure (biofarm) and vermicompost were used. As a result, it was recommended to use biofarm application in open field and vermicompost application in greenhouse in terms of yield. Oğur (2022) investigated the effects of some conventional and commercial organic fertilizers on seed emergence, plant growth and yield of arugula (*Eruca vesicaria*) plants in soil and soilless media. Sheep manure (300 ml pot^{-1}) and chicken manure (100 ml pot^{-1}) were used as conventional organic fertilizers; Algaren Twin (2.5 ml/L) Casolex (2.5 ml/L), Potasmin (3 ml/L) and Plantol (5 ml/L) were used as commercial organic fertilizers. It was observed that conventional organic fertilizer applications, especially chicken manure application, provided a significant increase in yield and other parameters examined in arugula compared to control and other treatments. Erhan (2022) determined the effect of cow and sheep organic fertilizers applied at different doses on yield and some quality characteristics of fennel (*Foeniculum vulgare L*.). Cow and sheep manures were effective on many yield values, 2250 kg da^{-1} cow manure amount was recommended for yield, 2250 kg da^{-1} sheep manure amount was recommended for volatile oil main component, 1500 kg da^{-1} sheep manure amount was suggested for fatty acids. Rahimi et al. (2023) investigated the effect of organic fertilizers (vermicompost, manure compost, animal manure) and irrigation level (60, 90 and 120 mm) on vegetative growth and physiological and antioxidant activity properties of thyme plants grown under stress. They explained that thyme showed a good response to organic fertilizers under water scarcity conditions and vermicompost was the most effective of the fertilizers used. Askary et al. (2023) investigated the effect of field age (one, two and three years of farming), different levels of organic and chemical fertilizers on the yield of Saffron (*Crocus Sativus L.*), which has great cytotoxic effects on cancer cells, high nutritional value, medicinal value and anticancer properties. The highest phytochemical, antioxidant and anti-cancer properties were obtained from organic farming (organic fertilizer and high level of fertilizer use).

Many researchers have recommended the use of inorganic and organic fertilizers together. It has been stated that the use of only organic fertilizer does not provide the desired yield in most cases, but it also has a positive effect on yield. For this reason, organic fertilizer can be used if low yield quality product is desired, and if yield is a more important option, the producer can use organic and inorganic fertilizers together. The use of organic fertilizers can control the overuse of chemical fertilizers in sustainable agriculture. The use of fertilizers that are compatible with nature and suitable for optimum plant development can have positive effects on the quantity and quality indices of the plant.

As a result, it is possible to say that yield and quality vary according to the parameters such as the type of plant to be grown, ecological conditions (temperature, humidity, etc.), soil characteristics (pH, physical-chemical properties, etc.), organic fertilizer characteristics (type, amount, time of use, etc.). The optimum values of these parameters must be decided before production is realized.

Conclusion

Public health is an issue of great importance due to the increasing number of health problems every day. TABs, which we have been using since ancient times, should be produced in a quality manner. Although inorganic fertilizers increase yield, they can cause environmental pollution (deterioration of soil structure, pollution of water resources, etc.) and prevent a healthy TAB production (causing accumulation of some toxic substances, etc.) (Sönmez et al., 2008; Yaldız et al., 2019a). The use of organic fertilizers in TAB production increases plant growth, green grass, dry grass and drug yield (Yaldız et al., 2019a). In addition, healthy TAB production reduces environmental pollution and improves soil quality. For this reason, the use of organic fertilizers should be increased.

Fertilizer use in plant production is a financial burden for the producer. In addition, most producers think that the yield will increase with the increase in fertilizer dosage (Yaldız et al., 2017). Therefore, in order to overcome this problem, trainings should be provided to the relevant people and organic fertilizer production and use should be encouraged. In short, organic fertilizer should be preferred in TAB production for both human and environmental (especially soil) health.

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CHAPTER II

Experimental Investigation of Radiocesium Sorptionon Sepiolite Clay Using Batch and Column Method

Fatma Aysun UĞUR[1]

Introductıon

Nuclear energy is a clean energy source that can minimize greenhouse gases and most importantly generate electricity 24 hours a day (Kim et al. 2021). Nuclear energy has three main advantages: low-cost energy generation, carbon-free, and reliability, and two disadvantages such as nuclear waste and operation risk (Pardo et al. 2020). Advanced management of radioactive waste can minimize the aforementioned disadvantages. Radioactive waste management refers to the safe processing, storage, and disposal of

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liquid, solid, and gas discharge from nuclear industry operations to protect people and the environment. Radioactive wastes originating from industry, medicine, and nuclear research are mostly released during nuclear energy production. Whatever the source, radioactive waste must be managed safely and economically (Lau et al. 2019). Generally speaking, based on the level of radioactivity and the hazardous residence time, radioactive waste is divided into three categories: low-level waste (LLW), intermediate-level waste (ILW), and high-level waste (HLW). All LLWs and most ILWs are mature applications, while most HLWs are securely stored in dedicated facilities. Permanent disposal of HLW in deep geological deposits is considered feasible by the scientific and technical community but has not yet been adopted by civil society in many countries (Okumura et al. 2018). The activities required for properly managing radioactive waste can be divided into the following steps: minimizing the amounts generated, conditioning and packaging to ensure safe handling and protection during transport, intermediate storage, and final disposal (Adeyemo et al. 2017). Owing to the harmful effects of radiation associated with these wastes on human health and the environment, radioactive waste treatment attracts worldwide attention. Until now, radioactive waste storage systems have been used to dispose of radioactive waste worldwide. Before storing radioactive waste, it is necessary to divide it into several categories (Keçeli 2015). The form of the waste, the radioactivity level of the waste, and the half-life of the waste to be stored are essentialparameters in storage. After these separations are determined, waste warehouses are created in the determined area. These warehouses are usually natural or artificial warehouses that are far from settlements and contain clay soil (Ibrahim et al. 2013). Clay material has the property of adsorbing substances as a structure. In experimental adsorption studies, the adsorption and desorption capacities of different clay minerals are specified. Adsorption is the retention of solid, liquid, or gaseous substances on the surface of a solid (Uğur et al. 2013).

Adsorption is the most commonly applied method for solidifying liquid radioactive wastes, which pose a great

A_0	counts per minute of standard solution	
A_f	count per minute of the measured solution after sorption	
C_0	initial concentration	mol l^{-1}
C_e	equilibrium concentration of adsorbate in solution	mol l^{-1}
E	adsorption energy	kJ mol^{-1}
Ɛ	Energy	J
K	energy constant	
K_d	distribution coefficient	l kg^{-1}
k_F	Freundlich adsorption constant	$[(mg\ g^{-1})(mg\ l^{-1})^n]$
k_L	Langmuir adsorption constant	
M	mass of sepiolite clay	G
m_{total}	total amount of cesium chloride sent to column	G
N	Freundlich adsorption constant	
Q	volumetric flow rate	ml min^{-1}
q_m	amount of adsorbed substance	$molg^{-1}$
q_{total}	total adsorbed cesium quantity	Mg
R	Constant	
S	area,under the breakthrough curve	m^2
T	Time	S
T	absolute temperature	K
t_{total}	total flow time	Min
V	volume of radioactive solution	L
V_{eff}	effulent volume	L

environmental risk, to occupy less volume and reduce waste activity. When the adsorption technique is placed on the ground and around the clay storage as a water-retaining insulation material in clay storage systems of certain thicknesses, it can prevent radioactive pollution from mixing with groundwater as well as soil pollution that may occur on the ground. Therefore, various clay samples' adsorption and desorption properties should be investigated.

