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# REMOVAL OF ALGAE FROM THERMAL MUD POOL: A CASE STUDY IN KOPRUKOY (ERZURUM, NORTHEAST (NE) TURKEY) THERMAL SPRING AREA

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**ABSTRACT**. Thermal spring areas, which are available globally, are used for recreational purposes or wellness applications because these areas have mineral-rich materials of thermal water and thermal muds. At the same time, thermal spring areas are one of the best habitats for algae among aquatic habitats. If algae formed on the surface of the thermal water in these areas, they create an ugly appearance and disrupt the aesthetics of the water because of their uncontrolled growth. The algae removal applications are the most effective methods for solution of these adversities in the thermal spring areas. In this work, experimental study was carried out to investigate the removal of algae from thermal water and thermal mud pools in the Delicermic-Koprukoy (Erzurum, NE Turkey) thermal spring area. For this purpose, some chemical materials were used for the removal of algae. The results of the experimental studies showed that the $Al_2SO_3$+CaO solution is a good material that provides 100% removal of algae from thermal water and thermal mud pools at pH 6.

**KEY WORDS**: Algae, Algae removal, Thermal water, Thermal mud, Spring area

## INTRODUCTION

Thermal muds known as peloids are geological materials and have rich clay minerals. Peloids presenting in nature with various water content are originated formed over many years by geological, biological, chemical and physical processes. In addition, they are defined as inorganic or organic matters or a mixture of them [1-4]. The peloids containing various amounts of clay minerals, non-clay minerals, organic matters, cations, anions and insoluble compounds are having suitability and potential for use in peloidotherapeutic applications in terms of physical, chemical, and mineralogical properties [4, 5].

Peloids used as thermal therapeutic agents in many spas and mostly thermal and occasionally natural waters mature thermal centers. Also, additional materials such as paraffin, humic matter can be added to the peloids [1, 6, 7]. According to Gomes *et al.* [8], peloids that can be used for healing or cosmetic purposes are divided into two classes. One of them is the mud or muddy suspension maturated in nature and the other is mud or muddy suspension taken place inside spas or research laboratories. Moreover, according to its components there are three groups named as essentially inorganic peloids, essentially organic peloids and mixed peloids [9].

Thermal therapy is known as pelotherapy and its using in spas is becoming increasingly popular. It is presented as the local or generalized application of thermal muds for recovering rheumatism, arthritis and bone-muscle traumatic damages. The pelotherapy applications are beneficial in treatment of great diversity of acute and chronic rehabilitative problems. In addition to bathing in hot waters, pelotherapy applications is also carried out [7, 10, 11].

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Turkey with its' a unique geographic location at the junction between Asia, Europe and Africa Continents is one of the richest countries in the world in terms of thermal water resources [12, 13]. The thermal waters of Turkey are remarkable geothermal fields that have with different physicochemical parameters [14]. In Turkey, direct use of geothermal energy is focused on district heating, greenhouse applications, and thermal tourism [15].

Algae, which are ubiquitous in surface waters, pose no threat to relatively low concentration water. However, they create serious visual pollution and people do not want to benefit from thermal treatments including algae. Also, algae massively emerging in lakes and reservoirs during summer emit an undesirable taste and odor [16, 17]. The mineral composition and water temperature of the spring plays a decisive role on the diversity of algae in thermal springs [18]. Generally, diversity of algal species increases from 0 °C to 25 °C and decreases at temperatures > 30 °C, while biomass increases with temperature from approximately 0 °C to 30 °C and decreases from 30 °C to 40 °C [19]. According to Atlas and Bartha [20], algae are restricted to growth below 55 °C, while Winterbourn [21] reported an upper temperature limit for algal growth of 68 °C. Because of the shallowness and clarity of most thermal waters and the exposure of many hot springs to high light intensities, various types of 'sun adaptations' may have occurred in many thermophilic organisms [22].

