



USAGE OF BILECIK LEFKE STONE AND BENTONITE CLAY FOR PHOSPHORUS REMOVAL IN WATER

Betül ÇANGA ¹ , Ramazan MERAL ² , Çayan ALKAN ^{2,*} 

¹ Department of Biotechnology, Institute of Postgraduate Education, Bilecik Şeyh Edebali University, Bilecik, Turkey

² Department of Biosystems Engineering, Faculty of Agriculture and Nature Science, Bilecik Şeyh Edebali University, Bilecik, Turkey

ABSTRACT

The rapid increase in the world population, the development of the industry, the excessive usage of fertilizers in agriculture, and the increase in detergents and chemicals used for cleaning accelerate the pollution of water resources. Conservation and recovery of damaged water resources along with the deteriorated ecosystem is of great importance for living things. An important part of water pollution in lakes and rivers is the increase in the content of nutrients. Nutrient elements, especially phosphorus, cause the transparency of water to decrease gradually. Over time, this situation, called eutrophication, causes an algae bloom and the aquatic ecosystem is disrupted. Uncontrolled discharge of wastewater containing phosphorus in high concentrations accelerates this process. These nutrients must be removed in order to maintain water quality and reduce the risk of eutrophication. The main ways of removing phosphorus from water are physical, chemical and biological methods. Among these, as an alternative to settling with chemical substances, the usage of clay (based on fixation) has an important place. In this study, different dosages of bentonite, Lefke stone and ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were used in water with three different pH values (4, 7, and 10) and three different phosphorus contents (20, 40, and 60 ppm). The per cent yields of the phosphorus removed with ferrous sulphate heptahydrate, Lefke stone and bentonite are 72%, 57% and 39%, respectively. In addition, it was determined that the dosage of additives used should be renewed depending on the phosphorus content of the environment and that the high pH value of the environment increased the efficiency, especially in the usage of ferrous sulphate heptahydrate. In conclusion, as an alternative to the usage of chemicals, it has been revealed that Lefke stone can be used for phosphorus removal in water, and its effectiveness can be further increased with further studies.

Keywords: Eutrophication, Bentonite, Phosphorus fixation

1. INTRODUCTION

The biggest reserves of Phosphorus (P), which is an important structural element for living creatures, in nature phosphatic rocks in the earth's crust, commercial fertilizers and water resources. Since non-volatile phosphorus does not pass into the atmosphere, the phosphorus cycle is different from other cycles (such as Oxygen, Nitrogen and Sulfur). Plants use and consume ortho-phosphates, which are the dissolved and ionized form of phosphorus. The only source of phosphorus for herbivorous animals is plants. Carnivorous animals meet their phosphorus needs by eating herbivorous animals [1].

Phosphorus is the second most abundant element in the human body, after calcium. Phosphorus is needed by all living creatures, it is the main component of ATP, DNA, NADPH, phospholipids, and nucleic acids. P is also needed for cellular activities in the body, energy production, contraction of the heart, muscle-nerve movements, tooth-bone tissue, and kidney [2].

Phosphorus is also a necessary nutrient element for aquatic plants and algae. However, excessive transport of phosphorus into water causes pollution called eutrophication. Increased phosphorus in water accelerates phytoplankton growth. And then, fish, other aquatic creatures, microorganisms, and insects are affected by these negativities, respectively. In other words, phosphorus disrupts the natural balance

*Corresponding Author: cayan.alkan@bilecik.edu.tr

Received:01.10.2023

Published: 29.11.2023

in water and increases the growth of toxic algae in water [1, 2]. The main cause of water pollution in lakes and rivers is nutrient excess. Phosphorus and other nutrients in water cause the transparency of water to decrease gradually, which disrupts the ecological balance. This situation, called eutrophication, disrupts the aquatic ecosystem by causing algal blooms and the death of fish [3].