Nomenclature

Furthermore, adsorption is an important industrial separation technique for the purification of waste media (Tsai et al. 2009). In recent years, low-cost, easily available, large surface area, non-toxic, and high ion exchange potential clay materials have been preferred instead of commercially available adsorbents. Clays exhibit two main interesting properties: low permeability causing very slow water movements in the bedrock, and the ability to retain radionuclides via physicochemical adsorption on clay minerals (Yılmaz et al. 2013; Kalkan and Bayraktutan M. S 2008; Lazarevic et al. 2007). Many clay minerals are widely used because of their organic molecule adsorption-desorption properties (Ibrahim et al. 2013; Kumar et al. 2006; Hu et al. 2005; Tsai et al. 2009).

In general, pollutants in the form of liquid waste adhere to the surface of the adsorbent material (clay) in two dimensions, allowing the cleaning of liquid waste. The contaminants adhering to the surface may leave the surface after a certain period, which is called desorption. It is desirable that the clays used in radioactive waste storage adsorb large amounts of radioactive waste in a short time and do not desorb as long as possible (Yılmaz et al. 2013; Sharma 2012). In these storage systems, if the area where radioactive waste is stored in these storage systems interacts with groundwater, radioactivity may leak into the environment as a result of corrosion. To prevent the extension of radioactive wastes to the environment from where they are buried, it is necessary to create multi-directional barriers, both natural and artificial. Since clay minerals are used as a suitable additive in radioactive waste storage, the holding properties of radioactive elements on clay minerals have been the subject of many experimental and theoretical studies (Uğur and Turhan, 2011).

Fission products are the most important source of radioactivity emitted into the environment due to nuclear tests, accidents in nuclear reactors, and leaks from nuclear waste. Experimental studies are primarily concerned with the removal of radioactive ^{90}Sr and ^{137}Cs, the most abundant fission products of uranium. Due to their long half-lives and high fission yields, the most effective radioisotopes are ^{137}Cs(30.17 years) and ^{90}Sr (28.8 years). ^{137}Cs is one of the alkali metals, the most reactive group of metals. Among its many isotopes, the most important are ^{137}Cs and ^{134}Cs. The gamma photon energy of ^{137}Cs is 661.8keV. It is classified as moderate radiotoxicity and has high solubility. It is one of the most important radionuclides in the form of waste (Chen et al. 2011).

Long-lived radionuclides in radioactive waste are considered hazardous pollutants, and their migration with groundwater is strongly influenced by surface runoff and adsorption of geological materials. When ^{137}Cs reaches the earth's surface, it is quickly and firmly absorbed by fine soil particles absorbed (Delage et al. 2010). It is known that the presence of radioactive substances in the aquatic environment causes various health problems in humans and animals. They can be absorbed and accumulated in the human body and cause serious health effects such as cancer, organ damage, nervous system damage, and, in extreme cases, death.

Sepiolite, as an adsorptive material in experiments, has widespread use among adsorbent clays due to its high surface area, fibrous and porous structure, and physicochemical activity. In recent years, it has been observed that clay minerals have received intense interest in environmental applications. While Spain is the largest sepiolite reserve in the world, Turkey ranks second (Al-Asheh et al. 2003).

In this study, the adsorption study of CsCI solution with moderate radioactivity was carried out on sepiolite samples received from Denizli province in Turkey. In experimental studies, two different methods (batch and column) were used for adsorption. In both adsorption methods, the experimental results were obtained by graphical and mathematical methods and then compared with the results.

Material and Methods

Adsorbent and adsorban

A sepiolite-based clay supplied from The Denizli region of Turkey was used as adsorbent for ^{137}Cs removal. The natural clay mineral used in this study was obtained from the Turkish General Directorate of Mineral Research and Exploration (MTA). Sepiolite is a hydrated clay mineral that attracts attention with its fibrous structure. The presence of micropores and channels, long and fine grains, high surface area, forms the basis for the accommodation of various organic and inorganic ions (Tsai et al. 2009). Sepiolite is a natural, fibrous clay mineral with 0.37 × 1.06 nm fine microporous channels running parallel to the length of the fibers. The size of the fibers is variable, but an average of 800 × 25 × 4 nm is typical, thus resulting in a solid with an outer surface area of the same size as the area of micropores. The structure of sepiolite is similar to that of other 2:1 trioctahedral silicates such as talc, but it has discontinuities and reversals of silica layers that give rise to structural tunnels and blocks. In the inner blocks, all the corners of the silica tetrahedral are connected to theadjacent blocks, but in the outer blocks, some corners are Si atoms attached to hydroxyls (Si-OH)(Pradas et al. 2005). Sepiolite is accumulated in two different structures in nature. The first of these; is alpha sepiolite resembling sea foam in the form of amorphous, compact, and massive nodules known as meerschaum, and the latter; beta sepiolite occurs as small, flat, and round particles or amorphous aggregate (Aksu and Gönen 2004). Alpha sepiolite is in tuber form and suitable for practical and commercial processing. Beta sepiolite has a layered structure. Sepiolite, which accumulates in two different polymorphic structures, differs from each other in terms of basic elements and physical properties (Andrello and Appoloni 2004). This unique structure allows organic and inorganic species to penetrate the structure and gives sepiolite industrial importance in adsorptive, rheological, and catalytic applications. Its hardness is around 2-2.5, and its color can be white, pinkish-white, or yellowish. These porous samples, which look like earth or paraffin, can float on water.

Sepiolite may contain aluminum, Fe^{+2}, Fe^{+3}, and Ni. It gelatinizes with HCl. When compact, its texture is smooth, but the refractive index is smaller. It is found in nature as a decomposition product of serpentines. Palygorskite is an orthorhombic or monoclinic chain unit with a sepiolite-like crystal structure. It appears as fibrous crystals in the electron microscope. When wet it is white, gray-white, yellowish-white, and gray-green (Stumm 1995).

All chemicals were analytical grade (Merck), while the radionuclide source ^{137}Cs was obtained from Amersham (U.K). The adsorbent used during the experiment was prepared with the radioactive tracer ^{137}Cs and CsCI at concentrations ranging from $1.68x10^{-4}Ml^{-1}$ to $5.88x10^{-4}Ml^{-1}$. Due to the long half-life, vertical decay correction was not performed in the experiments.

Batch method

The sorption experiment was carried out using a batch method under normal laboratory conditions (pH= 6.4, T = 20ºC, pressure=1013hPa). 0.02 g of absorbent sample of each particle size and 5 ml of $^{137}CsCl$ solution were combined in a 20 ml shaking tube. The mixture was then shaken periodically in selected time intervals in a thermostatic water bath. The aliquots of solution were taken for activity measurement after centrifugation at 3500 rpm for 30 min. The activity of ^{137}Cs in each aliquot sample was measured using a gamma-ray spectrometer with coaxial high-purity germanium (Hp-Ge) detector which has a relative efficiency of 16% and an energy resolution of 1.9 keV at the 1332.5 keV of ^{60}Co (McKay et al. 1997) (Reed and Cline 1994).

