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# Application of plant-based natural coagulant for sustainable treatment of steel and iron industrial wastewater, Karabuk, Turkey

Salem S. Abu Amr[a,b,*], Mohammed Shadi S. Abujazar[b,c], Sakine Ugurlu Karaağaç[b], Riyad Mahfud[a,d], Motasem Y.D. Alazaiza[e], Rami J.A. Hamad[a]

[a]*International College of Engineering and Management, 111 St., Seeb, Muscat, Oman, emails: salem.s@icem.edu.om (S.S. Abu Amr), riyad@icem.edu.om (R. Mahfud), rami@icem.edu.om (R.J.A. Hamad)*
[b]*Department of Environmental Engineering, Faculty of Engineering, Karabuk University, Karabuk 78050, Turkey, emails: shadiabujazar@gmail.com (M.S.S. Abujazar), sakineugurlu@karabuk.edu.tr (S.U. Karaağaç)*
[c]*Al-Aqsa Community Intermediate College, Al-Aqsa University, Gaza, Palestine – P.B.4051, email: ms.abujazar@alaqsa.edu.ps (M.S.S. Abujazar)*
[d]*Department of Chemical Engineering, College of Engineering, Sabratha University, Sabratha, Libya, email: riyad.mahfud@sabu.edu.ly (R. Mahfud)*
[e]*Department of Civil and Environmental Engineering, College of Engineering (COE), A'Sharqiyah University (ASU), 400 Ibra, Oman, email: my.azaiza@gmail.com (M.Y.D. Alazaiza)*

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**ABSTRACT**

This study examines the use of date stone powder-based plant natural coagulant in the treatment of iron and steel industrial effluent. Coagulation process was conducted using different dosage from date stone powdered (0.2–10 g/L) and different pH values (5–10) using orbital shaker at 200 rpm. The treatment efficiency was evaluated by examine the removal for chemical oxygen demand (COD), total suspended solids (TSS), ammonia-nitrogen ($NH_3$–N), manganese (Mn), iron (Fe), zinc (Zn), aluminum (Al), and nickel (Ni). The maximal removal for COD, TSS, $NH_3$–N, Mn, Fe, Zn, Al, and Ni were 59.4%, 99%, 92.1%, 87.1%, 97.7%, 94.8%, 65.8%, and 80.3%, respectively. Date stone powder has enormous promise as a plant-based natural coagulant for industrial effluent wastewater treatment and might be used to treat effluent from the iron and steel industries.

*Keywords:* Natural coagulant; Industrial; Wastewater; Treatment; Removal; Coagulation–flocculation

## 1. Introduction

Water is an essential natural resource for human life. Water covers about three-quarters of the earth's surface, with nearly 0.4% useable [1,2]. Water quantity and accessibility have historically played an essential role in determining where people may dwell and their style of living. The considerable growth in population, economic development, and industrialization reflected favorably in an increase in the people's living requirements and well-being, an increase in water demand, and excessive removal of freshwater resources [3,4]. The environment has degraded as a result of pollutants dumped into water bodies.

Fresh water is essential for human existence, and a shortage of it is the primary cause of most deaths and diseases. Water quality is a public health issue; water-related and waterborne illnesses account for more than 80% of all infections globally. As a consequence, clean water and a sanitary environment can save around 93% of deaths [5].

* Corresponding author.

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The industrial revolution and anthropogenic factors on our planet toward urbanization have severely impacted the environment in general, particularly water. Many companies create contaminated water as a result of industrialization processes, and this is one of the most significant water pollutants on our planet, not to mention the paucity of useable water supplies [6–9].

This compelled governments to act and adopt rules and regulations to limit water pollution caused by these industrial operations and others. Since many developed nations have expressed an interest in the environment and its preservation, it is essential to focus on offering more sustainable options for acceptable wastewater treatment solutions [10].

As a result of low cost and compactness of chemical processes; coagulation–flocculation process becomes popular with various wastewater treatment approaches, such as biological and physiochemical processes [11–16]. However, many inorganic coagulants (such as aluminum or iron salts) are used in water and wastewater treatment, which has some drawbacks, such as cost, environmental impact, toxicity, and significant sludge volume creation [17–19]. Therefore, natural coagulants are being employed more often to lessen the environmental impact of the coagulation–flocculation process [20–22].