As a result of the uncontrolled discharge of wastewater containing high concentrations of phosphorus into the receiving environment, significant deterioration in water quality may occur. It may be necessary to purify phosphorus as well as nutrients such as carbon and nitrogen to provide the necessary nutrient rates to protect water quality and reduce the risk of eutrophication in receiving environments. In general, the primary source of phosphorus is cleaning materials such as soap, detergent, and shampoo. Although some of it is retained in the soil, the retention percentage of P is low in soils with high permeability. Eutrophication is gradually increasing with the usage of phosphorus agricultural fertilizers [4, 5].

High phosphorus concentration especially accelerates the growth of cyanobacteria. Wastewater causes problems such as increased oxygen consumption, eutrophication, and toxicity in the receiving environment due to its high nutrient content. Eutrophication causes an increase in phytoplankton and microorganisms, algal blooms that include toxin-secreting cyanobacteria, and algae collapse, depleting the dissolved oxygen in the bottom water. Thus, eutrophication damages the taste and colour of water and causes a decrease in fish and crustacean species, which are useful food products. As organic materials decompose in an oxygen-free environment, foul-smelling gases such as methane, ammonia and hydrogen sulfide are produced. These gases also have a toxic effect on marine creatures. Due to eutrophication, seaweed increases, and blocks the passage of sunlight. With the cessation of photosynthesis, the oxygen in the liquid decreases. And then, invertebrate aquatic creatures and fish may disappear [2, 5, 6, 7, 8].

In terms of environment and human health, wastewater must be treated and reused. However, the applicability of technologies developed for the treatment and reuse of wastewater is low due to the price of installation, maintenance, and repair. For this reason, alternative purification methods, which are cheap and easy compared to expensive technological purification methods, are used. Industrial facilities must ensure optimum removal efficiency for nitrogen-phosphorus removal. According to legal regulations, the most suitable treatment technology for nutrient removal is biological treatment [8].

Although efforts are made to reduce phosphorus inflow into wastewater, success is not obtained due to the diversity of P sources. For this reason, advanced treatment of wastewater comes to the fore. Even so, technologies that aim to remove and recover P in wastewater by chemical, physical, and advanced biological methods are not very developed. Among physical methods, phosphorus crystallization, flotation, electrodialysis, and reverse osmosis are frequently used. Advanced biological phosphorus removal can remove 97% of the total phosphorus, although it is expensive. Chemical removal aims to precipitate phosphorus in the form of phosphate with salts of calcium, aluminium, and iron ions [1].

Some of the chemicals commonly used in phosphorus settling are Ca compounds and Mg, Al, and Fe salts [7]. *Acinetobacter*, one of the bacterial species found in activated sludge systems, is another alternative that can be used to remove P from water [8]. However basically, in the removal of P from wastewater, reverse osmosis, electrodialysis, usage of adsorbents, slag, sewage sludge, fly ash, kaolinite, and activated carbons obtained from agricultural waste are used. Some of the agricultural raw materials used in activated carbon production are corn cob, olive seed, cotton stalk, fruit waste, sugar cane, wheat straw, paddy husk, and sunflower seed-hazelnut-almond shell [7, 5]. Compared to other methods, adsorption is more successful and economical in P removal. Therefore, in recent years, attempts have been made to purify wastewater with easily accessible and cheap materials [2]. It is frequently used due to the cheapness and simplicity of the adsorption process. In removing P from wastewater, in particular,

biochar, coconut shell, calcium carbonate, calcium kaolinite, red mud, semi-burnt dolomite, fly ash, slag, zeolite, titanium dioxide, sand, and pumice are quite successful [7].

In particular, some clay types are frequently used in P removal. It is one of these examples, called bentonite in America, is also frequently encountered in the Montmorillon region of France. So, bentonite is also called montmorillonite. The general chemical formula of bentonite is $(\text{Na}, \text{Ca}) (\text{Al}, \text{Mg})_6 (\text{Si}_4\text{O}_{10})_3 (\text{OH})_{6 \times n} \text{H}_2\text{O}$ [1]. Bentonites are the most abundant clay-containing materials used in wastewater treatment. It is used successfully in both heavy metal removal (copper, lead, cadmium, and zinc) and phosphorus removal [9]. One of the most important factors affecting phosphorus adsorption is pH. Besides, decreasing temperature also increases the adsorption capacity [1]. In choosing the most suitable adsorbent to be used in phosphorus removal; Attention is paid to the physical and chemical properties of the adsorbent, its ability to adsorb phosphorus, cost, and simplicity of obtaining [2].