Batch methods calculations

Experimental Calculations

After the experimental results were obtained, *Ads%* (1), K_d (2), and X_m (3)values were obtained with the formula (Keçeli 2015).

$$\% Ads = \left(\frac{A_0 - A_f}{A_0}\right) \times 100 \qquad (1)$$

$A_0 = Counts\ per\ minute\ of\ standard\ solution$

$A_f = Count\ per\ minute\ of\ the\ measured\ solution\ after\ sorption$

$$K_d = \left(\frac{A_0 - A_f}{A_0}\right) \frac{V}{m} \qquad (2)$$

$K_d = Distribution\ Coefficient\ (lkg^{-1})$

$V = Volume\ of\ radioactive\ solution (ml)$

$m = Mass\ of\ sepiolite\ clay\ (g)$

$$q_m = \%Ads \left(C_0\ \frac{V}{m}\right) \qquad (3)$$

$q_m = Amount\ of\ adsorbed\ substance (molg^{-1})$

$C_0 = Initial\ concentration (moll^{-1})$

Freundlich equation

Freundlich isotherm was calculated by equation (4)

$$q_e = k_F C_e^{1/n} \qquad (4)$$

$q_e = Amount\ of\ adsorbed\ substance (molg^{-1})$

C_e =*Equilibrium concentration of adsorbate(solution) in solution* $(moll^{-1})$

The Freundlich isotherm does not give the maximum amount of adsorbed material. The constants k_F and n are related to the adsorptive bond strength and the distribution of bond strengths. If this equation is linearized so that the constants k_F and n can be easily obtained.

$$lnq_e = lnk_F + 1/nlnC_e \quad (5)$$

The slope of the graph drawn between lnq_e and lnC_e gives the constant n and the cutoff gives the constant k_F. When n< 1, the binding energy decreases with increasing surface concentration. This is due to the existence of different surface locations. As the amount of substance adsorbed on the surface increases, these different surface locations will be at the strongest binding sites, then at the weaker binding sites. The average bond strength will decrease. n<1; indicates that adsorption is preferred adsorption (Assemi and Erten 1994)(Palle et al. 2022).

Langmuir equation

It is used in cases of monolayer physical adsorption and adsorption from solution. Langmuir adsorption isotherm; It is effective when the surface contains a limited number of settlements, there is monolayer adsorption on the surface, and there is no adsorbate-adsorbate interaction on the surface (Zhang et al. 2021).

The Langmuir equation is given by equation (6).

$$q_e = \frac{q_m k_L C_e}{1+k_L C_e} \quad (6)$$

To find the constants $K_l$and C_e, this equation can be converted to equation (7).

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \quad (7)$$

The graph drawn between C_e and Ce/q_e gives a straight line. q_m and k_L are found from the slope and cut points of the east, respectively (McKay et al. 1997).

If we briefly summarize the assumptions made by the Langmuir isotherm;

• that the adsorbent surface consists of the same type of sites with constant energy,

• there is no interaction between adsorbed species,

• It assumes that the adsorbent surface is coated as a single layer when it reaches saturation.

D-R equations

D-R adsorption isotherms are used to calculate the adsorption energy. From the slope of these isotherms, the adsorption energy is found equation 9. These energy values give information about the adsorption mechanism. The D-R adsorption energy is defined as the energy released during the adsorbing of 1 mole of ions by the solution by the adsorbent.

$$q_{e=}\ q_m \exp\left(-K\varepsilon^2\right) \tag{8}$$
$$\varepsilon = RTexp\left(1+\frac{1}{C_e}\right) \tag{9}$$

C_e, is the solution concentration at equilibrium,
R, is the gas constant ($8{,}314x10^{-3} kJmol^{-1}K^{-1}$),
T, is the absolute temperature (K). If equation (8) is linearized;

$$lnq_e = lnq_m - K\varepsilon^2 \tag{10}$$

q_e
$= the\ equilibrium\ amount\ of\ solute\ adsorbed\ per\ unit\ weight\ of\ solid$
$q_m = the\ adsorption\ capacity\ of\ the\ adsorbent\ (mol.g^{-1})$

K
$= the\ constant\ related\ to\ the\ mean\ adsorption\ energy\ (E)$
$\varepsilon = the\ Polanyi\ potential$

A line is obtained from the graph drawn between $\mathcal{E}^2$ and lnq_e. K and q_m values are found from the slope and intersection point of the line, respectively. The K value is used to find the adsorption energy E ($kJmol^{-1}$).

$$E = (-2K)^{-1/2} \quad (11)$$

The adsorption energy value E gives information about the type of adsorption process. 2 types

adsorption can occur: physical and chemical adsorption. Physically equilibrium in adsorption is usually reached quickly and adhesion is reversible. Because it is necessary energy is low. If E<8 $kJmol^{-1}$, the adsorption process has a physical structure. Value of E between 8-16 kJmol-^{1}, the adsorption is in the form of ion-exchange. When E>16A very strong adhesion, which we call specific adsorption, takes place (Keçeli 2015).

Column method

Continuous fixed bed column studies were carried out in a fixed bed column reactor with an internal diameter of 2 cm and a column height of 20 cm. The adsorbent was placed on the column supported by glass wool from the top and bottom. CsCI solution at a concentration of $1.68x10^{-4}Ml^{-1}$ and $5.88x10^{-4}Ml^{-1}$ was fed to the bottom of the column with a Watson Marlow 120S brand peristaltic pump at a constant flow rate (20 ml/min) until a breakthrough curve was formed (Barragán-Peña et al. 2021). Samples were collected from the top of the column at certain time intervals at the exit and were measured at a gamma-ray spectrometer with coaxial high-purity germanium (HP-Ge) detector which has a relative efficiency of 16% and an energy resolution of 1.9 keV at the 1332. 5 keV of ^{60}Co (Uğur et al. 2013).

The performance of the column experiment is described through the concept of the breakthrough appearance and the shape of the breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining an adsorption column's operation and dynamic response. The general position of the breakthrough curve along the volume axis depends on the capacity of the column concening the feed concentration and flow rate. The breakthrough curve would be a step function for favorable separations, there would be an instantaneous jump in the effluent concentration from zero to the feed concentration at the moment the column capacity is reached (Assemi and Erten 1994; Pradas et al. 2005; Tsai et al. 2009) (Cornell 1993) (Aksu and Gönen 2004).

Column calculations

The breakthrough curves show the loading behavior of ^{137}Cs to be removed from the solution in a column and is usually expressed in terms of adsorbed cesium chloride concentration

(C_{ad} = inlet cesium chloride concentration (C_0) - Outlet cesium chloride concentration (C)) or normalized concentration, defined as the ratio of effluent cesium chloride concentration to inlet cesium chloride concentration (C/C_0) as a function of time or volume of effluent for a given bed height (Aksu and Gönen 2004). Effluent volume (V_{eff}) can be calculated from eq. (12).

$$V_{eff} = Qt_{total} \quad (12)$$

Where t_{total} and Q are the total flow time (min) and volumetric flow rate (ml min^{-1}). The area under the breakthrough curve (S) obtained by integrating the adsorbed concentration (C_{ad}; mg l^{-1}) versus t(hour) plot can be used to find the total adsorbed cesium quantity maximum column capacity). The total adsorbed cesium quantity (q_{total}; mg) in the column for a given feed concentration and flow rate is calculated from Eq. (13).

$$q_{total} = \frac{QS}{1000} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_{ad}\, dt \tag{13}$$

The total amount of cesium chloride sent to column (m_{total}) is calculated from Eq. (14).

$$m_{total} = \frac{C_0 Q t_{total}}{1000} \tag{14}$$

The total removal percent of cesium chloride (Column performance) concerning flow volume can be also found from the ratio of the total adsorbed quantity of cesium chloride (q_{total}) to the total amount of cesium chloride sent to column (m_{total}) Eq. (15).

$$\text{Total removal } \% = \frac{q_{total}}{m_{total}} \times 100 \tag{15}$$

RESULTS

Sepiolite, which is compact and spongy in structure, occurs in clusters. The elementary concentration of sepiolite clay naturally obtained from the Denizli region of Turkey was obtained by using X-ray fluorescence (XRF) (RIGAKU RIX2000) and iusing X-ray fluorescence (XRF) (RIGAKU RIX2000), as shown in Table 1. The chemical analysis of the dry adsorbent yielded the following weight percentages: SiO_2: 53.5%, MgO: 22.4%, Al_2O_3: 2.09%, CaO: 0.29%, Fe_2O_3: 0,55%, Na_2O: 0.16%, K_2O: 0.65%, MnO: 0.04%, TiO_2: 0.15%, P_2O_5: 0.05%, SO_3:0.03%, F: 0.81%, loss on ignition: 19.1% (Table 1).