Numerous studies have emphasized the use of natural coagulants in the treatment of wastewater from varied industries, showing that they are equally effective as chemical coagulants in treating a wide range of problematic parameters [23–25]. Industrial wastewater has also been successfully treated using plant-based natural coagulants [26,27]. Plant-based products can act as coagulants because they can carry out coagulation activities such polymer bridging and charge neutralization in colloidal particles [28–32]. Karaağaç et al. [33] employed olive stone powdered as a natural coagulant for industrial wastewater treatment and reported significant removal for organic and heavy metals from industrial effluent.

The present study aimed to examine the performance of date stone powder as a natural coagulant in treating wastewater from the iron and steel sector, specifically in terms of chemical oxygen demand (COD), total suspended solids (TSS), ammonia-nitrogen ($NH_3$–N), and heavy metals removal. This work examined the effect of date stone coagulant dose and pH variation on the removal efficiency. Furthermore, the chemical structure, thermal stability, and shape of date stone powder were investigated using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). This experimental investigation aimed to determine the effectiveness of the coagulation/flocculation process at the Karabuk iron and steel industry effluent near Karabuk University in Turkey.

## 2. Materials and methods

### 2.1. Sample collection

Karabuk Iron and Steel Factory's raw industrial effluent was collected in Karabuk, Turkey. The wastewater sample was collected at the discharge site and transported straight to the laboratory in a cool box within 1 h of collection and utilized; if not used immediately, the samples were stored at 25°C in the dark until use.

### 2.2. Preparation of date stone powder

Date stones (Fig. 1) were collected from a home in Gaza, Palestine, and transported to Karabuk University in Turkey. The date stone was cleaned with distilled water to remove any clinging bits. The stones were first allowed to dry at ambient temperature before being put in a 50°C oven for 8 h. The above procedures were done in order to make it easier to smash the date stones. As illustrated in Fig. 1, the date stones were grinded for size reduction using a (Retsch RS 200) grinder to get homogenize powder form employed as a coagulant in the tests.

### 2.3. Analytical study

The characterization parameters and procedures employed are shown in Table 1. During the tests, the pH of the samples was adjusted with a 1N $H_2SO_4$/NaOH solution [34].

### 2.4. Experimental procedure

In order to imitate the coagulation–flocculation process, Orbital shaker (Type: PSU-10i, No:010144-1404-0228, Latvia) and three 500 mL beakers were used to test the effect of the coagulant dose. Each beaker held 200 mL of sample. The timing and speed for rapid and slow mixing were set using the shaker apparatus's automated controller. The coagulation–flocculation process in this research comprised 15 min of rapid mixing at 200 rpm, followed by 30 min of slow


Fig. 1. Date stone and powder.

Table 1
Characterization parameters and methods

| Parameters | Method |
|---|---|
| pH | pH meter |
| Total suspended solids (mg/L) | SM 2540 D |
| Chemical oxygen demand (mg/L) | ASTM D1252-A |
| Ammonia-nitrogen (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 |

mixing at 60 rpm, and then 60 min of settling [35] for further testing for percentage removal of COD, TSS, $NH_3$–N, and heavy metals (manganese Mn, iron Fe, zinc Zn, aluminum Al, and nickel Ni). Throughout this experiment, the initial pH of the sample 8 was kept uncorrected, and coagulation was assessed based on the removal efficiency of COD, TSS, and $NH_3$–N.

The optimal date stone powder dose determined in the previous experimental stage was next assessed regarding the effect of pH (range from 5 to 10) on removal efficiency for the desired parameters. Before adding the coagulant, the pH was adjusted using 1 M of hydrochloric acid solution and 1 M of sodium hydroxide solution. To limit the risk of particle settlements, industrial wastewater samples were forcefully shaken prior to coagulation; removal efficiency is estimated as follows:

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

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

Table 2 shows the characteristics of the iron and steel factory effluent utilized in these tests.

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

| Industrial wastewater parameters | Results |
|---|---|
| pH | 8 |
| Color (Pt-Co) | 865.6 |
| Total suspended solids (mg/L) | 110 |
| Chemical oxygen demand (mg/L) | 840.24 |
| Ammonia-nitrogen (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 |

## 3. Results and discussion

### 3.1. Characterization of date stone powder using SEM imaging

Prior to and after the coagulation procedure, the morphological surface structure of date stone powder was studied. Date stone 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 [36]. The coagulant aggregated the particles, producing bigger flocs that were easily settled, as seen in Fig. 2b. As a result, SEM pictures of date stone powder revealed that bridging might be to blame for date stone powder's outstanding coagulation capabilities [36,37].

