Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28749

269 (2022) 57–64
September

Application of pinecones powder as a natural coagulants for sustainable treatment of industrial wastewater

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Received 28 April 2022; Accepted 18 July 2022

A B S T R A C T

Utilization of pinecone powder as a plant-based natural coagulant for the treatment of iron and steel factory effluent was examined. The concentrations of chemical oxygen demand (COD), total suspended solids (TSS), ammonia-nitrogen (NH_3–N), manganese (Mn), iron (Fe), zinc (Zn), aluminum (Al), and nickel (Ni) in effluent wastewater were investigated. Results showed that the maximal removal of COD, TSS, NH_3–N, Mn, Fe, Zn, Al, and Ni using pinecone powder were 83.3%, 99%, 83.9%, 86.8%, 93.7%, 89.7%, 73.7%, and 86.7%, respectively for effluent at natural pH 8 using a dosage of 3 g/L. The Fourier-transform infrared spectroscopy result showed the existence of various functional groups involved in the coagulation process. Overall, this study shows that pinecone powder has enormous promise as a natural coagulant for water treatment and it could be utilized to treat effluent from iron and steel plants.

Keywords: Natural coagulant; Industrial; Wastewater; Removal; Heavy metals

1. Introduction

Industrialization is an important factor for economic growth where the suitable management and disposal of industrial effluent is a key factor affecting the environmental health [1]. Heavy metal and organic chemical-containing wastewater is common in the iron and industrial applications [2]. Heavy metal tainted wastewater enters the environment, causing a harmful effect for human health and the ecology [3]. Heavy metals including cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn) are non-biodegradable and could be carcinogenic [4–7]. Thus, the existence of such metals in water in excessive concentrations might cause serious health problems for living creatures. To ensure ecological stability and public safety, successfully separating and enriching unwanted heavy metal ions from the environment remains a critical but difficult undertaking for environmental pollution management [8].

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Several conventional and current technologies, including chemical precipitation, reverse osmosis, ion exchange, and electrochemical removal, have been developed during the last several decades. These techniques have substantial drawbacks, such as partial removal, large energy consumption, and the creation of hazardous sludge [9–19].

Coagulation-flocculation is common used physicochemical method for the treatment of metal-bearing industrial wastewater since it removes colloidal particles with high efficiency, low cost, simple operation, and a wide range of coagulants [20,21]. Coagulation is often performed using chemicals coagulants. Coagulants employed in industrial wastewater treatment processes can be inorganic (such as aluminum sulfate and polyaluminium chloride), however, the primary disadvantages of such techniques are extra costs, toxic effects, enormous sludge volumes generated, and pH changes in the treated water [10,22]. Other issues highlighted about the usage of alum include the ecotoxicological effects of sludge, the toxicological effects of residue aluminum in treated water, and the cost of chemical imports [23,24].

Consequent upon the aforementioned challenges, several studies have indicated that the use of natural plant-based materials for coagulation in lieu of chemicals is a promising alternative for the treatment of different industrial wastewaters to alleviate the issues associated with chemical coagulants [16,25,26]. To alleviate the worldwide water crisis, researchers are currently focusing on extracting coagulants from naturally existing indigenous minerals, were natural coagulants are biodegradable in environment, and can be obtained from plants, animals, and microorganisms [27,28]. Many recent studies have highlighted the importance of natural coagulants. Plant-based materials are capable of acting as coagulants because they can perform some of the coagulation mechanisms, namely neutralization of charge in colloidal particles and polymer bridging [29,30].

The main objective of this study was to evaluate the efficacy of pinecone powder as a natural coagulant for iron and steel factory wastewater treatment, especially in terms of chemical oxygen demand (COD), total suspended solids (TSS), ammonia-nitrogen NH_3–N and heavy metals removal. Specifically, several coagulant dosages were applied to study the pH effect on removal efficiency. In addition, pinecones powder was characterized using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) to elucidate the chemical structure, thermal stability, and morphology, respectively.

2. Materials and methods

2.1. Sample collection

Industrial wastewater samples were taken using high-density polyethene (HDPE) containers from Karabuk iron and steel factory nearby Karabuk University. Wastewater sample was collected manually by grab sampling and immediately transferred into a cold room of 4°C, at Department of environment engineering, faculty of engineering, Karabuk University, Turkey.