Many studies have been conducted on this subject. Ayar [1] tried to remove P in water with bentonite clay. He determined that the best removal was at neutral pH. After all, He observed that physical and chemical interactions were effective together in P removal. Li, W. et al. [10] tried P removal with a mixture of kaolin clay and ferric chloride with different moles. They found that phosphates were completely removed by iron at neutral pH. Dirim [6] in the Lower Kelkit Watershed, aimed to remove P from water with plants in his laboratory study. As a result, he determined that the highest phosphorus removal was in *Lemnaminor* species with 84%, *Ceratophyllum demersum* species with 75% and that other plant species could only remove around 50% phosphorus. *Typhaangustifolia* showed lower performance than other species with a rate of 18%.

In this study, for the purpose of P removal in water, bentonite clay, which is a natural adsorbent and abundant in Bilecik, and Lefke stone, which is specific to the Bilecik Osmaneli region, were used.

2. MATERIAL AND METHOD

2.1. Material

For the research experiments, Lefke stone located in Osmaneli county of Bilecik province, bentonite extracted by ESAN Clay and Bentonite factory from Bozüyük county of Bilecik province and Tekkim brand ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were used.

2.1.1. Bentonite

Bentonites are the chemical decomposition of volcanic ash, tufa and lava containing glassy material. Montmorillonite, which creates bentonite and consists of layers, is an octahedral structure located between two tetrahedral layers. There are water molecules and exchangeable cations in this structure. Water and organic matter enter between these unit layers and extend the structure. The main components of Ca-bentonite and their approximate ratios are as follows: (66%) SiO_2 and (13%) Al_2O_3 [14].

Pure Ca-bentonite was used in the study. Bentonite mineral contains 50% montmorillonite. After the crushing and drying stages, it was ground below 75 microns. Two different concentrations (5% and 10%) were tried in the experiments (Figure 1).



Figure 1. A sample of the dust of bentonite clay

2.1.2. Lefke stone

Lefke stone, a type of sandstone, was used in the construction of mosques, madrasahs and inns during the Seljuk and Ottoman Empires periods. Besides, this stone was used in Eskişehir government mansion, Istanbul Haydarpaşa train station, Bebek and Bostancı mosques. Lefke stone is a type of sandstone found naturally in the Osmaneli county of Bilecik province, and the ratio of clay and silt materials is less than approximately 15%. The grains in the stone consist of quartz, feldspar, lithic fragments, hematite, and other opaque minerals [15, 16]. After the Lefke stone was crushed and sieved at 250 microns, it was dried in the oven at 105°C for 24 hours and its moisture was removed. Two different concentrations (5% and 10%) were tried in the experiments.

Lefke stone is especially used in the restoration of historical buildings and the design of special structures (such as fountains and bridges) (Figure 2).



Figure 2. A sample of the dust of Lefke stone

2.1.3. Ferrous sulphate heptahidrat ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

10 mg/ml (10.000 ppm) ferrous sulphate heptahydrate was prepared as stock. Three different initial concentrations (100 mg/l, 150 mg/l, 200 mg/l) were tried in the experiments.

2.2. Method

In the research, for three materials in different concentrations (Ferrous Sulphate Heptahydrate, Bentonite, and Lefke Stone), phosphorus removal efficiencies were examined at three different dosages of phosphorus concentration (20, 40, and 60 mg/l) and at three different pH values (4, 7, 10) at the end of 30 minutes. Vanadomolybdophosphoric acid colourimetric method was applied for phosphorus analyses [18]. For the colourimetric method used for the determination of total orthophosphate in

samples, solution A+B was prepared by combining solution A and solution B reagents and HCl. Standard solutions were obtained using stock phosphorus solution (1000 ppm P). It was prepared as 0, 5, 10, 20 ppm for 20 ppm P concentration, 0, 10, 25, 50 ppm for 40 ppm P concentration, and 0, 20, 40, 60 ppm for 60 ppm P concentration [17].