### 3.2. FTIR analysis

To further investigate the existence of the powdered date stone's main possible functional groups, the corresponding infrared (IR) spectrum using FTIR spectroscopy was generated, as shown in Fig. 3. FTIR analysis was adequately done to simplify and possibly spotlight its main functional groups. To ease the analysis of the IR spectrum obtained for date stone powder, the bands' range- where its functional groups could highlight within the range of wavelength peaks. In the range of 300–2,500 cm$^{-1}$, the detected peak may suggest the presence of strong amine salts (N–H), which are engaged in the bridging mechanism employed by particles during the coagulation process and may help to improve the removal of

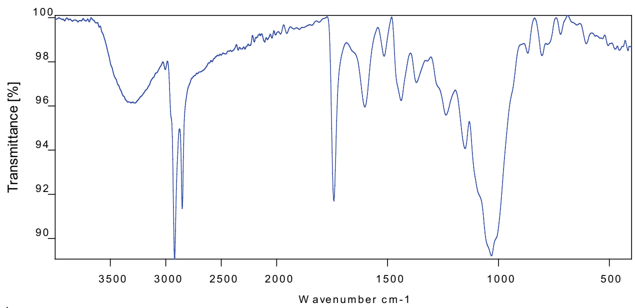
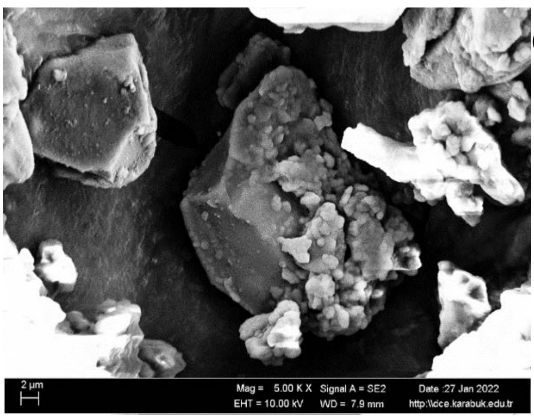



Fig. 3. Fourier-transform infrared spectroscopy curve for date stone powder.

(a)


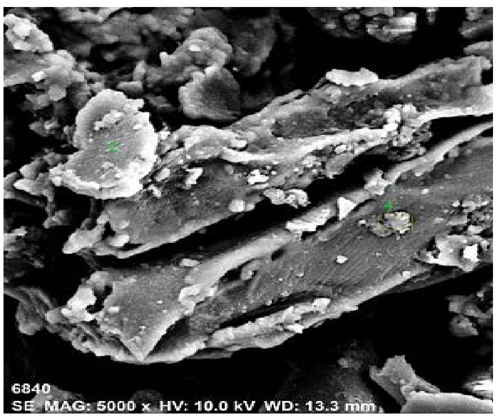

(b)



Fig. 2. Scanning electron microscopy image (2 μm) of date stone powder (a) before and (b) after the coagulation procedure.

ammonia and organics from wastewater. The peak between 1,750–1,650 cm$^{-1}$ shows the C–N link, whereas the ones from 1,650–1,550 cm$^{-1}$ either confirm a primary amine N–H or the aromatic C=C. The peak between a green region of 1,300–1,250 cm$^{-1}$ indicates an aromatic ester C–O bond, while the one between 1,200–1,000 cm$^{-1}$ shows the N–H aliphatic amine.

### 3.3. Effect of date stones powder dosage

The effect of date stone powder on the removal efficiency of targeted parameters was evaluated. Therefore, different dosages of 0.2, 0.6, 1, 3, 5, 7, and 10 g/L of coagulants were adopted. The highest COD and $NH_3$–N removal performance was 59.4% and 92.1%, respectively, using 7 g/L of coagulant, maintaining the initial pH 8 for industrial effluent (Fig. 4).

As shown in Fig. 4, there was a progressive trend in removing up to 7 g/L dosages; then, it began to decline as the date stone powder dose was increased (up to 10 g/L).

The decrease in COD and $NH_3$–N removal takes place. This is due to the overcrowding of coagulants; This might be because when the coagulant was introduced, there has been increased availability of coagulation processes to take place, resulting in a proportional rise in removal; at 7 g/L dosage, the coagulation process may have achieved equilibrium, so that further dose did not affect removal [38–40].

On the other hand, TSS removal performance was shown to be consistent at 99% at all doses throughout the tests. Date stone powder effectiveness in COD, TSS, and $NH_3$–N removal can be linked to coagulant chemicals in this date stone powder. Indeed, solid particles in industrial wastewater effluent agglutinate grow in size and decant in the backer.