2.2. Preparation of pinecones powder

Pinecones were collected from Karabuk university garden, Turkey. The pinecones were washed by distilled water to remove adhering and unwanted parts. The pinecones were dried at room temperature first, then in an oven at 50°C for around 8 h. This was done to make it easier to smash the pinecones. The crushed pinecones were ground using a (Retsch RS 200) grinder to obtain powder form to be used as a coagulant in the experiments as shown in Fig. 1.

2.3. Analytical analysis

All analytical methods were carried out in accordance with the Standard Method of Water and Wastewater, as stated in Table 1. During the tests, the pH of the samples was adjusted with a 1 N H_2SO_4/NaOH solution [31].

2.4. Coagulation experiments

The working conditions of the coagulation/flocculation experiments were conducted using Orbital shaker

Fig. 1. Pinecones and powder.

(Type: PSU-10i, No:010144-1404-0228, Latvia). With regard to the effect of coagulant dose, 500 mL beakers were used. The operational parameters utilized were determined by reviewing the literature. A 200 mL of sample were loaded in 500 mL beakers and placed in the plate of the shaker, the rapid mixing was 200 rpm at 15 min, slow mixing was 90 rpm at 30 min, and settling time was 60 min on 200 mL of sample.

After 60 min of sedimentation, the samples were using Whatman circle ashless/white ribbon filter paper to ensure clarification of sample from impurities, for farther testing for removal treatment efficiency of COD, TSS, ammonia-nitrogen NH_3–N and heavy metals (manganese "Mn", iron "Fe", zinc "Zn", aluminum "Al" and nickel "Ni", at original pH 8 of the iron and steel industry wastewater collected sample.

Eq. (1) was used to calculate the percentage removal of the respective parameters by considering the initial concentration of raw industrial wastewater sample and the final concentration industrial wastewater.

Table 1
Characterization parameters and methods

Parameters	Method
pH	pH meter
Color (Pt-Co)	SM 2120 C
TSS (mg/L)	SM 2540 D
COD (mg/L)	ASTM D1252-A
Ammonia-nitrogen NH_3–N (mg/L)	TS EN ISO 11732
Manganese "Mn" (mg/L)	TS EN ISO 11885
Iron "Fe" (mg/L)	TS EN ISO 11885
Zinc "Zn" (mg/L)	TS EN ISO 11885
Aluminum "Al" (mg/L)	TS EN ISO 11885
Nickel "Ni" (mg/L)	TS EN ISO 11885

$$\text{Removal efficiency}(\%) = \left[1 - \left(\frac{C_f}{C_i}\right)\right] \times 100 \quad (1)$$

where C_i and C_f refer the original and the obtained levels of each parameter.

3. Results and discussion

3.1. Pinecones powder characterization scanning electron microscopy imaging

Before and after the coagulation procedure, the morphological surface structure of pinecone powder was examined. Pinecone powder has a condensed crystalline brick-shaped structure, as seen in Fig. 2a. The structure functioned as an attachment point for suspended particles and cations [32]. As seen in Fig. 2b, the coagulant aggregated the particles, resulting in bigger flocs that settled easily. As a result, SEM images of pinecone revealed that bridging may be key for the pinecone's exceptional coagulation characteristics [32,33].

3.2. Fourier-transform infrared spectroscopy analysis

As shown in Fig. 3, the corresponding infrared (IR) spectrum was achieved using FTIR to further examine the existence of the main possible functional groups in powdered pinecone. The FTIR analysis was adequate for simplifying and maybe emphasizing its primary functional groups. The bands range-where its functional groups may perhaps be accentuated within the range of wavelength peaks-were chosen to enable the investigation of the IR spectra produced for pinecone. The observed peak in the 3,000–2,500 cm^{-1} range may indicate the presence of strong amine salts (N–H), which contribute in the particle bridging mechanism during the coagulation process and may assist in the removal of ammonia and organics from wastewater.

