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The potential use of olive seeds powder as plant-based natural coagulant for sustainable treatment of industrial wastewater

Sakine Ugurlu Karaağaç[a], Mohammed Shadi S. Abujazar[a,b,*], Mahmut Kopan[a], Salem S. Abu Amr[a,c], Motasem Y.D. Alazaiza[d]

[a]*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), mamutkopan@hotmail.com (M. Kopan), salemabuamro@karabuk.edu.tr (S.S. Abu Amr)*
[b]*Al-Aqsa Community Intermediate College, Al-Aqsa University, Gaza, P.B.4051, Palestinian Authority, email: ms.abujazar@alaqsa.edu.ps*
[c]*International College of Engineering and Management, 111 St, Seeb, Muscat, Oman, email: salem.s@icem.edu.om*
[d]*Department of Civil and Environmental Engineering, College of Engineering (COE), A'Sharqiyah University (ASU), 400 Ibra, Oman, email: my.azaiza@gmail.com*

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ABSTRACT

The use of olive seed powder as a plant-based natural coagulant in treating iron and steel factory wastewater was studied. 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. Coagulation experiments on the effects of iron and steel factory wastewater, pH, and olive seed powder dosage on coagulation efficacy were conducted using an orbital shaker and a flocculation device. The maximum removal percentages of COD, TSS, NH_3–N, Mn, Fe, Zn, Al, and Ni by olive seeds powder were 86.3%, 99%, 72.4%, 80.9%, 91.5%, 92.6%, 73.7%, and 84.3% for effluent at natural pH 8 using a 5 g/L dosage, respectively. The Fourier-transform infrared spectroscopy study showed the presence of several functional groups involved in the coagulation process. It is possible to argue that olive seed powder has enormous potential as a plant-based natural coagulant for wastewater treatment and that it might be used to treat wastewater from iron and steel factories.

Keywords: Industrial wastewater; Natural coagulant; Heavy metals; Removal efficiency

1. Introduction

The significant increase in the population in the previous decades reflected positively on the increase in the life requirements and well-being of the population. Accordingly, industries increased significantly to meet the population's needs [1,2]. Consequently, environmental deterioration occurs due to contaminants being released into bodies of water, either through the disposal of these pollutants directly or through mistreatment [3,4].

Fresh water all around the globe is getting more polluted due to the discharge of untreated waste from various industrial operations [5]. Many companies use fresh water and emit wastewater as waste [6]. Wastewater is not only one of the primary sources of irreparable harm to environmental balances, but it also contributes to the loss of the world's freshwater reserves [7,8]. Water is extensively used in iron and steel factories for several purposes, including cooling, dust suppression, cleaning, temperature regulation (heat treatment), and waste material transfer (ash, sludge, scale,

* Corresponding author.

etc.). Using a sizeable volume of water results in a large amount of wastewater discharge, which may contain suspended materials and various dissolved compounds and chemicals.

Suppose untreated wastewater from the iron and steel industry is released into water bodies. In that case, the principal environmental consequences include organic contaminants and heavy metals such as copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), and molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn) [9–12].

Growing environmental consciousness and more stringent regulatory regulations have compelled several industries to focus on developing more sustainable options for acceptable wastewater treatment solutions [13].

Currently, many wastewater treatment technologies with certain advantages and disadvantages are in use [14,15]. Biological treatment, such as nitrification and denitrification removal [16], physio-chemical treatment, such as adsorption [17,18], ion exchange [19,20], precipitation [21,22], reverse osmosis [23,24], coagulation–flocculation, and electrocoagulation, are the most commonly used wastewater treatments [25–29].

Coagulation–flocculation processes, in particular, are attracting scientific attention due to their high efficiency, low cost, ease of handling, and high availability of various coagulants [26,30,31]. They are widely used for wastewater treatment in various textile, chemical, pharmaceutical, metal-working, and petrochemical industries [30,31].

In the coagulation process, inorganic coagulants such as chemical coagulants (i.e., aluminium or iron salts) are used in the industrial wastewater treatment process [32,33]. However, the disadvantages of such a method were a high costs, toxicity, the formation of vast amounts of sludge, and the changing of the pH value of the treated water [34]; other issues highlighted about the usage of alum include the ecotoxicological effects of sludge, the toxicological effects of residual aluminum in treated water, and the cost of chemical imports [35].