XRD pattern of adsorbent presented in Fig. 1 showed that it contains 87% sepiolite, 12% palygorskite, and 1% other impurities such as CaO and MgO.

In batch experiments; first of all, it is necessary to determine the time to reach equilibrium. For this, 0.02 g of sepiolite samples in

120, 100, 70, 45, and 30-micrometer sizes are taken, and $4.20x10^{-4}$ (mol. l^{-1}) CsCI solution is added to each, in a thermostated shaker (GFL 1083) for periods ranging from 1 minute to 16 hours, agitated. Then, the liquid and solid phases were separated by centrifugation at 3500 rpm for 30 minutes and filtered. 2 ml of the filtered solution was taken and put into plexiglass tubes for counting. The CsCI activity of the resulting solution was counted in gamma spectrometry. This process was repeated for all clay sizes. Ads% values were obtained from Eq.1, in Figure 2, the shaking time was obtained by plotting the Ads % versus the timegraph. According to the results of the time graph with ads % in all sepiolite clay sizes, it was observed that ads % did not change after 60 minutes. Therefore, the shaking time was taken as 60 minutes in all adsorption experiments.

In the adsorption study of the CsCI solution with all dimensions of the sepiolite clay, the amount of clay was changed by keeping the volume constant to find the solid/liquid ratio. 5 ml of $4.20x10^{-4}$mol CsCI solution at 20°C was added to the clay samples weighed 0.01g, 0.02g, 0.04g, 0.1g, 0.2g, 0.4g, and the shaking time was 60 minutes, and the batch method was used. The graph drawn between LogKd% and V/m showed that the Adsorption % did not change after the value of V/m of 250 ml. g^{-1}(Figure 3a). For the batch experiments, it was decided to take the solid-liquid ratio as 250 mlg^{-1}.

In addition, after the K_d value has been found, the loading curves drawn between the log K_d at 20ºC and the concentrations in the solid for the clay sample are given in Figure 3.b.

Experimental results were applied to the linear form of the Freundlich isotherm. The n_F and $k$constants were calculated from the slope and ordinate cutoff value of the graphs drawn between lnq_e and lnC_e (Table 2). For CsCI adsorption, n<1 was found (Figure 4)

When the adsorption results were applied to the linear form of the Langmuir adsorption isotherm, adsorption equilibrium constant k_L, adsorption capacity q_m and correlation coefficients were found from the slopes and ordinate cutoff values ofthe lines drawn between C_e / q_e and C_e (Table 3). In addition, the maximum amount of adsorbed substance was found at a k_L value (Figure 5).

The linear shape of the D-R isotherm was obtained by plotting between Lnq_e and $\mathcal{E}^2$. In these graphs, adsorption capacity q_m and adsorption energy constant K were obtained from the slope and shear point of the lines (Figure 6). (Table 4).

Developing a model to accurately describe the dynamic behavior of adsorption in a fixed bed system is inherently difficult. The successful design of a column adsorption process requires the prediction of the concentration-time shape or breakthrough curve for the effluent. Since the concentration of the adsorbate as the feed moves through the bed, the process does not operate at a steady state (Aksu and Gönen 2004; Stumm 1995; Ibrahim et al. 2013).

While performing the column experiments, the breakthrough curve was obtained from the graphs drawn between the flow time t (hour) of the solution passing through the column and C_t / C_0 for two different concentrations and three different particle sizes. In these curves, depending on the initial concentration of the solution, it was observed that the percentage of transition at the high initial concentration ($5.88x10^{-4}$M) was around 80% and around 40% at low concentration ($1,68x10^{-4}$M) (Figure 7) (Table 5).

With the same experimental results, the variation of the outlet volume V_{eff} *(l)*versus $C_t/C_0$was also graphically obtained for two different solution concentrations ($5.88x10^{-4}$-$1.68x10^{-4}$M), and three different particle sizes. The results of these graphs are given in Table 6. The sorption capacity has a big impact on the position of the breakthrough curve. By increasing the sorption capacity the breakthrough curve will be shifted to longer breakthrough times (to the right) because the adsorbent will hold back more adsorptive molecules. This is not the case if the sorption kinetics on the sample is too slow and a spontaneous breakthrough occurs.

In contrast to the sorption capacity, the sorption kinetics, affect the shape of the breakthrough curve. For faster kinetics the breakthrough curve becomes steeper (sharper) and the mass transfer zone will be smaller. A fast mass transfer from the gas phase to the adsorption sites leads to short local equilibrum times and a smaller concentration front enlargement.

In the 1st breakthrough curve (Figure 7), obtained in this study, the transition to the mass transfer region started after about two hours when the time parameter is examined. Around 20 hours, the transition to the saturated region occurred due to the saturation of the solution. Experiments were continued for up to 45 hours. However, no change was observed in the saturation rate of the solution between 20 hours and 45 hours. Experiments were terminated after 45 hours.

In this study's 2nd breakthrough curve (Figure 8), the output volume transitioned to the mass transfer region after 500ml. The steepness of the curve; mass transfer are affected by axial distribution, isotherm shape, heat effects and heat transfers. The region after 1800 ml can be described as a saturated region at all sepiolite sizes and both concentrations. A determination of saturation capacity is found with in this region. The unsaturated region is observed around the 0-500 ml volume. In industrial applications, keeping the unsaturated region short is preferred by optimizing the target, adsorbent, particle size and process conditions.

DISCUSSION

In batch adsorption experiments, at the stage of determining the solid/liquid ratio, initially, K_d was determined depending on *V/m*, until it increased rapidly and this increase reached the maximum (250ml/g) of *V/m* continues, after this value, K_d does not change seen, although *V/m* increases. This result shows that clay samples get better in liquid as the volume to mass ratio increases. It can be explained that it is dispersed and adsorbed more on the inner surfaces of the solid. Increasing values of *V/m* and K_d did not change the results after all suitable surfaces were coated with cesium (Assemi & Erten, 1994).

Since it is in the chlorite group as a mineral, it is possible to observe the typical properties of this group in cesium adsorption. Moreover, palygorskite (attapulgite) found in sepiolite is in the mixed layer clay group. It is chain structured. It contains small amounts of Fe^{+2}, Fe^{+3} and Ca besides Mg, chemically. The presence of Ca in terms of cation exchange provides an advantage (Pradas et al., 2005).