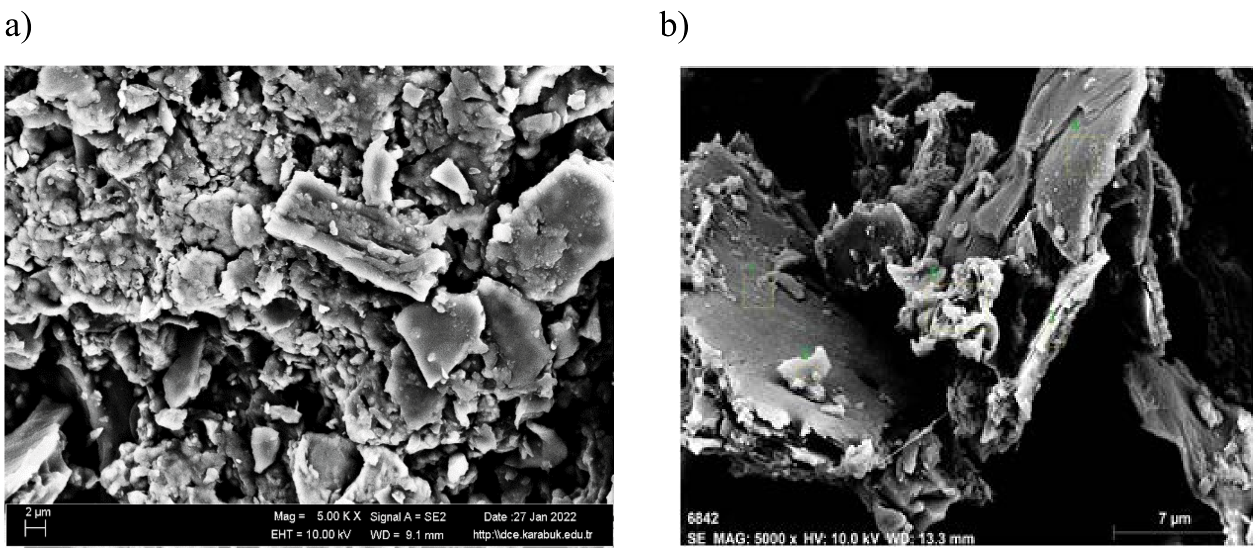

Fig. 2. Microscopic image (2 µm) for pinecones powder (a) before (b) after coagulation process observed by scanning electron microscopy.

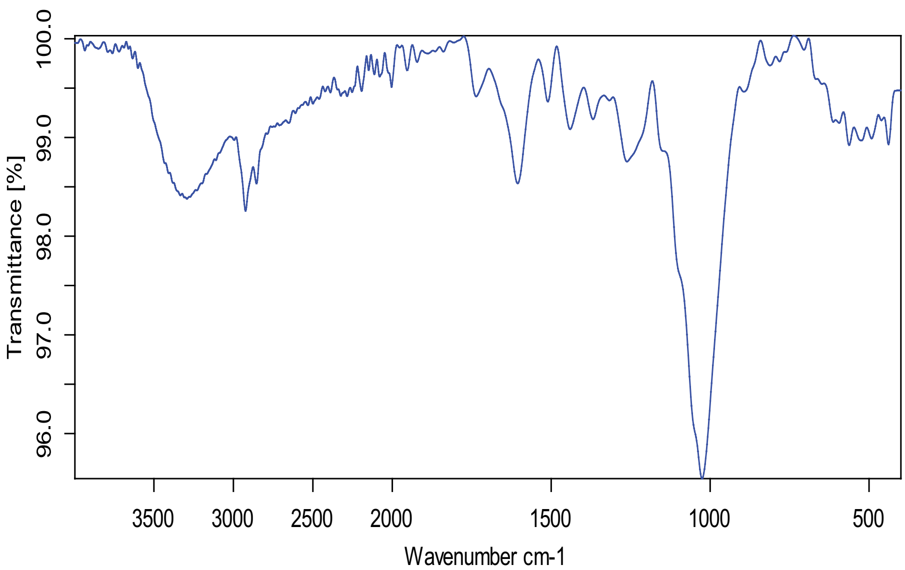

Fig. 3. Fourier-transform infrared spectroscopy curve for pinecone powder.

The C–N link is demonstrated by the peak between 1,750–1,650 cm^{-1}, whilst the one between (1,650–1,550) cm^{-1} confirms either a primary amine N–H or the aromatic C=C. The peak between 1,300–1,250 cm^{-1} in the green area indicates an aromatic ester C–O bond, whereas the one between 1,200–1,000 cm^{-1} shows an N–H aliphatic amine [34,35].

3.3. Effect of pinecones powder dosage

The characterization of the iron and steel industry wastewater used for these experiments is listed in Table 2.