Consequent to the above-mentioned challenges, using natural coagulants instead of chemicals for coagulation is a viable approach for treating diverse industrial wastewater [36]. Researchers are currently focusing on extracting coagulants from naturally existing indigenous minerals to alleviate the worldwide water crisis. Natural coagulants are biodegradable in the environment and can be obtained from plants, animals, and microorganisms. Many recent studies have highlighted the importance of natural coagulants. Plant-based materials can act as coagulants because they can perform coagulation mechanisms, namely neutralization of charge in colloidal particles and polymer bridging. [10,37].

Numerous research studies indicate the potential of natural coagulants in wastewater treatment from diverse sectors, demonstrating that they are comparable to chemical coagulants in terms of treatment efficiency for several parameters of importance [38]. Coagulation with natural plant-based coagulants has also been utilized successfully in treating industrial effluent [39,40].

On the other hand, the current study aims to test the efficacy of olive seed powder as a natural coagulant in iron and steel factory wastewater treatment, specifically in terms of chemical oxygen demand (COD), total suspended solids (TSS), ammonia-nitrogen NH_3–N, and heavy metals removal. More specifically, the goal was to determine the most appropriate coagulant dose, study the pH effect on removal efficiency, and characterize olive seeds powder using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) to elucidate the chemical structure, thermal stability, and morphology, respectively. This experimental investigation was carried out to assess the efficacy of the coagulation/flocculation process in the wastewater of the Karabuk iron and steel factory located near Karabuk University in Turkey.

2. Materials and methods

This research was carried out at an environmental laboratory at Karabuk University's College of Engineering Department of Environmental Engineering. Industrial wastewater samples were collected from Karabuk iron and steel factory, nearby Karabuk University, situated at coordinates: 41°11′N 32°38′E; the collected samples were put in dark brown plastic bottles from the discharge point and transported to the laboratory in a cool box within 1 h of collection and used; if not used immediately, the samples were kept at 25°C in the dark until use.

2.1. Preparation of olive seed powder

Olive seeds were gathered from a restaurant near Karabuk University in Turkey. The olive seeds were rinsed with distilled water to remove the adherent olive. The seeds were initially dried at room temperature before being placed in an oven for 8 h at 50°C, and this was done to make it easier to smash the olive seeds; by using a mortar and pestle, the olive seeds were crushed to reduce their size. The crushed seeds were processed in a (Retsch RS 200) grinder to generate olive seed powder, which was utilized as a coagulant in the tests (Fig. 1). olive seed can also contain cellulose (37.5%), hemicelluloses (26 wt.%), lignin (21.5 wt.%), moisture (8 wt.%), minerals (1 wt.%), and proteins, pectines [3,41].

2.2. Analytical analysis

The characterization parameters and procedures employed are shown in Table 1. During the tests, the pH of the samples was adjusted with a 1 N H_2SO_4/NaOH solution [42].

2.3. Coagulation experiments

Coagulation/flocculation studies were carried out utilizing an Orbital shaker (Type: PSU-10i, No: 010144-1404-0228, Latvia) and three 500 mL beakers to test the impact of a coagulant dose. The operational parameters utilized were determined by reviewing the literature. On the shaker's plate, 500 mL beakers with 200 mL of industrial effluent were put on the shaker. To each beaker, various amounts of olive seed powder were added and shaken for 5 min at 200 rpm to ensure rapid mixing. For another 15 min, the mixing speed was reduced to 90 rpm. After that, all

Fig. 1. Olive seeds and powder.

Table 1
Characterization parameters and methods

Parameters	Method
pH	pH meter
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

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

Industrial wastewater parameters	Units	Results
pH	–	8
TSS	mg/L	110
COD	mg/L	840
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

suspensions were left to settle. After 30 min of sedimentation, the samples were filtered using Whatman circle ashless/white ribbon filter paper to ensure impurity removal and further testing for removal 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.

All tests were duplicated at room temperature (21°C ± 2°C) for uniformity, and the average findings are provided below. Finally, a series of coagulation/flocculation experiments were carried out in 500 mL beakers filled with 200 mL of iron and steel factory effluent under optimal conditions. Table 2 shows the characteristics of the iron and steel factory effluent used in these tests [43].