Soluble compounds have a strong affinity for CsCI solution. For adsorption to occur, the molecule must be separated from its solvent, and adhere to the adsorbent. The stronger the solute is attached to the solvent system, the weaker its hydrophobic properties, the less the adsorption. Inorganic compounds are generally less hydrophobic due to their hydrophilic nature, preferentially more adsorbed. However, some easily soluble compounds are sometimes easily adsorbed, while many poorly soluble compounds are not easily adsorbed (Lazarevic et al. 2007). This is seen in the variation between initial concentration(C_0) and K(d) in Fig 3b. While the CsCl concentration ranges from $1.68x10^{-4}$ M to $5.88x10^{-4}$ M, the change in K_d value is not linear.

Figure 4 shows the Freundlich isotherm values of clay for five different clay sizes. In this clay sample of 120µm, very small shifts from the isotherm in 100µm and 70µm dimensions were observed. This result shows that the adsorption sites are wider in small-sized and homogeneous clay samples. But R^2 was found to be very close to 100% in these samples.

Langmuir adsorption isotherm of clay is shown in Figure 5. The results from the graph are summarized in Table 3. According to the experimental results, as the particle size of the clay decreases, the surface area expands. As the particle size of the clay decreased, the adsorption capacity q_m, the maximum amount of adsorbed material k_L and R values increased.

Table 4, summarizes the D-R isotherm results. As the clay size decreases, the adsorption capacity q_m, the energy constant K, and the energy value E increase. In the D-R isotherm, the variation between q_m and energy is seen for all clay sizes, even at very close values of the CsCl solution. No temperature-dependent experiments were performed in the D-R isotherm, however, positive energy values prove that the process is exothermic, spontaneous, and physical adsorption. Physical adsorption occurs due to Van der Waals forces. It is among the most important types of adsorption. Physical adsorption can occur when the low temperature range is sufficient for weak and reversible ligaments. Indeed, the adsorbed component the adsorbed molecules desorb with the change of their concentration in the solution. Adsorptionit is multi-layered. It is easy to regenerate.

The column studies used the lowest and highest CsCI concentrations used in the batch studies. The amount of adsorbate (clay) used in the column experiments was taken as 5g. During these experiments, the relationships between effective volume and Ct/C_0 and between time and C/C_0 were determined.

The flow rate of the solution from the column was observed for each sample. Although the flow rate varies from clay to clay, it has been observed that the flow rate slows down as the clay size gets smaller. Because as the clay size decreases, the surface area expands and traps more solution within itself. Therefore, a long time and solution were required to reach the initial concentration (equilibrium concentration). At high CsCI concentrations, the amount of substance adsorbed in the column, m_{top}, is less than the amount of substance adsorbed at low concentrations was observed to be lower. At high concentrations, the volume of solution used to reach initial activity is smaller than at low concentrations. Most of the available information indicates that the adsorption percentage decreases as the cesium concentration increases. The percentage of cesium adsorbed depends on the Cs+ ion concentration in the solution. High concentrations (>0.1M Cs) retention by smooth leaching, particle control mechanism; at low concentrations, it walks with a film mechanism (Tsai et al. 2009). Low cesium concentrations (<10-8M, actual limits vary from mineral to mineral) the distribution coefficient is independent of the cesium concentration. At high cesium concentrations, the adsorption is not linear, that is, the retention is not proportional to the cesium concentration (Cornell 1993).

CONCLUSIONS

The present study aimed to investigate the adsorption behavior of ^{137}Cs on sepiolite clay using both the bath and column methods. Despite the use of two CsCI solutions that were very similar in terms of radioactivity, the results obtained from the adsorption experiments were remarkably significant. The findings indicated that the adsorption capacity of sepiolite clay was influenced by the particle size, with the smallest particle size showing the highest adsorption capacity. This suggests that sepiolite clay can be a promising insulation material in radioactive waste storage systems, as it can effectively adsorb radioactive cesium and prevent it from leaching into the environment. The results of this study contribute to the understanding of the adsorption behavior of ^{137}Cs on sepiolite clay and provide valuable insights for the development of efficient and sustainable radioactive waste management strategies.

Table 1. Chemical analysis of the sepiolite sample investigated in this study

[a]LOI: lose in ignition

Composition	SiO_2	MgO	Al_2O_3	CaO	Fe_2O_3	Na_2O	K_2O	MnO	TiO_2	P_2O_5	SO_3	F	LOI[a]
Content(wt%)	53.5	22.4	2.09	0.29	0.55	0.16	0.65	0.04	0.15	0.05	0.03	0.81	19.1

Table 2. Freundlich Isotherm Results

Size(μm)	k(mg l^{-1})	n	R^2
120	2.77	0.17	0.976
100	3.10	0.29	0.981
70	3.16	0.24	0.989
45	3.66	0.22	0.983
30	3.75	0.17	0.983

Table 3. Langmuir Isotherm Results

Size(μm)	q_m(mol g^{-1})	k_L	R^2
120	9.8	0.023	0.965
100	13	0.025	0.997
70	18	0.042	0.996
45	19.7	0.049	0.988
30	23.5	0.062	0.993

Table 4. D-R Isotherm Results

Size(μm)	q_m(mol g^{-1})	EE(KJ mol^{-1})	R^2
120	0.09	4.47	0.996
100	0.20	5.47	0.997
70	0.41	5.47	0.998

45	*0.53*	*5.47*	*0.997*
30	*0.61*	*5.47*	*0.996*

Table 5. Breakthrough curve results 1

m(g)	***size(μm)***	***C_0(mol l^{-1})***	***t(hour)***	***V_{eff} (l)***
5	*100*	*$1.68x10^{-4}$*	*20*	*0.35*
5	*70*	*$1.68x10^{-4}$*	*20*	*0.37*
5	*30*	*$1.68x10^{-4}$*	*20*	*0.39*
5	*100*	*$5.88x10^{-4}$*	*20*	*0.66*
5	*70*	*$5.88x10^{-4}$*	*20*	*0.74*
5	*30*	*$5.88x10^{-4}$*	*20*	*0.78*

Table 6. Breakthrough curve results 2

m(g)	***size(μm)***	***C_0(mgl^{-1})***	***Q(m dk^{-1})***	***q_{top}(mg)***	***m_{top}(mg)***	***%R***
5	*100*	*$1.68x10^{-4}$*	*20*	*4.40*	*15*	*30*
5	*70*	*$1.68x10^{-4}$*	*20*	*4.70*	*15*	*31*
5	*30*	*$1.68x10^{-4}$*	*20*	*5.16*	*15*	*34*
5	*100*	*$5.88x10^{-4}$*	*20*	*31*	*53*	*59*
5	*70*	*$5.88x10^{-4}$*	*20*	*34*	*53*	*64*
5	*30*	*$5.88x10^{-4}$*	*20*	*36*	*53*	*68*