Regarding optimal dose, the coagulation efficiency of date stone powder in COD and $NH_3$–N removal differed. As a result, it is essential to determine the optimal coagulant dose to reduce material costs and sludge formation while ensuring peak performance in the treatment process.

The capacity of natural polyphenols in date stone powder to adsorb organics and metal ions increased the removal of organic contaminants [41]. The improvement in organic and ammonia removal might be attributed to the action of electric double layers generated by carboxylic, phenolic, and amino groups [42]. When more significant doses of a date stone (>7 g) were used, the removal effectiveness of targeted parameters decreased. Date stone's positively charged primary amino groups increased the bridging mechanism of the particles and colloids in the wastewater and improved the flocculation process [43]. Date stone powder has a high molecular weight and is unhydrolyzed in wastewater. Using a larger dosage of date stone results in the rapid precipitation of a considerable powder volume, which may reduce flocculation effectiveness [44].

The performance of date stone powder on heavy metal removals from industrial effluent is presented in Fig. 5. The highest removal efficiencies for Fe, Zn, Al, and Ni were 97.7%, 94.9%, 65.8%, and 80%, respectively, at 7 g/L. In contrast, the highest removal efficiency of Mn was 87.2% of Mn at 5 g/L, in the same time the removal efficiency of Mn shows significant removal efficiency of 87.1% at 7 g/L. Therefore, we consider that the optimal dosage of date stone powder is 7 g/L for all tested heavy metals in this experiment; furthermore, when the dosage added was more significant than the recommended volume of 7 g/L, no significant reduction was found in this experiment.

By linking with date stone powder particles, cations in wastewater can increase the coagulation process by neutralizing and destabilizing the negative charges of the coagulant functional group residue [45]. The presence of monovalent and multivalent cations in wastewater, such as $Mg^{2+}$, $Ca^{2+}$, $Na^{+}$, and $Fe^{2+}$, enhanced flocculation. These findings are similar to those published by Okaiyeto et al. [46], Wang et al. [47], and Zhang et al. [48], who observed that multivalent cations such $Ca^{2+}$, $Mn^{2+}$, and $Al^{3+}$ boosted flocculation activities. Nwodo and Okoh [49], similarly found that $Ca^{2+}$, $Mg^{2+}$, and $Mn^{2+}$ increased flocculating ability.

### 3.4. Effect of pH variance

The effect of pH ranges 5–10 was evaluated, maintaining the optimum coagulant dosage of 7 g/L. The pH was adjusted using 1 N $H_2SO_4$/NaOH solution. As illustrated in Fig. 6, the maximum removal performance for the parameters was observed at pH 8.0 with 59% COD removal and 92.1% $NH_3$–N removal. The removal of COD and $NH_3$–N increased steadily as pH values climbed until the optimum

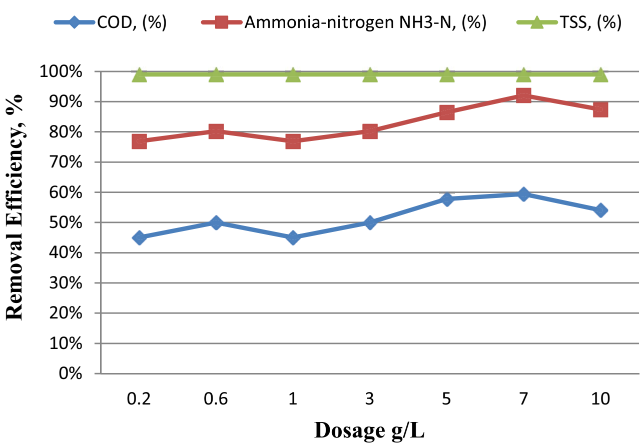



Fig. 4. Effects of date stone powder dose on chemical oxygen demand, total suspended solids, and ammonia-nitrogen removal (pH: 8).

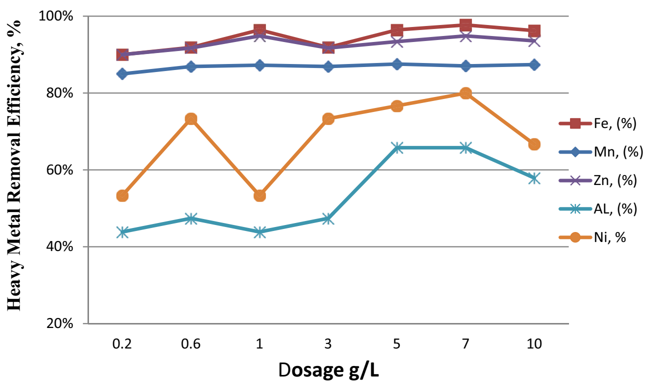



Fig. 5. Effects of date stone powder dose on heavy metals Mn, Fe, Zn, Al and Ni removal (pH: 8).