Algae known the most common indicator of eutrophication in rivers and lakes are a diverse group of plant-like organisms that occur in a wide range of environmental habitats. They grow faster in warm water and slow-flowing rivers. A combination of high temperatures, stagnant water and nutrient overload can result in excessive algae growth. This can lead to a depletion of oxygen in the water, release of toxins and taste and odor problems. Therefore, it is important to control algal blooms for a healthy ecosystem. There are many methods developed for removal of algae, such as ozone treatment method, bottom dredging operations, nanofiltration technology, ultrasound and plasma [23-26]. They undergo physical or chemical treatment before being discharged into the environment, such as adsorption, microwave-assisted extraction, ozonation, Fenton reagent, membrane-based technologies, and electrochemical processing [27-35].

In this study, it is aimed to investigate the problem of algae on the surface of muddy water in thermal mud pool and remove the algae from the environment. This thermal mud is located in the Koprukoy (Erzurum, NE Turkey) thermal spring area. The *Bacillariophyta* is the dominant algae type in the region and its surroundings according to the algological studies [36]. The water of thermal mud pool should be cleaned from the algae, because it is not hygienic and creates image pollution. For this purpose, the removal of algae from thermal sludge using $Al_2(SO_3)_3$, CaO, $FeCl_3$ and $Na_2CO_3$ chemical materials was investigated. Removal of algae from the water of thermal mud pool has been achieved by experimental studies carried out in the laboratory conditions.

## EXPERIMENTAL

The location of Delicermik-Koprukoy (Erzurum, NE Turkey) geothermal area is shown in Figure 1. The Koprukoy hot spring and mud bath, whose local name is Delicermik, is located 3.5 km north of Koprukoy district. This area is 18 km from Pasinler district and 58 km away from Erzurum city center.

### *Thermal water*

Delicermik hot spring water has a 26 °C of temperature and a flow rate of about 3 L/s. However, the mud and pool water temperature vary between 2 °C and 7 °C according to the seasons. The pH value of the thermal water is 7.0. Delicermik thermal water source has hot water with sodium-calcium-bicarbonate-carbon dioxide in chemical classification. His place in physical classification is hypothermic and hypotonic water. In addition, Delicermik source has a total molten mineral content of 2879 mg/L [37, 38]. Thermal water used in the experimental studies was supplied from this area (Figure 2a).

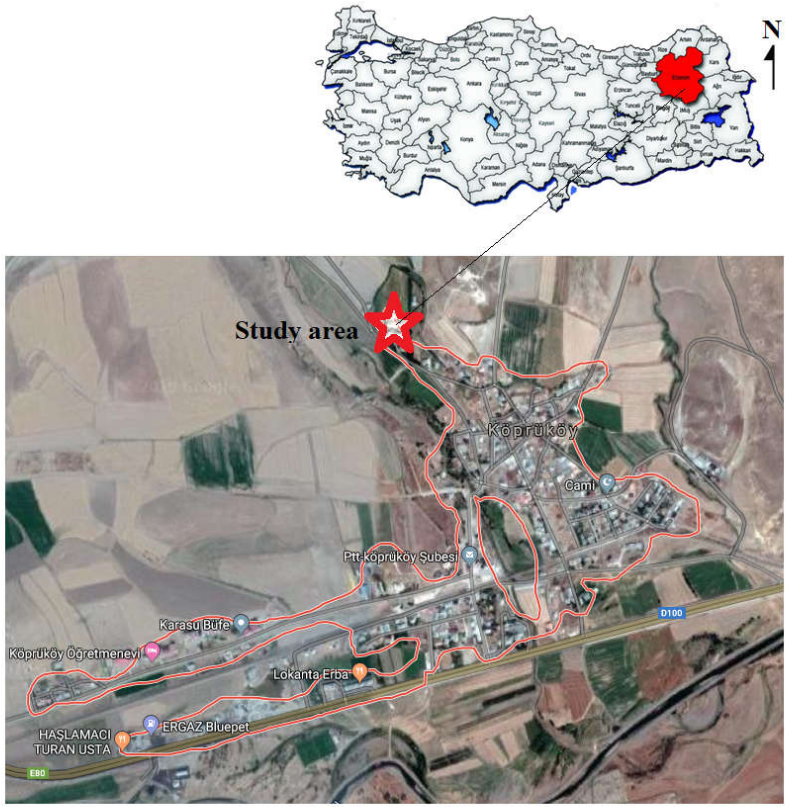



Figure 1. Location map of Koprukoy (Erzurum; NE Turkey) geothermal area [46].