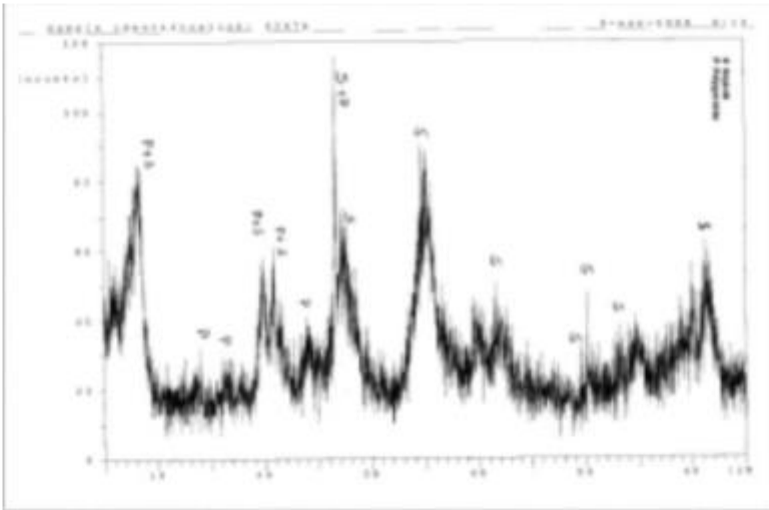

Fig. 1 XRD analysis of sepiolite clay

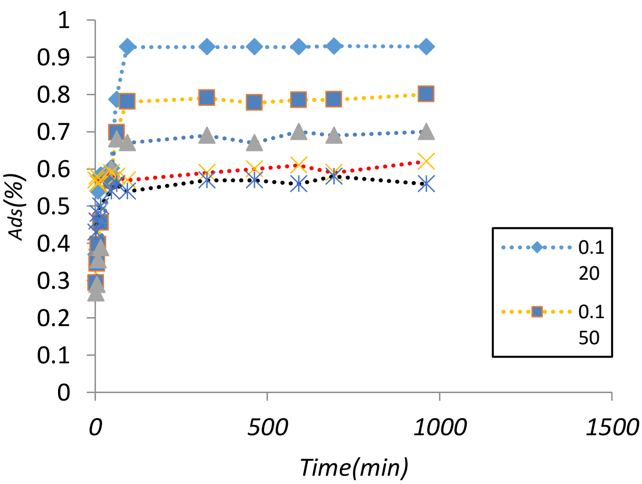

Fig.2 Finding the time to reach equilibrium

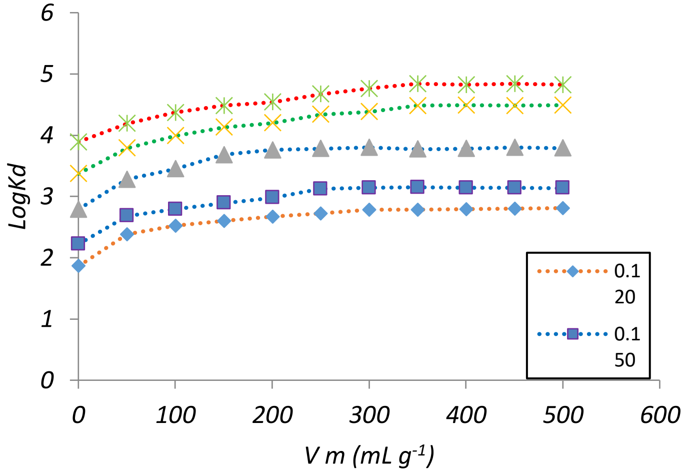

Fig.3a Adsorption of sepiolite clay with CsCl solution variation of distribution coefficient Kd with V/m ratio

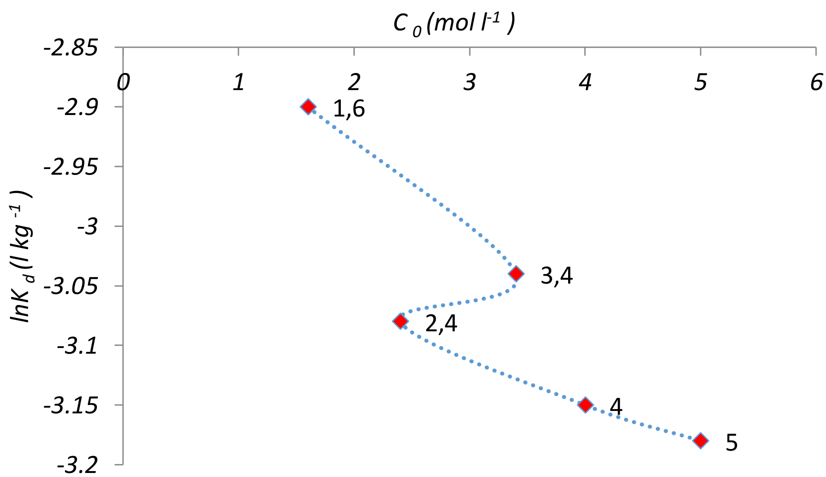

Fig.3b Adsorption of sepiolite clay with CsCl solution variation of distribution coefficient $\ln K_d$ with C_0 ratio