The optimal olive seed powder dose determined in the previous experimental stage was assessed regarding the effect of pH (ranging from 5 to 10) on removal efficiency for the specified parameters. Before adding the coagulant, the pH was adjusted using 1 M hydrochloric acid solution and 1 M sodium hydroxide solution. In order to reduce the possibility of particles settling, industrial wastewater samples were forcefully shaken prior to coagulation; removal efficiency is estimated as follows:

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

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

3. Results and discussion

3.1. Olive seeds powder characterization SEM imaging

The morphological surface structure of olive seed powder was investigated both before and after the coagulation procedure. As seen in Fig. 2a, olive seed powder has a condensed crystalline brick-shaped structure. The structure functioned as a point of attachment for suspended particles and cations [36]. The coagulant aggregated the particles, resulting in larger flocs that could be readily settled, as seen in Fig. 2b. As a result, SEM pictures of olive seeds revealed that bridging might be to olive seeds powder's outstanding coagulation properties [44,45].

3.2. FTIR analysis

The related infrared (IR) spectrum was created using FTIR to analyze further the presence of the main potential functional groups in powdered olive seeds, as shown in Fig. 3. The FTIR analysis was sufficient to simplify and maybe highlight its major functional groups. To facilitate the study of the IR spectra produced for olive seeds

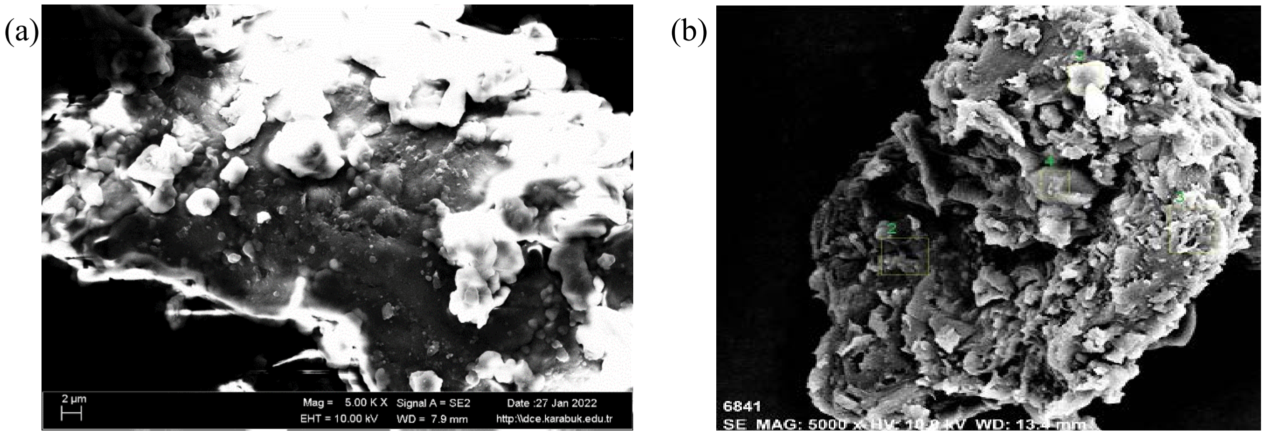

Fig. 2. Scanning electron microscopy image (2 μm) of olive seeds powder (a) before and (b) after the coagulation procedure.

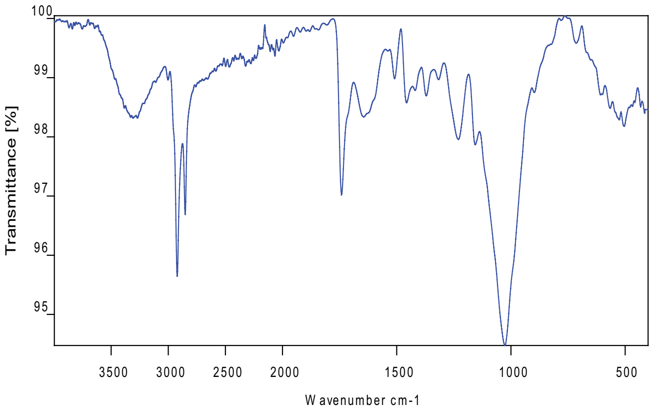

Fig. 3. FTIR curve for olive seeds powder.