Figure 2. Some photos from Delicermik thermal area; a) thermal water pool, b) thermal mud pool and c) thermal water and mud pools with algae.

*Thermal mud*

Thermal mud material of Delicermik thermal mud pool has moderate, high and very high plasticity together with a high content of clay-size particles, high content of quartz and feldspars and high swelling [1]. Thermal mud consisting of smectite mineral and water mixtures are the best materials for thermal pelotherapy applications [39, 40]. The high-swelling index and water limit [41], plasticity, specific surface, exchange capacity and mineral content make it suitable to use as thermal mud [10, 38]. Thermal mud was supplied from this area (Figure 2b).

*Algae*

Because the amount of smectite clay mineral is too high, the mud media of thermal mud pool is very suitable media for the growth of microorganisms [1, 42]. Dense algae growth indicates that the thermal mud contains abundantly smectite clay minerals. Delicermik thermal mud pool hosts algae belonging to *Bacillariophyta*, *Chlorophyta*, *Cyanophyta* and *Euglenophyta* types [36, 38, 43]. The algae samples were taken from this area (Figure 2c).

*Chemicals*

In this laboratory studies; iron(III) chloride ($FeCl_3$), calcium oxide (CaO), aluminum sulfite ($Al_2(SO_3)_3$, sodium carbonate ($Na_2CO_3$) and hydrochloric acid (HCl) were used in experimental studies. These chemical materials were obtained from Sigma Aldrich. The melting points of these chemicals are 2614 °C, 770 °C, 851 °C, 318 °C and -27.32 °C for iron(III) chloride, calcium oxide, aluminum sulfite and sodium carbonate, respectively.

*Experimental program*

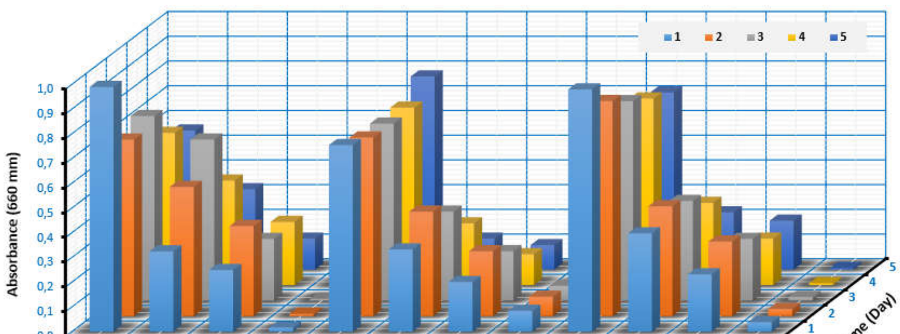
In the algae removal by chemical method study, 4 different experimental study groups were prepared from algae samples and subjected to tests under laboratory conditions. In Group 1; The reaction mixture was formed by adding 0.2 g $Al_2(SO_3)_3$ and CaO to 100 mL thermal water containing 10 g algae and 15 g thermal mud. The pH value was adjusted to be the same in each reaction medium. The changes in the experimental environment were noted by measuring every day at 660 nm. Then, the most suitable temperature, time and pH were determined for algae removal by creating a reaction medium at different pH values. In the first group, 10 g of algae, 15 g of thermal sludge and 0.2 g of $Al_2SO_3$ and CaO were mixed and then observation was carried out for one week in hot water baths at different temperatures. The measurements were made at 660 nm daily and optimum temperature, time and pH values were determined. In the second group, 0.2 g of CaO was added to 100 mL of water including algae and stirred with magnetic stirrer for two minutes. Then 0.2 g of $FeCl_3$ was added and the mixture was stirred for a further 30 min. The mixture was allowed to settle for 15 min. In the third group, 100 mL of water including algae was taken into the four glass beakers. 0.2 g CaO was added to the first reaction medium, 0.2 g $Al_2(SO_3)_3$ to the second reaction medium, and 0.2 g CaO and 0.2 g $Al_2(SO_3)_3$ to the third reaction medium, respectively. Then, magnetic mixer mixed them for 30 min and the mixture was allowed to subside for 15 min. In Group 4, the temperature and pH of mixture of thermal water and thermal sludge were adjusted in accordance with the conditions in the field (T: 23.3 ºC, pH: 6.0). Changes in the water were checked every other day by observing for a week without adding any chemical materials.