For the analysis, 7ml sample + 1ml pure water + 2ml A+B solution were combined and after ten minutes waiting period, the absorbance was read on the spectrophotometer at 470 nm.

Equation 1 was used in the calculation of phosphorus removal efficiency [17].

$$\text{Phosphorus removal efficiency (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

C_i: Initial phosphorus concentration (mg/l)

C_f: Final phosphorus concentration (mg/l)

2.2.1. Statistical analysis

One-way ANOVA was used to analyze the means of the final P concentrations for the different applications. Differences were evaluated at the 0.05 significance level and the Duncan post hoc test was used with the software program SPSS17.0.

3. RESULTS AND DISCUSSION

The results obtained in the study were tabulated for each pH value along with each absorbent type and dosage (Table 1-3). Final P concentrations and one-way ANOVA results were also added to the table.

The lowest value was obtained in the application of ferrous sulphate (200mg/l), the second lowest value was obtained in the application of Lefke stone (10%), and the pH value was effective in the application of ferrous sulphate (Table 1)

Table 1. Final concentration and removal per cent obtained for initial phosphorus content of 20 ppm

| Additive Material | Dosage | pH | | | | | |
|-------------------|----------|---------|-----------|---------|-----------|---------|-----------|
| | | 4 | | 7 | | 10 | |
| | | ppm | Removal % | ppm | Removal % | ppm | Removal % |
| Bentonite | 5% | 12.80 c | 36 | 13.71 d | 31 | 12.29 e | 39 |
| | 10% | 13.54 d | 32 | 9.78 c | 51 | 11.21 c | 44 |
| Lefke stone | 5% | 11.38 b | 43 | 9.43 b | 53 | 11.55 d | 42 |
| | 10% | 8.88 a | 56 | 8.53 a | 57 | 9.55 b | 52 |
| Ferrous sulphate | 100 mg/l | 15.29 f | 24 | 13.55 d | 32 | 13.81 f | 31 |
| | 150 mg/l | 14.52 e | 27 | 12.13 d | 39 | 9.55 b | 52 |
| | 200 mg/l | 14.13 d | 29 | 12.19 d | 39 | 5.51 a | 72 |

Remark: Columns with different letters significantly differed from each other as indicated by the Duncan test ($p \leq 0.05$).

Likewise, the lowest value was obtained in the application of ferrous sulphate (200mg/l), and the second lowest value was obtained in the Lefke stone (10%) application (Table 2).

Table 2. Final concentration and removal per cent obtained for initial phosphorus content of 40 ppm

| Additive Material | Dosage | pH | | | | | |
|-------------------|----------|---------|-----------|---------|-----------|---------|-----------|
| | | 4 | | 7 | | 10 | |
| | | ppm | Removal % | ppm | Removal % | ppm | Removal % |
| Bentonite | 5% | 33.90 d | 15 | 28.27 b | 29 | 33.17 f | 17 |
| | 10% | 32.95 c | 18 | 28.42 b | 29 | 30.40 c | 24 |
| Lefke stone | 5% | 29.00 b | 28 | 30.24 d | 24 | 31.64 d | 21 |
| | 10% | 25.93 a | 35 | 26.66 a | 33 | 29.60 b | 26 |
| Ferrous sulphate | 100 mg/l | 38.14 g | 5 | 33.73 f | 16 | 32.49 e | 19 |
| | 150 mg/l | 37.05 f | 7 | 32.56 e | 19 | 30.55 c | 24 |
| | 200 mg/l | 36.12 e | 10 | 28.85 c | 28 | 25.91 a | 35 |

Remark: Columns with different letters significantly differed from each other as indicated by the Duncan test ($p \leq 0.05$).