The industrial wastewater pH was set at natural pH 8 for the purpose of testing the effect of pinecones coagulant dose, as indicated in Table 2. Various coagulant dosages (1, 3, 5, 7, and 10 g/L) were immediately mixed into multiple beakers of wastewater samples. The suspension was slowly stirred and then allowed to settle.

The effect of coagulant dosages on COD, TSS, ammonia-nitrogen NH_3–N and heavy metals (manganese Mn, iron Fe, zinc Zn, aluminum A" and nickel Ni from iron and steel industry wastewater sample for sufficient treatment.

3.3.1. Effects of dosage on COD, TSS and ammonia-nitrogen NH_3–N removal efficiency

To investigate the efficacy of coagulant dose, A series of experiments were conducted by varying pinecones powder doses ranges (1, 3, 5, 7, and 10 g) are mixed with 1 L of iron and steel industry wastewater and agitated using an orbital shaker under conditions mentioned in section 2.2. According to Ramavandi and Farjadfard [36], because of the mass of the coagulant, surface charge can have a considerable impact on coagulation performance. Economical optimization of coagulant dosage and best-needed coagulant mass for scale-up, as well as the design of large-scale equipment, are necessary. Therefore, the effect of pinecones powder dose on COD and ammonia-nitrogen NH_3–N removal was studied at an original iron and steel industrial wastewater pH of 8, and the findings are shown in Fig. 4.

Table 2
Characteristic of industrial (iron and steel factory) wastewater

Industrial wastewater parameters	Results
pH	8
Color, Pt-Co	865.6
TSS, mg/L	110
COD, mg/L	840.24
Ammonia-nitrogen NH_3–N, mg/L	42.8
Manganese Mn, mg/L	6.27
Iron Fe, mg/L	5.30
Zinc Zn, mg/L	5.44
Aluminum Al, mg/L	0.38
Nickel Ni, mg/L	0.15

Pinecones powder coagulant showed its effectiveness when used as coagulant with the optimal dose of 3 g/L. The highest efficiency removal for COD was 83.3%, as shown in Fig. 4.

Fig. 1 illustrates that by increasing the pinecones powder dosage (up to 10 g/L), the decrease on COD removal take place. This is due to coagulant overloading, which limits the quantity of accessible adsorption parts for colloidal particle bridging by covering the surface of the natural coagulant [36,37].

The result of batch test in Fig. 4 demonstrate the effect of pinecones powder coagulant dosage on the of ammonia-nitrogen NH_3–N efficiency removal. The maximum two treatment efficiency was found at dosage of 3 and 7 g/L with 83.9% and 84.4%, however; from an economical perspective, and to reduce the of sludge produced from the

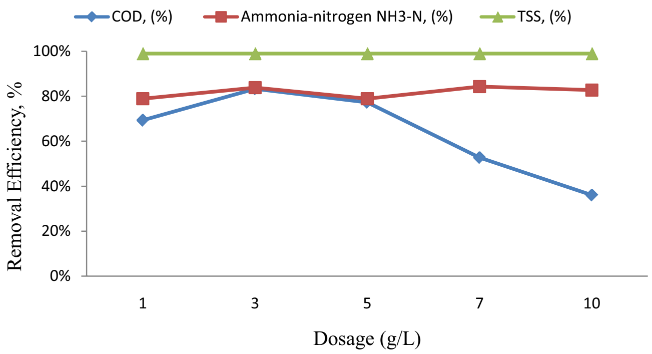

Fig. 4. Effects of pinecones powder dose on COD, TSS and NH_3–N removal (pH: 8).

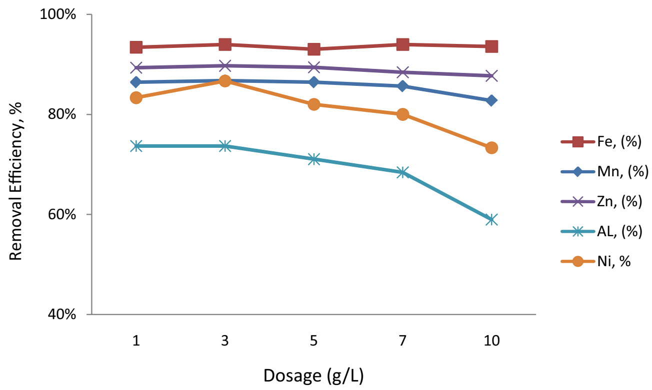

Fig. 5. Effects of pinecone powder dose on heavy metals removal (pH: 8).

process, the optimal dosage could be 3 g/L as no considerable difference in removal efficiency between both dosages. Furthermore, when the dose increased was larger than 3 g/L, no significant removal was found in this study.