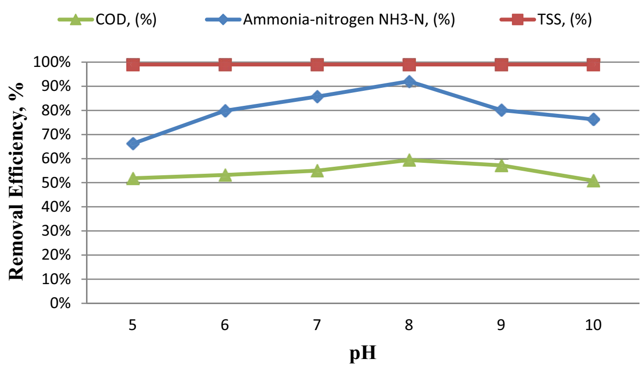



Fig. 6. Effects of pH on chemical oxygen demand, total suspended solids, and ammonia-nitrogen removal.

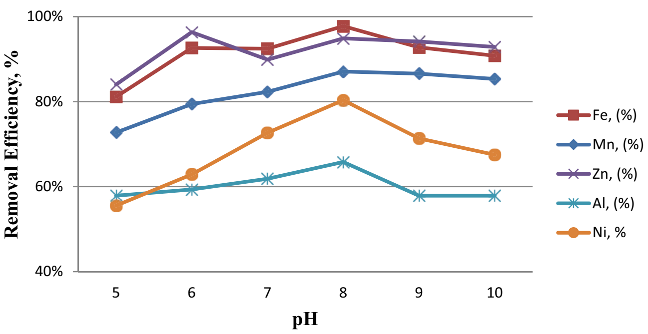



Fig. 7. Effects of pH on heavy metals removal.

value was achieved. The percentage removal of COD and $NH_3$–N dropped when pH increased above the optimum.

The pH of each beaker was corrected to the requested pH before the coagulation treatment took place using date stones powder during the trials; as shown in Fig. 6, the percentage removal for COD and $NH_3$–N were 59% and 92.1%, respectively, at pH 8, as illustrated in Fig. 6 the percentage removal begins to increase with pH increase from 5 to 10 and then decrease trend occurs.

On the other hand, the percentage removal of TSS was observed to be constant at 99% as pH changed from 5–10 throughout the experiments. Because of the neutral electric charge of COD and $NH_3$–N, the adsorption capacity of the particles is strong at pH levels ranging from 7 to 9 [50].

Experiments were then carried out at various pH levels using the optimal dosage of date stone powder (7 g/L) to determine the best pH range. It was discovered that the ideal pH was 8 and that employing the coagulant resulted in improved removals. The removals of Mn, Fe, Zn, Al, and Ni using date stones powder were 87.1%, 97.7%, 94.8%, 65.8%, and 80.3%, respectively, at pH 8 (Fig. 7).

Due to the organic structure of date stones powder, the pH of industrial effluent remained unchanged after its addition. As a result, no pH correction was necessary throughout the treatment process when date stone powder was used as a coagulant.

## 4. Conclusion

Date stone powder has shown substantial potential as a plant-based natural coagulant in iron and steel mill treatment in COD, TSS, $NH_3$–N, Mn, Fe, Zn, Al, and Ni removal. The experiment demonstrated the date stone's substantial coagulation properties. The specific findings of the research are as follows. The presence of various functional groups involved in the coagulation process was confirmed by FTIR analysis. The date stone powder removed a high proportion of COD, TSS, $NH_3$–N, Mn, Fe, Zn, Al, and Ni from effluent at pH 8 at a concentration of 7 g/L, with percentages of 59.4%, 99%, 92.1%, 87.1%, 97.7%, 94.8%, 65.8%, and 80.3%, respectively. The impacts of pH ranges from (5–10) demonstrate that the best removal efficiency was 59.45% COD, 99% TSS, and 92.1% $NH_3$–N, while the percentage removal of heavy metals was 87.1%, 97.7%, 94.8%, 65.8%, and 80.3% for Mn, Fe, Zn, Al, and Ni, respectively. Due to its organic nature, industrial effluent pH remained unaltered after adding date stones powder. As a result, no pH adjustment was required throughout the treatment when date stone powder was utilized as a coagulant.