Absorbance measurements were made at UV-Vis spectrophotometer at 660 nm using Beckman coulter to determine optimum time, temperature and pH values. Also, changes in the amount of turbidity and algae were observed by using some chemical materials.

## RESULTS AND DISCUSSION

*Effect of time*

In this experimental study, algae removal processes have been carried out up to five days to observe the effect of time on the algae removal in the thermal springs. The results obtained from experiments clearly indicated that better removal rates of algae could be expected with increasing application time. In these experiments, absorbance measurements were made at different time such as 1, 2, 3, 4 and 5 days. The effect of various times on algae removal by chemical material was tested (Figure 3). Algae removal efficiency increased obviously even in a short preoxidation time, and the removal efficiency further increases with the continuing extension of the contacting time [24]. As is shown in Figure 3, it is possible to have complete reduction of algae at optimum time conditions and this optimum time is 5 days for this experimental study.




| | Control 20 °C | Al2SO3 20 °C | CaO 20 °C | Al2SO3+ CaO 20 °C | Control 25 °C | Al2SO3 25 °C | CaO 25 °C | Al2SO3+ CaO 25 °C | Control 30 °C | Al2SO3 30 °C | CaO 30 °C | Al2SO3+ CaO 30 °C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0,99 | 0,325 | 0,25 | 0,017 | 0,755 | 0,333 | 0,201 | 0,085 | 0,98 | 0,398 | 0,232 | 0,039 |
| 2 | 0,714 | 0,523 | 0,365 | 0,01 | 0,723 | 0,423 | 0,263 | 0,079 | 0,87 | 0,445 | 0,302 | 0,029 |
| 3 | 0,747 | 0,652 | 0,25 | 0,008 | 0,716 | 0,36 | 0,2 | 0,06 | 0,807 | 0,403 | 0,25 | 0,015 |
| 4 | 0,616 | 0,423 | 0,256 | 0,006 | 0,718 | 0,25 | 0,125 | 0,055 | 0,755 | 0,333 | 0,188 | 0,008 |
| 5 | 0,563 | 0,325 | 0,125 | 0 | 0,781 | 0,125 | 0,099 | 0,037 | 0,716 | 0,232 | 0,198 | 0,006 |

Solutions

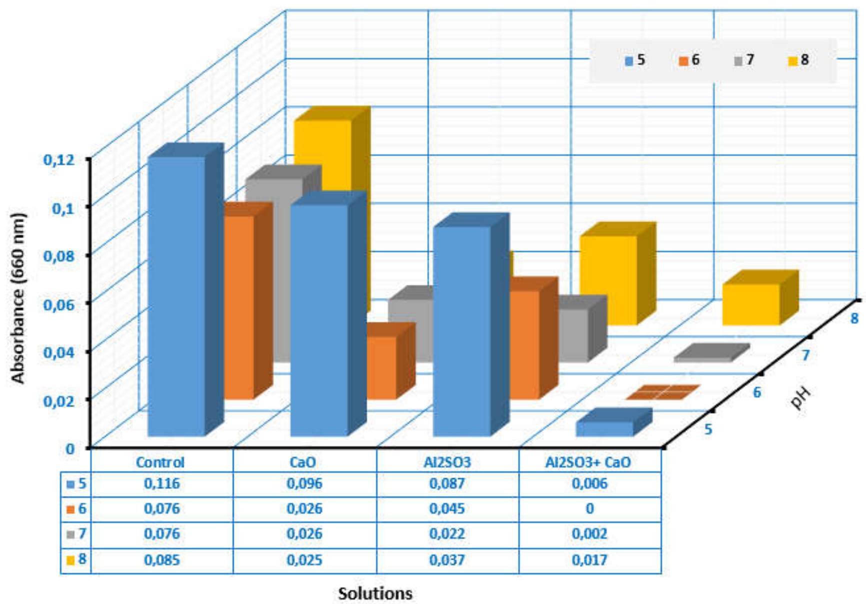
Figure 3. Effect of time and temperature on the algae removal.