powder, the band's range, where its functional groups might be emphasized within the range of wavelength peaks, was chosen. The observed peak in the range of 3,000–2,500 cm^{-1} might suggest the presence of strong amine salts (N–H), which are involved in the bridging mechanism employed by particles during the coagulation process and may help to improve the removal of ammonia and organics from wastewater. The peak between 1,750–1,650 cm^{-1} demonstrates the C–N connection, while the one between 1,650–1,550 cm^{-1} confirms either a primary amine N–H or the aromatic C=C. The peak in the green regions of 1,300–1,250 cm^{-1} suggests an aromatic ester C–O bond, whereas the one between 1,200–1,000 cm^{-1} indicates an N–H aliphatic amine.

3.3. Effect of olive seeds powder dosage at industrial wastewater treatment

Coagulant dose is an essential element in the wastewater coagulation/flocculation process. As a result, a series of tests were conducted to determine the influence and amount of coagulant dosage required to remove COD and ammonia-nitrogen NH_3–N, as well as heavy metals (manganese Mn, iron Fe, zinc Zn, aluminum Al, and nickel Ni) from iron and steel industry wastewater samples for adequate treatment. The impact of the dose was investigated using a natural pH of 8 and olive seeds powder coagulant dosages ranging from (1, 3, 5, 7, and 10 g/L).

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

Coagulation performance can be significantly impacted by a surface charge due to the mass of the coagulant, according to Ramavandi and Farjadfard [46]. Economically, the optimization of coagulant dose and the best-needed mass of the coagulant for scale-up and the design of large-scale equipment are required. Consequently, the effect of olive seed powder dose on COD removal was investigated at an original iron and steel industry effluent pH of 8; the findings are shown in Fig. 4.

The experiment's range of the olive seed powder dosage was 1, 3, 5, 7, and 10 g/L. The highest removal efficiency was 86.9% and 86.3% at 7 and 5 g/L of olive seeds powder dosage.

In terms of an economic point of view, the optimal dosage could be 5 g/L, as there is no big deferent in removal efficiency compared with 7 g/L, and in order to decrease the quantity of dosage used for the treatment process, which will reflect on decreasing on the sludge generation as well. As shown in Fig. 4, by increasing the olive seeds powder dose (up to 10 g/L), a decrease in COD removal takes place; This occurs due to coagulant overloading, which reduces the number of potential adsorption sites for colloidal particle bridging by covering the surface of the natural coagulant [46,47].

As well-known insufficient dosage or overdose would result in poor performance in flocculation [48].

According to the batch test results, as shown in Fig. 4, the removal rate first increases with increasing dosage, followed by a declining trend in ammonia-nitrogen NH_3–N removal with increasing dose level. The highest effective dose of olive seed powder was shown to be 5 g/L with a 72.4% removal rate; initially, there was a constantly rising trend in removal up to 5 g/L. However, excess coagulant in particles causes the aggregated particle to redistribute and disrupts particle settling.

This might occur because when the coagulant was introduced, there was an increased availability of coagulation

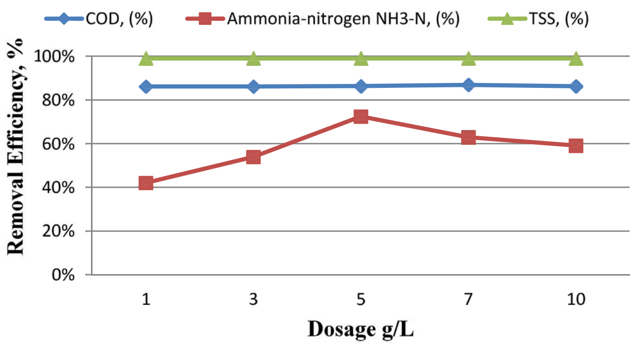

Fig. 4. Effects of olive seeds powder dose on COD, TSS and NH_3–N removal (pH: 8).