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## References


[1] S.N. Ugwu, A.F. Umuokoro, E.A. Echiegu, B.O. Ugwuishiwu, C.C. Enweremadu, Comparative study of the use of natural and artificial coagulants for the treatment of sullage (domestic wastewater), Cogent Eng., 4 (2017) 1–13, doi: 10.1080/23311916.2017.1365676.

[2] W.M. Desta, M.E. Bote, Wastewater treatment using a natural coagulant (*Moringa oleifera* seeds): optimization through response surface methodology, Heliyon, 7 (2021) e08451, doi: 10.1016/j.heliyon.2021.e08451.

[3] M. Kumar, A. Kushwaha, L. Goswami, A.K. Singh, M. Sikandar, A review on advances and mechanism for the phycoremediation of cadmium contaminated wastewater, Cleaner Eng. Technol., 5 (2021) 100288, doi: 10.1016/j.clet.2021.100288.

[4] M.S.S. Abujazar, S. Fatihah, A.E. Kabeel, S. Sharil, S.S. Abu Amr, Evaluation quality of desalinated water derived from inclined copper-stepped solar still, Desal. Water Treat., 131 (2018) 83–95.

[5] M.O. Fatehah, S. Hossain, T.T. Teng, Semiconductor wastewater treatment using tapioca starch as a natural coagulant, J. Water Resour. Prot., 5 (2013) 1018–1026.

[6] H.-G. Hoang, C. Lin, H.-T. Tran, C.-F. Chiang, X.-T. Bui, N.K. Cheruiyot, C.-C. Shern, C.-W. Lee, Heavy metal contamination trends in surface water and sediments of a river in a highly-industrialized region, Environ. Technol. Innovation, 20 (2020) 101043, doi: 10.1016/j.eti.2020.101043.

[7] R. Setia, S.S. Dhaliwal, V. Kumar, R. Singh, S.S. Kukal, B. Pateriya, Impact assessment of metal contamination in surface water of Sutlej River (India) on human health risks, Environ. Pollut., 265 (2020) 114907, doi: 10.1016/j.envpol.2020.114907.

[8] R.R. Ayangunna, S.O. Giwa, A. Giwa, Coagulation-flocculation treatment of industrial wastewater using tamarind seed powder, Int. J. ChemTech Res., 9 (2016) 771–780.