TSS removal effectiveness, on the other hand, was shown to be consistent at 99% when pH varied from 5–10 throughout the studies. Because of the neutral electric charge, the particles have a strong coagulation capacity at pH levels ranging from 7 to 9 [38], implying that the particles' adsorption capability for COD and ammonia-nitrogen NH_3–N will be high.

The capability of pinecone powder's natural polyphenols to adsorb organics and metal ions improved organic contamination removal [39]. The improvement in organic and ammonia removal might be attributed to the action of electric double layers generated by carboxylic, phenolic, and amino groups [40]. When larger doses of pinecone powder (>3 g) were used, the removal effectiveness of the target parameters decreased. The positively charged primary amino groups in pinecone powder increased the bridging mechanism of the particles and colloids in the wastewater, which aided in flocculation [41]. The pinecone powder has a high molecular weight and has not been hydrolyzed in wastewater. A higher dose of pinecones powder results in the quick precipitation of a significant amount of powder, which may limit flocculation efficacy [42].

3.3.2. Effects of dosage on heavy metal removal percentage (Mn, Fe, Zn, Al and Ni)

Fig. 5 shows that optimal dosage of pinecone for heavy metals (Mn, Fe, Zn, Al and Ni) in the iron and steel industry wastewater, were obtained at 3 g/L dose of pinecone powder in coagulation flocculation experiments with highest removal efficiency (86.8%, 94%, 89.7%, 73.7%, and 86.7%) for Mn, Fe, Zn, Al and Ni respectively.

Furthermore, when the dosage added was larger than the suggested value of 3 g/L, no significant removal was found in this study.

3.4. Effect of variance pH at industrial wastewater treatment

The pH of the wastewater was adjusted from 5 to 10, and the coagulation test was performed at room temperature with an initial characteristic of the industrial sample as shown in Table 2 and a coagulant dose of 3 g/L. A 1 N H_2SO_4/NaOH solution was used to alter the pH of the samples.

3.4.1. Effects of pH on COD, ammonia-nitrogen NH_3–N removal efficiency

The effects of pH (4–10) on COD and NH_3–N removal using 3 g/L pinecone powder are shown in Fig. 6. At pH 8.0, the maximum coagulation efficiency was attained, with 83.3% COD removal efficiency and 83.9% NH_3–N removal. The removal of COD and NH_3–N increased gradually as pH climbed until the maximum value was reached. As the pH raised slightly above optimal, the percentage removal of COD and NH_3–N decreased.

During the studies, samples in beakers were adjusted to the proper pH before any additional coagulation procedures using pinecone powder. At pH 8, the maximum COD and NH_3–N removal efficiencies for were 83.3% and 83.9%, respectively, as illustrated in Fig. 6, the removal efficiency improves from 5 to 10 and then decreases. The organic nature of pinecone powder ensured that the pH of industrial effluent remained unchanged after its addition. As a result, no pH adjustment was required throughout the treatment procedure when pinecone powder was utilized as a coagulant.

Because of their neutral electric charge, the particles have a good coagulation capacity at pH values ranging from 7 to 9 [38]. By interacting with pinecone particles, cations in wastewater can increase coagulation by neutralizing and reducing the negative charges of the coagulant functional group residue [43]. The addition of monovalent and multivalent cations to wastewater, such as Mg^{2+}, Ca^{2+}, Na^{+}, and Fe^{2+} increased flocculating activity. These findings are consistent with those of [44–46], who found that multivalent cations such as Ca^{2+}, Mn^{2+}, and Al^{3+} increased flocculation activity [46,47] revealed that the presence of Ca^{2+}, Mg^{2+} and Mn^{2+} increased flocculating activity.