A decrease was observed in the effect levels of the dosages used in response to the increasing phosphorus content. This effect was especially observed in the effectiveness of ferrous sulphate (Table 3).

Table 3. Final concentration and removal per cent obtained for initial phosphorus content of 60 ppm

| Additive Material | Dosage | pH | | | | | |
|-------------------|----------|---------|-----------|---------|-----------|---------|-----------|
| | | 4 | | 7 | | 10 | |
| | | ppm | Removal % | ppm | Removal % | ppm | Removal % |
| Bentonite | 5% | 56.12 d | 6 | 57.63 f | 4 | 59.06 f | 2 |
| | 10% | 48.53 c | 19 | 50.98 e | 15 | 57.26 e | 5 |
| Lefke stone | 5% | 44.86 b | 25 | 50.24 d | 16 | 54.08 d | 10 |
| | 10% | 40.94 a | 32 | 46.90 b | 22 | 49.10 b | 18 |
| Ferrous sulphate | 100 mg/l | 58.26 e | 3 | 52.89 | 12 | 51.59 c | 14 |
| | 150 mg/l | 56.23 d | 6 | 47.60 c | 21 | 48.74 b | 19 |
| | 200 mg/l | 55.74 d | 7 | 44.59 a | 26 | 44.83 a | 25 |

Remark: Columns with different letters significantly differed from each other as indicated by the Duncan test ($p \leq 0.05$).

As a result of the applications made for an initial phosphorus concentration of 20 ppm, the lowest content was obtained in the application of ferrous sulphate (200mg/l) with 5.51 ppm, and the second was in the application of Lefke stone (10%) with 8.53 ppm. The dosage differences used in each application were also found to be significant statistically. Considering the percentage of the removal values, it varied between 24% and 72%. Bentonite application reached 51% value at pH:7 condition and gave

proportionally lower values in other conditions. Lefke stone application showed dosage-dependent changes, regardless of pH value. The most striking thing is that the application of ferrous sulphate gave the highest value only for the pH:10 condition. Elgarhy et al. [11] achieved the highest efficiency of 85% for pH 6 value in their sodium-bentonite clay studies. Among the 20.5-10% adsorbent dosages, 10% gave the best results. El Refaey [12] found that the P sorption value varied depending on the thermal process applied to bentonite in their study with Ca-modified Bentonite. Besides, the sorption ability of phosphorus decreased with the increasing temperature of the thermal treatment. Markou et al. [13] stated that Ca-bentonite applied at 5% reduced the phosphorus content in wastewater by over 80%. In our study, Ca-bentonite, which was supplied as a commercial product, was produced for different purposes and it is thought that its effect was limited depending on the details of the production processes.

Although the content values obtained as a result of the applications made for the initial phosphorus concentration of 40 and 60 ppm (Tables 2 and Table 3), showed statistical differences, the percentage removal values were limited between 3% and 35%. This situation shows the need to re-determine the adsorbent dosages to be used for high P concentrations.

4. CONCLUSION

This study investigated the possibilities of using Lefke stone extracted from Bilecik province and Ca-bentonite clay produced for phosphorus removal in wastewater. First of all, it was understood that Lefke stone with its natural form could be an alternative against to chemical usage. The advantage of not being affected much by the ambient pH value, as well as being easily available and economical, has brought the method to the fore. Although bentonite clay contributed to P removal at some levels, further studies are needed to increase its effectiveness. It is necessary to investigate more effective usage possibilities by examining the production processes of Ca-bentonite, particle size selection and carrying out some modification studies. Similar pre-treatments can increase the effectiveness of Lefke stone. Besides, better results in water with high P content can be obtained by using different combinations of these adsorbents when they are used in appropriate dosages.

AUTHORS' CONTRIBUTIONS

Ramazan MERAL: Literature survey, data collection and analysis, writing, supervising and reviewing.
Betül ÇANGA: Literature survey, data collection and analysis and writing.
Çayan ALKAN: Literature survey, writing and editing.
All authors read and approved the final manuscript.

CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

REFERENCES

- [1] Ayar E. Removal of phosphorus by adsorption from aqueous medium using bentonite clay. MSc, Süleyman Demirel University, Isparta, Turkey, 2009.
- [2] Çetin P. Development of new methods for phosphorus analysis in drinking water. MSc, İstanbul Technical University, İstanbul, Turkey, 2013.
- [3] Li Y, Nan X, Li D, Wang L, Xu R, Li Q. Advances in the treatment of phosphorus-containing wastewater. In IOP Conference Series: Earth and Environmental Science 2021; 647 (1): 012163.

- [4] Tunçal T, Pala A, Uslu O. Investigation of enhanced biological phosphorus removal characteristics in İzmir Wastewater Treatment Plant. *J Water Pollut Con* 2008; 18 (1): 17–31.
- [5] Atıcı G. Determination of the nitrogen and phosphorus removal performance of zeolite and sawdust in wastewater. MSc, Erciyes University, Kayseri, Turkey, 2023.
- [6] Dirim S. Removal of phosphorus by plants in natural wetlands of Kelkit downbasin. MSc, Sakarya University, Sakarya, Turkey, 2006.
- [7] Zeybek Ş. Activated carbon production from walnut shell and phosphorus removal by adsorption method. MSc, Kocaeli University, Kocaeli, Turkey, 2019.
- [8] Erdoğan ÖK. Evaluation and optimization of nitrogen-phosphorus removal performances in domestic wastewater treatment facilities in Antalya province. MSc, Süleyman Demirel University, Isparta, Turkey, 2022.
- [9] Visa M. Tailoring fly ash activated with bentonite as adsorbent for complex wastewater treatment. *Appl Surf Sci* 2012; 263: 753-762.
- [10] Li W, Ouyang F, An G, Yang C, Zhong R, Xiao F, Peng D, Wang D. Mechanism insight into the role of clay particles on enhancing phosphate removal by ferrate compared with ferric salt. *Environ Sci Pollut Res* 2021; 28: 45414–45421.
- [11] Elgarhy AH, Mahran BNA, Liu G, Salem TA, ElSayed EE, Ibrahim LA. Comparative study for removal of phosphorus from aqueous solution by natural and activated bentonite. *Sci Rep* 2022; 12: 19433
- [12] El Refaey A. Effect of calcination and Ca-modified bentonite and zeolite, with respect to phosphorus removal from aqueous solution. *Egyptian J Soil Sci* 2021; 61(4): 433-444.
- [13] Markou G, Mitrogiannis D, Inglezakis V, Muylaert K, Koukouzas N, Tsoukalas N, Kamitsos E, Palles D, Baziotis I. Ca(OH)₂ Pre-treated bentonite for phosphorus removal and recovery from synthetic and real wastewater. *Clean- Soil, Air, Water* 2018; 46 (2): 1-10.
- [14] Kalpaklı Y. Determination of reaction conditions of the zinc adsorption onto raw Ca-bentonite. *OHU J Eng Sci* 2018; 7(2): 1004-1012.
- [15] Şahin G, Akova SB. Turkey's geological values in geographical indications. *Asia Minor Studies* 2019; 7 (2): 335-354.
- [16] Selim HH, Karakaş A, Coruk Ö. Geological and engineering properties of Lefke Stone (Osmaneli /Bilecik) used as a natural building stone in old structures. *Dumlupınar University Engineering Faculty J. of Engineering* 2019; 10 (3): 1019-1032.
- [17] Tüzüner A. *Soil and Water Analysis Laboratories Handbook*. Ministry of Agriculture, Forestry And Rural Affairs 1990; 375.
- [18] Kitson RE, Mellon MG. Colourimetric determination of phosphorus as molybdivanadophosphoric acid. *Ind Eng Chem Anal Ed* 1944; 16: 379-383.