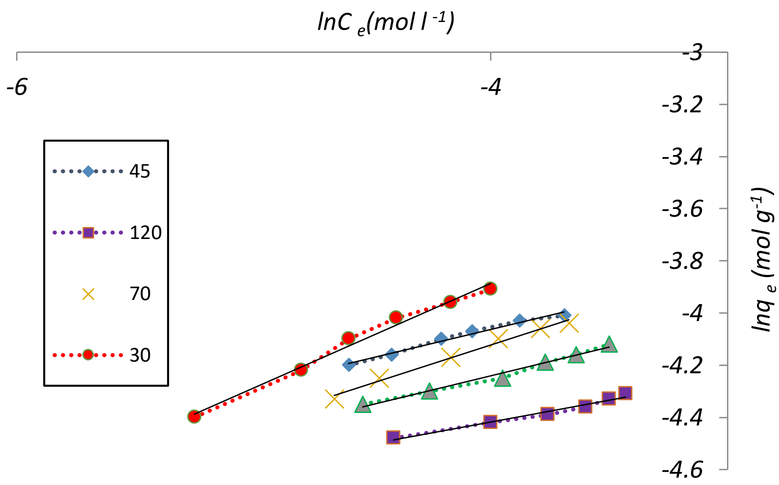

Fig.4 Freundlich Isotherm of sepiolite clay in five different sizes

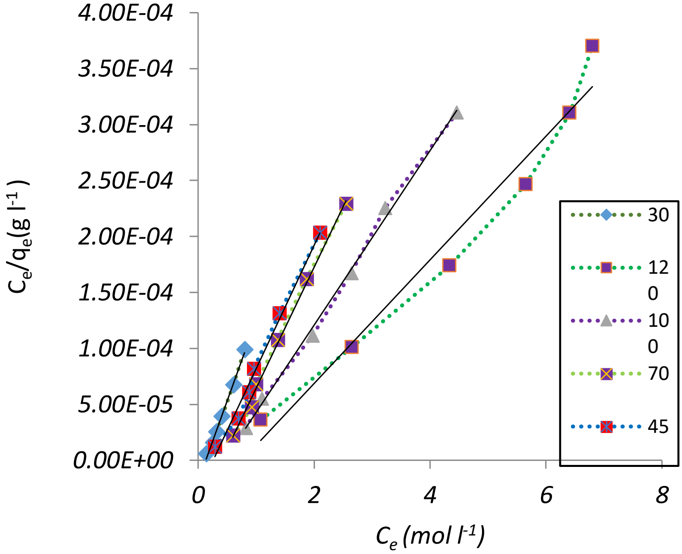

Fig. 5 Langmuir Isotherm of Sepiolite clay in five different sizes

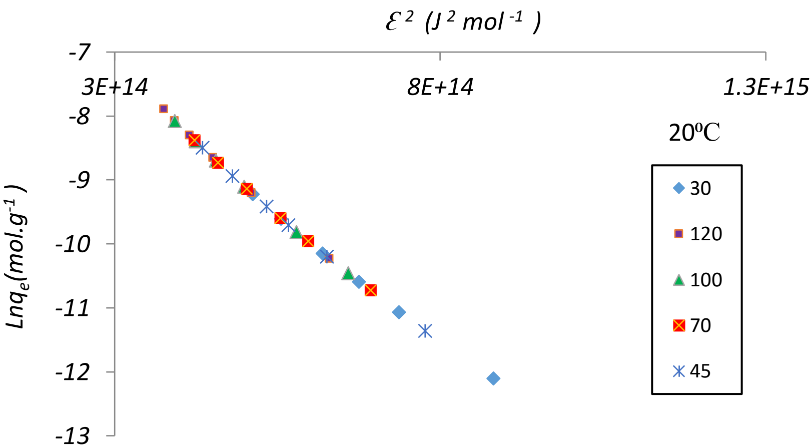

Fig. 6 D-R Isotherm of Sepiolite clay in five different sizes

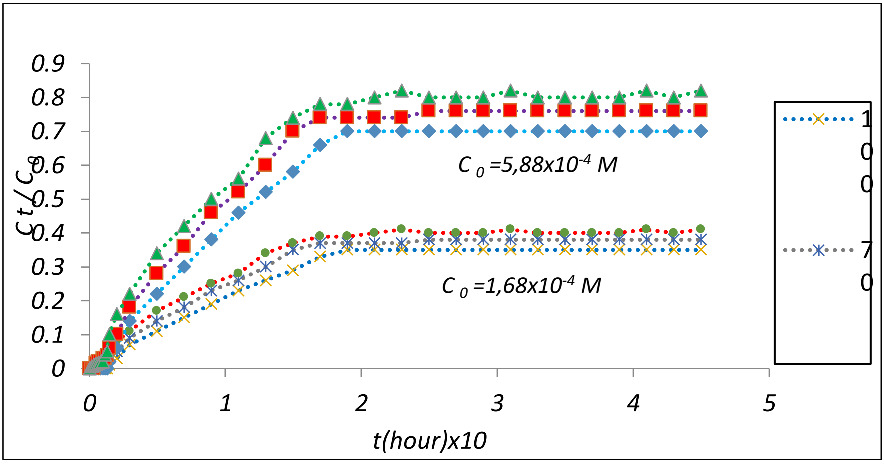

Fig .7 Time and C_t /C_0 dependent the breakthrough curve for two different initial concentrations (5,88.10^{-4}M and 1,68.10^{-4}M) and three different clay sizes

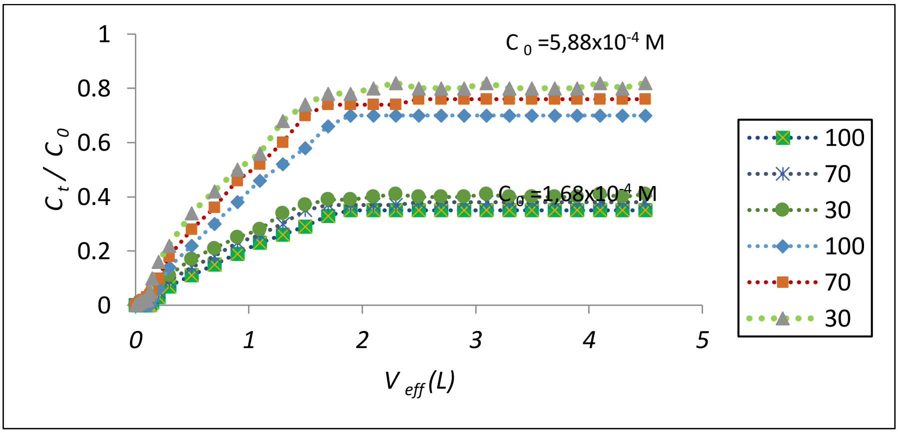

Fig .8 The effulent volume and C_t /C_0 dependent the breakthrough curve for two different initial concentrations (5,88.10^{-4}M and 1,68.10^{-4}M) and three different clay sizes.

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CHAPTER III

Toxicity Assessment Of Cypermethrin İn Chub *Squalius Orientalis* Spermatozoa: Oxidative Stress And Sperm Quality

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Introduction

The pesticide Cypermethrin (CYP) is heavily applied in agricultural practices as one of most-used chemicals in the world due

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to be broad spectrum pyrethroid. The pesticide is commonly detected in water although it is banned. CYP and its byproducts resulting from industrial, domestic and agricultural activities enter to water sources with different ways (groundwater, drainage, run-off, forest-spraying procedures, evapotranspiration, rainwater, accidental overspray) and non-target aquatic animals are negatively influenced by their interactions with chemical agents or contaminants. In surface water, the realistic concentration of CYP has been revealed between 0.100 and 1.000 µg/L (Kumari et al., 2007) while it can reach to 2.8 µg/L (Jindal and Sharma, 2019). The reported 96 h LC50 values of CYP in fish were in the range of 0.7 and 350 µg/L (URL-1, 2008; Sarıkaya, 2009).

The prediction of *in vivo* toxicity could be realized by means of *in vitro* assays and the toxicity mechanisms of pollutants. The monitoring of contaminated areas could be realized *in vitro* evaluation with sperm cells as a usefully tool (Repetto et al., 2000, Jonsson and Aoyama, 2007). The reactive oxygen species (ROS) overproduction and oxidative stress occur when spermatozoa were exposed to contaminants (Kocabaş et al., 2020). Particularly, the excessive ROS production cause impairment in sperm quality and structure (Amidi et al. 2016). Moreover, ROS-mediated attack cause lipid peroxidation due to contain a high amount of PUFAs (polyunsaturated fatty acids) of sperm cells (Sharma and Agarwal 1996). Within this context, CYP-induced changes were evaluated on quality and oxidative stress of *Squalius oriantalis* spermatozoa.

The chub (*S. oriantalis*) is Cyprinid fish species. In barbel zone, *S. orientalis* populations are abundant naturally. As model organism, S. orientalis is used in toxicity tests owing to be bio-indicator species (Kupren et al., 2015). Hence, we selected the species as test organisms for our experiments. Thus far, *in vitro* impacts of CYP on sperm cells have been only conducted in *Oncorhynchus mykiss* (Kutluyer et al., 2016) and *Salmo coruhensis* (Kutluyer et al. 2018). Thus far, there is no information about changes of CYP on sperm quality of *S. oriantalis*. Moreover, fertilization rate depends on sperm quality. For these reasons, pollutants can cause adverse effects on embryonic and larval development. The presented study objected to investigate CYP-induced changes on quality and oxidative stress indices of *S. oriantalis* spermatozoa.

Material and methods

Test chemicals and reagents

All chemicals and Cypermethrin (C22H19Cl2NO3, 99.5 % of purity) were provided by Sigma-Aldrich (St. Louis, MO, USA). CYP was dissolved in Dimethyl sulfoxide (1 mg/L) and added to an immobilization medium. Until analysis, stock solutions were kept at 4°C in the dark

Obtainment of experimental animals

The sexually mature chub *S. oriantalis* (n=10, 2-3 years old) were obtained from wild with electro-shocker during spawning period. All animal procedures were approved by our institute ethical committee (protocol number 2017/8). An aesthetic (Benzocaine, 0.5 mg/l) was applied to fish for stripping. For sperm collection, 2.0 mL tubes were used after gentle pressure abdominally. The contamination of sperm samples was avoided by drying the abdominal area. Samples were stored on crush ice (4–6°C) for analysis.

CYP exposure

The medium [NaCl (75 mM), $NaHCO_3$ (2.3 mM), $CaCl_2$ (1.5 mM), and $MgCl_2$ (0.4 mM), KCl (83 mM)] was used for immobilization of the pooled sperm. The dilution ratio was 1:5 (semen:extender). For exposure experiments, different doses (1 μg/l, 2 μg/l and 4 μg/l) of CYP were applied to spermatozoa (n=6) for 2 h.