3.4.2. Effects of pH on heavy metal (Mn, Fe, Zn, Al and Ni) removal efficiency

Experiments were then conducted at various pH levels using the optimal dosage of pinecone powder (3 g/L) to

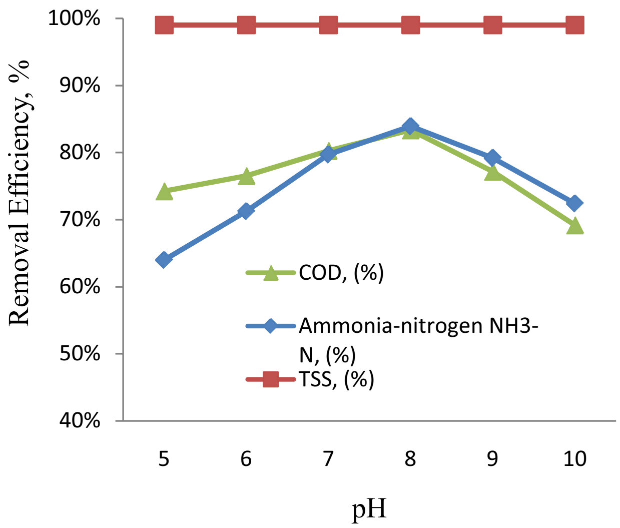

Fig. 6. Effects of pH on COD, TSS and ammonia-nitrogen NH_3–N removal.

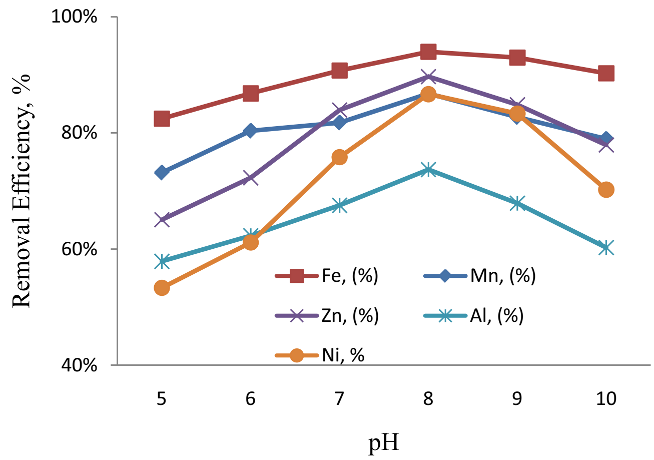

Fig. 7. Effects of pH on heavy metals removal.

find the best pH range. It was discovered that the optimal pH was 8 and that using the coagulant resulted in better removals. Mn, Fe, Zn, Al and Ni reductions by pinecone stone powder were 86.8%, 93.7%, 89.7%, 73.7% and 86.7%, respectively, at pH 8 (Fig. 7). The organic structure of pinecone powder preserved the pH of industrial effluent after its addition.

As a result, no pH adjustment was required throughout the treatment procedure when pinecone powder was utilized as a coagulant.

4. Conclusion

In general, the removal effectiveness of COD, TSS, NH_3–N, Mn, Fe, Zn, Al, and Ni by pinecone powder shown significant promise as a plant-based natural coagulant in iron and steel factory treatment. The experiment proved the significant coagulation characteristics of pinecone powder. The following are the study's specific results. FTIR research indicated the presence of several functional groups involved in the coagulation process.

At 3 g/L, the pinecones powder removed a significant number of COD, TSS, NH_3–N, Mn, Fe, Zn, Al, and Ni from effluent at pH 8, with percentages of 83.3%, 99%, 83.9%, 86.8%, 93.7%, 89.7%, 73.7% and 86.7%, respectively. The impacts of pH ranges from (5–10) demonstrate that the natural pH of the wastewater sample shows that the greatest feasible removal efficiency. Because pinecone powder is organic, its addition had no effect on the pH of industrial effluent. Therefore, no pH adjustment was necessary throughout the treatment phase when pinecone powder was used as a coagulant.

Acknowledgments

The authors wish to express sincere thanks to the many individuals and organizations for their kind support in the study Karabuk University Turkey, Scientific Research Projects Coordination Unit through its KBÜBAP-22-YL-033 funding, as well as the Institute of International Education-Scholar Rescue Fund, (IIE –SRF). New York, NY 10007 USA, for supporting this work. Also, the research leading to these results has received funding from Ministry of Higher Education, Research, and Innovation (MoHERI) of the Sultanate of Oman under the Block Funding Program, MoHERI Block Funding Agreement No. MoHERI/BFP/ASU/01/2021.

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