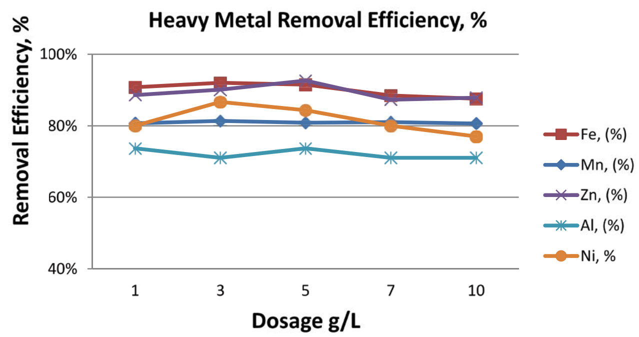

Fig. 5. Effects of olive seeds powder dose on heavy metals Mn, Fe, Zn, Al and Ni removal (pH: 8).

mechanisms, increasing removal. The coagulation process may have achieved equilibrium at 5 g/L dosages, in which case an additional dose will not affect removal [49].

On the other hand, TSS removal effectiveness was shown to be consistent at 99% when pH varied from 5–10 throughout the trials. Because of the neutral electric charge, the particles have a strong coagulation capacity at pH levels ranging from 7–9 [50], implying that the particles' adsorption capability for COD and ammonia-nitrogen NH_3–N will be high.

The capacity of natural polyphenols in olive seed powder to adsorb organics and metal ions increased the elimination of organic contaminants [51]. The action of electric double layers created by carboxylic, phenolic, and amino groups may be responsible for improving organic and ammonia elimination [52]. When more significant doses of olive seeds (>5 g) were used, the removal effectiveness of the desired parameters decreased. The positively charged primary amino groups in olive seeds improved the flocculation process by increasing the bridging mechanism of the particles and colloids in the wastewater [53]. The powdered olive seeds have a high molecular weight and have not been hydrolyzed in wastewater. Using a larger dose of olive seeds results in the rapid precipitation of a considerable powder volume, which may impair flocculation effectiveness [54].

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

The concentration of heavy metals of Mn, Fe, Zn, Al, and Ni in the iron and steel industry, Karabuk, Turkey, are shown in Table 1 to determine the optimum dosage of olive seeds powder in iron and steel industry wastewater at pH 8 a different dosages (1, 3, 5, 7, and 10 g/L) were tested.

As illustrated in Fig. 5, the recommended dosage for olive seeds powder was 5 g/L with the highest removal efficiency (80.9%, 92.6%, 73.7%, 91.5%, and 84.3%) for Mn, Zn, Al, Fe, and Ni respectively. Furthermore, when the dosage was supplied above the recommended limit of 5 g/L, no appreciable elimination was found in this investigation.

Cations in wastewater can promote coagulation by neutralizing and weakening the negative charges of the coagulant functional group residue by interacting with olive seed powder particles [55]. Including monovalent and multivalent cations such as Mg^{2+}, Ca^{2+}, Na^{+}, and Fe^{2+}, in wastewater increased flocculating activity. These findings are comparable to [56–58], who discovered that multivalent cations such as Ca^{2+}, Mn^{2+}, and Al^{3+} increased flocculation activity. Zhang et al. [58] and Nwodo and A.I. Okoh [59] similarly found that Ca^{2+}, Mg^{2+}, and Mn^{2+} increased flocculating activity. However, Al reported limited removal efficiency compared with other parameters due to its limited initial concentration (0.38 g/L) in raw wastewater and may due to its higher solubility, lead to reducing the precipitation of Al ions.

3.4. Effect of variance pH on industrial wastewater treatment

The influence of pH was investigated by adjusting the pH of the wastewater from pH 5 to pH 10, and the coagulation test was carried out at room temperature with an initial profile of the industrial sample as indicated in Table 2 and a coagulant dosage of 5 g/L. The pH of the samples was adjusted using a 1 N H_2SO_4/NaOH solution.

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

Fig. 6 depicts the effects of pH (5–10) on COD and NH_3–N removal using a 5 g/L olive seed powder dosage. The highest coagulation efficiency was obtained at pH 8.0, with 59% COD removal and 92.1% NH_3–N removal. COD and NH_3–N removal increased steadily as pH increased until the maximum value was achieved. As the pH raised slightly above optimal, the percentage removal of COD and NH_3–N decreased.

Samples in the beakers were adjusted to the desired pH before any other coagulation process using olive seeds powder during the experiments; as seen in Fig. 6, the removal efficiencies for COD and NH_3–N were 86.1 and 72.4%, respectively, at pH 8. The adsorption capability of the particles will be high due to the neutral electric charge [47]. Cations in wastewater can improve the coagulation process by neutralizing and destabilizing the negative charges of the residue of the coagulant functional groups by linking with tannin particles [52].