*Effect of temperature*

It is clear from literature that temperature have a profound effect on various chemical processes. The temperature has a pronounced effect on the adsorption capacity of the adsorbent [44, 45]. The effects of temperature influencing the algae removal was studied at the 20, 25 and 30 ºC and obtained results were illustrated in the Figure 3. It was observed that higher temperature increased the impact of ferrate on algae. This is probably the reason why fully damaged algae were observed already after the addition of chemical solutions compared to the system at laboratory conditions [46]. The water temperature is one of the most important environmental factors that might influence algae removal. As shown in Figure 3, it was found that the algae removal was dramatically improved at the initial stage with increased temperature. The removal efficiency of algae was obtained at the temperature of 30 ºC. Higher temperature increased the impact of chemical materials on algae. This is probably the reason why fully damaged algae were observed already after the addition of $Al_2(SO_3)_3$+CaO solution compared to the solution without chemical material [47].

*Effects of pH*

It has been long recognized that the solution pH is one of the key parameters influencing the performance of algae removal process [47]. In this study, the effect of initial pH on the algae removal was also examined, with the values of pH varied in the range of 5.0-8.0. The solution pH had a great influence on turbidity and algae removal. The effects of pH on the removal of algae are illustrated in Figure 4. When pH was 5.0, coagulation had little effect on turbidity and algae removal. The major reason may be that coagulant hydrolysis was inhibited under an acidic condition [17]. It was seen from the results that removal of algae increased with the increasing of pH values up to 7.0 and then it decreased. Similar results were also obtained for the removal of algae by using some chemical materials [48-50].




| | Control | CaO | Al2SO3 | Al2SO3+ CaO |
|---|---|---|---|---|
| 5 | 0,116 | 0,096 | 0,087 | 0,006 |
| 6 | 0,076 | 0,026 | 0,045 | 0 |
| 7 | 0,076 | 0,026 | 0,022 | 0,002 |
| 8 | 0,085 | 0,025 | 0,037 | 0,017 |

Figure 4. Effect of pH on the algae removal for 5 days and 30 ºC temperature.

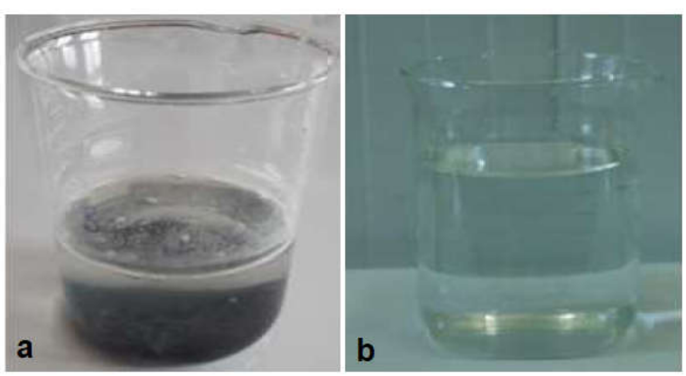



Figure 5. The photos of water (a) before removal of algae and (b) after removal of algae.

In this study, the removal of algae from thermal spring areas was investigated and obtained results were presented. It was observed from the results of experimental study that the maximum value of removal algae was obtained at the end of 5th day, at the 30 ºC and at the pH value of 7.0. The photos of water with algae; (a) before removal of algae (Figure 5a) and after removal of algae (Figure 5b)

## CONCLUSION

This study was carried out for Delicermik-Koprukoy (Erzurum, NE Turkey) geothermal area located 58 km east of Erzurum province. It was aimed to remove algae from thermal mud pool and this experimental study was conducted for this purpose. Thermal water, thermal mud and algae supplied from geothermal area were subjected to the experimental procedure to solve problem of algae formation in the thermal mud pool. Thermal water of this area has property of low enthalpy geothermal area. The algae belonging to *Bacillariophyta*, *Chlorophyta*, *Cyanophyta* and *Euglenophyta* types are dense in this area. Thermal water resources have temperature of 26 °C and gaseous effluents flow rate of 3.1 L/s. Thermal water is used for sludge blanket because it is from the area where Pliocene clay levels belonging to Horasan Formation are found. The experimental study was performed to remove the algae from the thermal spring area. It was observed from the results of experimental study that the maximum value of removal algae was obtained at the end of 5th day, at the 30 °C and at the pH value of 7.0.

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