[9] Ş. Şener, E. Şener, A. Davraz, Evaluation of water quality using water quality index (WQI) method and GIS in Aksu River (SW-Turkey), Sci. Total Environ., 584–585 (2017) 131–144.
[10] S. Tong, H. Li, M. Tudi, X. Yuan, L. Yang, Comparison of characteristics, water quality and health risk assessment of trace elements in surface water and groundwater in China, Ecotoxicol. Environ. Saf., 219 (2021) 112283, doi: 10.1016/j.ecoenv.2021.112283.
[11] A.A. Owodunni, S. Ismail, Revolutionary technique for sustainable plant-based green coagulants in industrial wastewater treatment—a review, J. Water Process Eng., 42 (2021) 102096, doi: 10.1016/j.jwpe.2021.102096.
[12] M. Kumari, S.K. Gupta, A novel process of adsorption cum enhanced coagulation-flocculation spiked with magnetic nanoadsorbents for the removal of aromatic and hydrophobic fraction of natural organic matter along with turbidity from drinking water, J. Cleaner Prod., 244 (2020) 118899, doi: 10.1016/j.jclepro.2019.118899.
[13] A.D. Barbosa, L.F. da Silva, H.M. de Paula, L.L. Romualdo, G. Sadoyama, L.S. Andrade, Combined use of coagulation (*M. oleifera*) and electrochemical techniques in the treatment of industrial paint wastewater for reuse and/or disposal, Water Res., 145 (2018) 153–161.
[14] M.I. Ejimofor, I.G. Ezemagu, M.C. Menkiti, Biogas production using coagulation sludge obtained from paint wastewater decontamination: characterization and anaerobic digestion kinetics, Curr. Res. Green Sustainable Chem., 3 (2020) 100024, doi: 10.1016/j.crgsc.2020.100024.
[15] Z.Z. Abidin, N. Ismail, R. Yunus, I.S. Ahamad, A. Idris, A preliminary study on *Jatropha curcas* as coagulant in wastewater treatment, Environ. Technol., 32 (2011) 971–977.
[16] K.P.Y. Shak, T.Y. Wu, Coagulation–flocculation treatment of high-strength agro-industrial wastewater using natural *Cassia obtusifolia* seed gum: treatment efficiencies and flocs characterization, Chem. Eng. J., 256 (2014) 293–305.
[17] P. Vega Andrade, C.F. Palanca, M.A.C. de Oliveira, C.Y.K. Ito, A.G. dos Reis, Use of *Moringa oleifera* seed as a natural coagulant in domestic wastewater tertiary treatment: physicochemical, cytotoxicity and bacterial load evaluation, J. Water Process Eng., 40 (2021) 101859, doi: 10.1016/j.jwpe.2020.101859.
[18] H. Guven, R.K. Dereli, H. Ozgun, M.E. Ersahin, I. Ozturk, Towards sustainable and energy efficient municipal wastewater treatment by up-concentration of organics, Prog. Energy Combust. Sci., 70 (2019) 145–168.
[19] B. Tawakkoly, A. Alizadehdakhel, F. Dorosti, Evaluation of COD and turbidity removal from compost leachate wastewater using *Salvia hispanica* as a natural coagulant, Ind. Crops Prod., 137 (2019) 323–331.
[20] W.L. Ang, A.W. Mohammad, State of the art and sustainability of natural coagulants in water and wastewater treatment, J. Cleaner Prod., 262 (2020) 121267, doi: 10.1016/j.jclepro.2020.121267.
[21] S. Maurya, A. Daverey, Evaluation of plant-based natural coagulants for municipal wastewater treatment, 3 Biotech., 8 (2018) 77, doi: 10.1007/s13205-018-1103-8.
[22] M. Alazaiza, A. Albahnasawi, G. Ali, M. Bashir, D. Nassani, T. Al Maskari, S. Amr, M. Abujazar, Application of natural coagulants for pharmaceutical removal from water and wastewater: a review, Water, 14 (2022) 140, doi: 10.3390/w14020140.
[23] A. Ahmad, S.R.S. Abdullah, H.A. Hasan, A.R. Othman, N. 'Izzati Ismail, Plant-based versus metal-based coagulants in aquaculture wastewater treatment: effect of mass ratio and settling time, J. Water Process Eng., 43 (2021) 102269, doi: 10.1016/j.jwpe.2021.102269.
[24] G.L. Muniz, A.C. Borges, T.C.F. da Silva, Performance of natural coagulants obtained from agro-industrial wastes in dairy wastewater treatment using dissolved air flotation, J. Water Process Eng., 37 (2020) 101453, doi: 10.1016/j.jwpe.2020.101453.
[25] M.S.S. Abujazar, S.U. Karaağaç, S.S. Abu Amr, M.Y.D. Alazaiza, M.J. Bashir, Recent advancement in the application of hybrid coagulants in coagulation-flocculation of wastewater: a review, J. Cleaner Prod., 345 (2022) 131133, doi: 10.1016/j.jclepro.2022.131133.
[26] M.B. Fard, D. Hamidi, K. Yetilmezsoy, J. Alavi, F. Hosseinpour, Utilization of *Alyssum* mucilage as a natural coagulant in oily-saline wastewater treatment, J. Water Process Eng., 40 (2021) 101763, doi: 10.1016/j.jwpe.2020.101763.
[27] K.E. Lee, N. Morad, T.T. Teng, B.T. Poh, Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: a review, Chem. Eng. J., 203 (2012) 370–386.
[28] A. Hariz Amran, N. Syamimi Zaidi, K. Muda, L. Wai Loan, Effectiveness of natural coagulant in coagulation process: a review, Int. J. Eng. Technol., 7 (2018) 34, doi: 10.14419/ijet.v7i3.9.15269.
[29] E.N. Ali, H. Tien Seng, Heavy metals (Fe, Cu, and Cr) removal from wastewater by *Moringa oleifera* press cake, MATEC Web Conf., 150 (2018) 02008, doi: 10.1051/matecconf/201815002008.
[30] S.-C. Chua, F.-K. Chong, C.-H. Yen, Y.-C. Ho, Valorization of conventional rice starch in drinking water treatment and optimization using response surface methodology (RSM), Chem. Eng. Commun., 208 (2021) 613–623.
[31] M. Dehghani, M.H. Alizadeh, The effects of the natural coagulant Moringa oleifera and alum in wastewater treatment at the Bandar Abbas Oil Refinery, Environ. Health Eng. Manage., 3 (2016) 225–230.
[32] M.S.S. Abujazar, S.U. Karaağaç, S.S. Abu Amr, S. Fatihah, M.J.K. Bashir, M.Y.D. Alazaiza, E. Ibrahim, The effectiveness of rosehip seeds powder as a plant-based natural coagulant for sustainable treatment of steel industries wastewater, Desal. Water Treat., 270 (2022) 44–51.
[33] S.U. Karaağaç, M.S.S. Abujazar, S.S.A. Amr, S. Fatihah, M.J.K. Bashir, M.Y.D. Alazaiza, E. Ibrahim, The potential use of olive seeds powder as plant-based natural coagulant for sustainable treatment of industrial wastewater, Desal. Water Treat., 270 (2022) 44–51.
[34] S. Veli, A. Arslan, M. Isgoren, D. Bingol, D. Demiral, Experimental design approach to COD and color removal of landfill leachate by the electrooxidation process, Environ. Challenges, 5 (2021) 100369, doi: 10.1016/j.envc.2021.100369.
[35] A. Ghaffari, C.C. Miller, B. McMullin, A. Ghahary, Potential application of gaseous nitric oxide as a topical antimicrobial agent, Nitric Oxide, 14 (2006) 21–29.
[36] H. Salehizadeh, S.A. Shojaosadati, Extracellular biopolymeric flocculants: recent trends and biotechnological importance, Biotechnol. Adv., 19 (2001) 371–385.
[37] N. He, Y. Li, J. Chen, S. Lun, Identification of a novel bioflocculant from a newly isolated *Corynebacterium glutamicum*, Biochem. Eng. J., 11 (2002) 137–148.
[38] Z. Daud, B. Ahmad, H. Awang, M.H. Abubakar, N. Nasir, H.A. Tajarudin, Ammoniacal nitrogen removal using flamboyant pods (*Delonix regia*) adsorbent for natural rubber wastewater treatment, Int. J. Integr. Eng., 10 (2018) 184–189.
[39] B. Ramavandi, S. Farjadfard, Removal of chemical oxygen demand from textile wastewater using a natural coagulant, Korean J. Chem. Eng., 31 (2014) 81–87.
[40] M. Besharati Fard, D. Hamidi, J. Alavi, R. Jamshidian, A. Pendashteh, S.A. Mirbagheri, Saline oily wastewater treatment using *Lallemantia mucilage* as a natural coagulant: kinetic study, process optimization, and modeling, Ind. Crops Prod., 163 (2021) 113326, doi: 10.1016/j.indcrop.2021.113326.
[41] G. Palma, Removal of metal ions by modified *Pinus radiata* bark and tannins from water solutions, Water Res., 37 (2003) 4974–4980.
[42] P. Scho, D.M. Mbugua, A.N. Pell, Analysis of condensed tannins: a review, Anim. Feed Sci. Technol., 91 (2001) 21–40.
[43] A.S. Mangrich, M.E. Doumer, A.S. Mallmannn, C.R. Wolf, Green chemistry in water treatment: use of coagulant derived from *Acacia mearnsii* tannin extracts, Rev. Virtual Química, 6 (2014) 2–15.
[44] T.J. Kim, J.L. Silva, M.K. Kim, Y.S. Jung, Enhanced antioxidant capacity and antimicrobial activity of tannic acid by thermal processing, Food Chem., 118 (2010) 740–746.
[45] B. Zhang, H. Su, X. Gu, X. Huang, H. Wang, Effect of structure and charge of polysaccharide flocculants on their flocculation