As illustrated in Fig. 6, the removal efficiency increases from 5–10 and decreases. Due to the organic composition of olive seed powder, the pH of industrial effluent remained unaltered after its addition. As a result, no pH correction

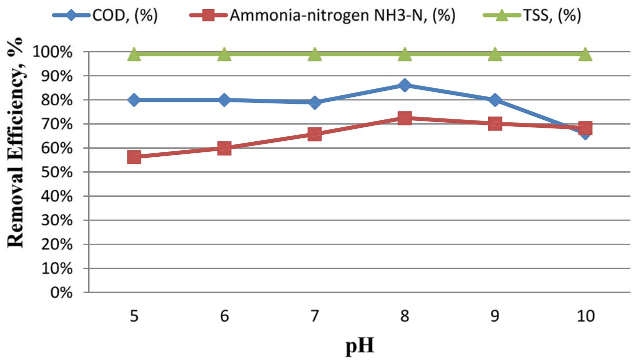

Fig. 6. Effects of pH on COD, TSS and ammonia-nitrogen NH_3–N removal.

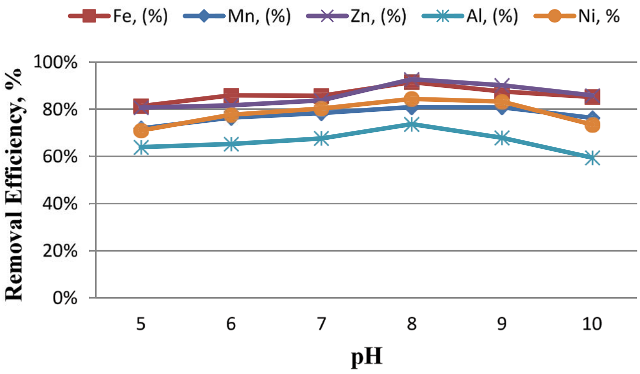

Fig. 7. Effects of pH on heavy metals removal.

was necessary throughout the treatment process when olive seeds powder was used as a coagulant.

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

Experiments were conducted at different pH levels using the optimum dosage of olive seed powder (5 g/L) to determine the best pH range. It was revealed that the ideal pH was 8 and that employing the coagulant resulted in improved removals. At pH 8, the Mn, Fe, Zn, Al, and Ni reductions by olive seeds powder were 80.7%, 91.5%, 92.6%, 73.7%, and 84.3%, respectively (Fig. 7).

Due to the organic structure of olive seeds powder, the pH of industrial effluent remained intact after its addition. As a result, no pH correction was necessary throughout the treatment process when olive seeds powder was used as a coagulant. Although several studies reported the possible leaching of heavy metals and some other parameters from olive seed powder [57], Zhang et al. [58] reported limited leached parameters were leaching tests conducted for olive seed ash. In the current work, the raw olive seed powdered was used, which led to minimizing the parameters leaching from the raw material.

4. Conclusion

In general, the percentage removal of COD, TSS, NH_3–N, Mn, Fe, Zn, Al, and Ni by olive seed powder shows substantial potential as a plant-based natural coagulant in iron and steel mill treatment. The experiment demonstrated the olive seed's substantial coagulation properties. The specific findings of the research are as follows. The existence of various functional groups involved in the coagulation process was confirmed by FTIR analysis. The olive seeds powder eliminated a large proportion of COD, TSS, NH_3–N, Mn, Fe, Zn, Al, and Ni from effluent at pH 8, with percentages of 86.3, 99, 72.4, 80.9, 91.5, 92.6, 73.7 and 84.3%, respectively, at 5 g/L. The effects of pH range from (5–10) show that the natural pH of the wastewater sample shows that the best possible removal efficiency was 86.1%, COD, 99% TSS, and 72.4% NH_3–N. In comparison, the removal efficiency of heavy metals was 80.7%, 91.5%, 92.6%, 73.7%, and 84.3% for Mn, Fe, Zn, Al, and Ni, respectively. Because of the organic nature of olive seed powder, the pH of industrial effluent remained unaltered after its addition. As a result, no pH modification was required during the treatment procedure when olive seed powder was utilized as a coagulant.

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