Sperm analysis

Sperm analyses (fresh and post-exposure) were realized with SCA (Sperm Class Analyzer system) (Microptic S.L., Barcelona, Spain). The solution (0.3% NaCl) was activated of sperm cells. The percent of motile spermatozoa (%) was described as the motility rate. The motility duration was determined as the time complete stopping movement.

Biochemical assays

LD5–2B centrifuge was used for centrifugation (3000×g and 4°C for 15 min) of the sperm samples and then KCl (1.15%, 1:10 ratio) was used homogenization in an ice bath of the pellets. Thiobarbituric acid reacting substances (TBARS) was determined as described by Placer et al. (1966) for lipid peroxidation. The amount of total protein was assessed as described by Lowry (1951). Assay Kits (CAYMAN, Chemical Company, Michigan, ABD) were used as described by the manufacturer guidelines for analysis of level of MDA (10009055), the activity of SOD (706002), GPx and CAT (707002). The used absorbance for TBARS (Thiobarbituric Acid Reactive Substances), SOD, CAT and GPx were 532, 560, 240 and 412 nm, respectively.

Data analysis

Results were given as mean ± SD (standard deviation) and analyzed with SPSS (14.0). Variance analysis (One-way ANOVA) was used for statistical comparison, followed by posthoc Duncan test to assess the differences between exposed groups and control. The Kruskal–Wallis variance analysis was performed for the nonparametric data. All analyses were realized in triplicate and, the significance level was $p<0.05$.

Results and Discussion

The percentage (%) and duration (s) of motile sperm cells are given in Figure 1. Movement rate of sperm cells significantly reduced after CYP exposure ($p=0.000$, $p<0.05$). A reduction in motility duration was determined in exposed groups ($p=0.000$, $p<0.05$).

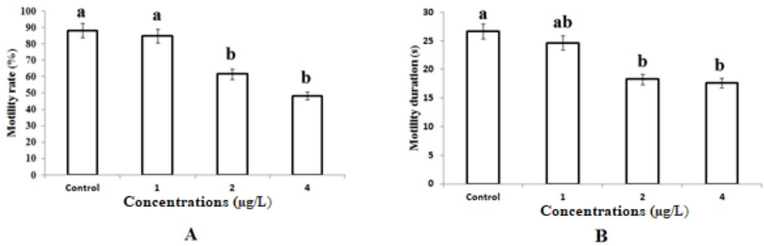

Figure 1. The effects of CYP on spermatozoa A) motility rate (%) and B) motility duration (s) in Squalius oriantalis (n = 6). Data are presented as means ± SD. Superscript letters (a, b, c) indicate significant differences.

Figure 2 shows lipid peroxidation (MDA) and the enzymatic activities (GSH-Px, SOD and CAT). Our data indicated that GSH-Px and SOD activity of *S. oriantalis* spermatozoa declined by increasing CYP doses ($P < 0.05$) while CAT activity and MDA levels increased ($P < 0.05$).

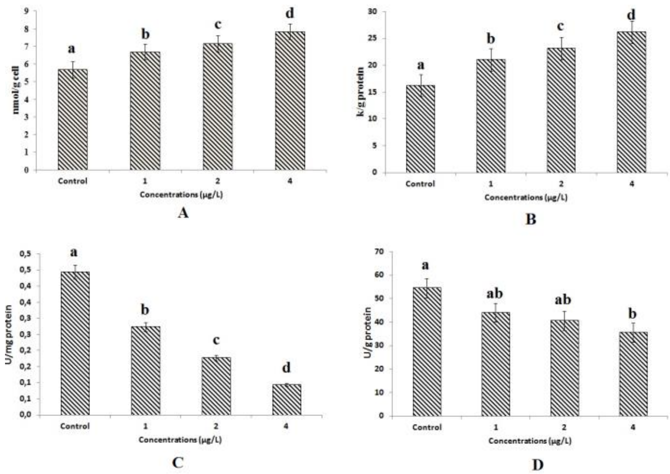

Figure 2. The effects of CYP on spermatozoa a) MDA, b) CAT, c) SOD and d) GSH-Px in Squalius oriantalis (n = 6). Data are presented as means ± SD. Superscript letters (a, b, c) indicate significant differences.

In previous studies, disruption in DNA integrity, disorders in sperm structure and morphology, and changes in adenosine triphosphate content after exposure to pollutants have been reported by researchers in different fish species (Kocabaş et al., 2020). In particular, CYP poses a serious threat for sperm function and quality of aquatic animals. In support, Kutluyer and colleagues (2016, 2018) reported CYP-induced adverse effects on percentage of motile cells and duration of motility of *O. mykiss* and *S. coruhensis*. Until now, there is no study about impact of CYP on sperm quality and reproduction of *S. oriantalis* as *in vivo* or *in vitro*. This is first report on the impacts of CYP on sperm of *S. oriantalis*. According to our in vitro experimental results, a reduction in sperm motility rate and duration were evaluated when sperm cells were treated with CYP. This can be explained with dysfunction of sperm cells by CYP (Farrell et al., 1996; Lopes et al., 2019). Recently, researches have been documented that calcium channels were affected by pyrethroids through activating the return transport of Ca^{2+} ions (Chen et al., 2018; Hsu et al., 2018; Wang et al., 2019). Therefore, energy-linked mitochondrial functions in sperm cells might be inhibited by high mitochondrial Ca^{2+} uptake (Wang et al., 2019).

For the assessment of oxidative stress and monitoring antioxidant status, MDA, CAT, GSH-Px and SOD activity are evaluated as markers. Cell death can be caused by oxidative stress (Wang et al., 2019). Recently, the negative effects of toxicants have been well-reported in the fish sperm cells (Kocabaş et al., 2020). In an earlier study, Kutluyer and colleagues (2016) demonstrated that CAT activity in rainbow trout spermatozoa decreased depending on increasing concentration of CYP while MDA and GSH levels, GSH-Px activity elevated. Kutluyer and colleagues (2018) determined that activity of SOD and GSH-Px decreased in sperm cells of Çoruh trout as a result of CYP exposure while levels of MDA and, GSH and CAT activity elevated in sperm cells. Based on our data, MDA and CAT activity were increased depending on concentration and, GPx and SOD activities were significantly reduced. The increase in activities of CAT and MDA of sperm cells might show protection against oxidative damage and extremely ROS (reactive oxygen substances) production. The reason of the reduction in SOD activity may be inadequate defense to oxidative damage in consequence of conversion of O^{2-} (superoxide anion) to H_2O_2 (hydrogen peroxide) (Aitken and Roman, 2008). A reduction in the activity of GSH-Px might be regarding to inadequate protection against oxidative stress (Kocabaş et al., 2018).

In conclusion, movement rate and duration of *S. oriantalis* spermatozoa were affected by 2 h in vitro exposure to CYP at concentrations 2-4 μg/L Even at low concentrations, the oxidative damage increased as a result of exposure to CYP as a dangerous chemical agent. The male reproduction and subsequent progeny can impair through high exposure to CYP and its byproducts. The malformations and delayed development in embryo and larvae can occur as a result of adverse impacts of toxicants on sperm cells. The study about CYP-induced reproductive toxicity provides data and a new perception for further studies. Further efforts are required to effect on fertility, embryonic development and larval growth.

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