performance for bentonite suspensions, Colloids Surf., A, 436 (2013) 443–449.

[46] K. Okaiyeto, U. Nwodo, L. Mabinya, A. Okoh, Characterization of a bioflocculant produced by a consortium of *Halomonas* sp. Okoh and *Micrococcus* sp. Leo, Int. J. Environ. Res. Public Health, 10 (2013) 5097–5110.

[47] L. Wang, Z. Feng, X. Wang, X. Wang, X. Zhang, DEGseq: an R package for identifying differentially expressed genes from RNA-seq data, Bioinformatics, 26 (2010) 136–138.

[48] D. Zhang, Z. Hou, Z. Liu, T. Wang, Experimental research on *Phanerochaete chrysosporium* as coal microbial flocculant, Int. J. Min. Sci. Technol., 23 (2013) 521–524.

[49] U.U. Nwodo, A.I. Okoh, Characterization and flocculation properties of biopolymeric flocculant (glycosaminoglycan) produced by *Cellulomonas* sp. Okoh, J. Appl. Microbiol., 114 (2013) 1325–1337.

[50] T. Xia, M. Kovochich, M. Liong, L. Mädler, B. Gilbert, H. Shi, J.I. Yeh, J.I. Zink, A.E. Nel, Comparison of the mechanism of toxicity of zinc oxide and cerium oxide nanoparticles based on dissolution and oxidative stress properties, ACS Nano, 2 (2008) 2121–2134.