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The effectiveness of rosehip seeds powder as a plant-based natural coagulant for sustainable treatment of steel industries wastewater

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ABSTRACT

This study aims to investigate the performance plant-based natural coagulant from rosehip seed powder in the treatment of iron and steel factory wastewater. The concentrations of 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 examined. Coagulation investigations were carried out using an orbital shaker and a flocculation apparatus to investigate the effects of iron and steel factory effluent, pH, and rosehip seeds powder dosage on coagulation efficacy. The rosehip powder removes a large amount of COD, TSS, NH_3–N, Mn, Fe, Zn, Al, and Ni from effluent at pH 8 with percentages of 86.1%, 99%, 79%, 86%, 91.7%, 90.6%, 73.7%, and 100%, respectively, at 1 g/L. The effects of pH ranges ranging from (5–10) reveal that the wastewater sample's natural pH (8) demonstrates the maximum practicable removal effectiveness. FTIR analysis revealed the presence of numerous functional groups involved in the coagulation process. One may argue that rosehip seed powder holds great potential as a natural plant-based coagulant for water treatment and could be used to treat effluent from iron and steel factories.

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

1. Introduction

Many waterways have become unwholesome and harmful to man and other living resources as a result of population growth [1], unplanned fast urbanization, industrial and technical advancement, energy use, and waste creation from home and industrial sources. Due to the discharge of significant volumes of industrial wastewater, the most dangerous industries are those that include organic pollutants and heavy metals, such as copper (Cu), chromium (Cr), iron (Fe),

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magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn) [2–5].

Living organisms can absorb heavy metals due to their high solubility in a watery environment. Heavy metals may accumulate in high amounts in the human body once they reach the food chain. If the metals are consumed over the allowable concentration, they can cause significant health problems [6,7].

Therefore, industrial effluent must be treated before being discharged into the environment. Heavy metal removal from inorganic effluent can be accomplished by traditional treatment methods such as chemical precipitation, ion exchange, and electrochemical removal. These techniques have substantial drawbacks, such as partial removal, large energy consumption, and the creation of hazardous sludge [8–17].

Numerous techniques have recently been investigated to develop environmentally friendly and more effective solutions to reduce the amount of wastewater generated and enhance the effluent quality [18].

Several conventional and current technologies have been developed during the last several decades, including chemical precipitation, reverse osmosis, ion exchange, and electrochemical removal. These processes have significant disadvantages, such as being generally expensive, complicated, time consuming, and requiring skilled personnel, as well as producing toxic sludge [8–17], so coagulation flocculation processes are attracting scientific attention primarily due to their high efficiency, low cost, easy handling, and high range of various coagulants [19,20], and are widely implemented for treating industrial wastewater [21,22].

In the coagulation-flocculation process using, inorganic coagulants such as chemical coagulants (i.e., aluminum or iron salts) are used in the industrial wastewater treatment process, but the main drawback of such process are include high running costs, carcinogenic, massive sludge output generation, and pH value adjustment of the treated water [23], other issues 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 [24]. Therefore, cheaper alternatives to natural and low-cost coagulants such as chitosan, *Moringa oleifera*, okra, Surjana seed were used [25–27].

Consequent to the challenges mentioned above, Several studies have indicated that using natural plant-based materials for coagulation instead of chemicals is a promising alternative for treating different industrial wastewaters to alleviate the issues associated with chemical coagulants [28–31]. 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 [32,33]. Many recent studies have highlighted the importance of natural coagulants. Plant-based materials can act as coagulants because they can perform some coagulation mechanisms, namely neutralization of charge in colloidal particles and polymer bridging [34,35].

To address the worldwide water crisis, researchers are currently focusing on extracting coagulants from naturally existing indigenous minerals, where natural coagulants are biodegradable in environment, and can be obtained from plants, animals, and microorganisms. 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. [3,34].

Thus, the goal of this research is to experimentally evaluate the efficiency of rosehip seeds powder as a natural coagulant in iron and steel factory wastewater treatment, especially in terms of COD, ammonia-nitrogen NH_3–N and heavy metals removals. Furthermore, this study focuses on the most appropriate coagulant dose, and the pH effect on removal efficiency. Rosehip seeds powder and the flocs produced after treatment were characterized using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) to elucidate the chemical structure, thermal stability, and morphology. This experimental investigation was carried out to assess the effectiveness of the coagulation/flocculation process in the wastewater of the Karabuk iron and steel factory.

2. Materials and methods

2.1. Sample collection

This study was conducted out in environmental laboratory at the department of environment engineering, faculty of engineering, Karabuk University, Turkey. 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 sample were but 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 dark until using.

2.2. Perpetration of rosehip seeds powder

Rosehip seeds were collected from near plantation to the Karabuk University, Turkey. The rosehip seeds were wash away by distilled water to take out unwanted adhering, then were dried under atmospheric temperature first followed by oven for about eight 8 h at 50°C. This was carried out to make the rosehip seeds ready for crushing. The crushed rosehip seeds were ground using a grinder (Retsch RS 200) to obtain powder form to be used as a coagulant in the experiments as shown in Fig. 1.

2.3. 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 [36].

2.4. Coagulation experiments

A laboratory using Orbital shaker (Type: PSU-10i, No: 010144-1404-0228, Latvia) was utilized in coagulation tests. Experiments in the laboratory were carried out using

500 mL beakers filled with 200 mL of industrial effluent and put in the shaker's plate. For 15 min, the industrial wastewater samples in the beakers were mixed at a high speed of 200 rpm. The shaker speed was then dropped to 90 rpm for 30 min. The high-speed mixing was utilized to equally disperse the coagulant, while the slow-speed mixing was employed to maintain the floc particles suspended in the water uniformly. The beaker's contents were left to settle for 1 h.

After 60 min of sedimentation, the samples were using whatman circle ashless/white ribbon filter paper to insure clarification of sample from impurities, for farther 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 of the tests were carried out in duplicate.

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.

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

Fig. 1. Rosehip 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

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

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

3. Results and discussion

3.1. Rosehip seeds powder characterization scanning electron microscopy (SEM) imaging

Before and after the coagulation procedure, the morphological surface structure of rosehip seeds powder was examined. Rosehip seeds 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 [37,38]. As seen in Fig. 2b, the coagulant aggregated the particles, resulting in bigger flocs that sank easily. As a result, SEM images of rosehip seeds powder one revealed that bridging may be responsible for the rosehip seeds powder's exceptional coagulation properties [37,39,40].

3.2. Fourier transformed infrared (FTIR) analysis

The matching infrared (IR) spectrum was produced using Fourier transform infrared (FTIR) spectroscopy, as shown in Fig. 3, to further investigate the presence of the main potential functional groups in powdered for rosehip seeds. The FTIR analysis sufficed for simplifying and maybe accentuating the major functional groups. To investigate the IR spectra produced for rosehip seeds powder, the bands range – where its functional groups may possibly be emphasized within the range of wavelength peaks – were chosen. The observed peak in the 3,000–2,500 cm^{-1} range might be due to the presence of strong amine salts (N–H), which are involved in the particle bridging mechanism during the coagulation process and may relief in the removal efficiency of ammonia and organics from wastewater.

The peak between 1,750–1,650 cm^{-1} demonstrates the C–N connection, whilst 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 region between 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 [40,41].

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

Industrial wastewater parameters	Units	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

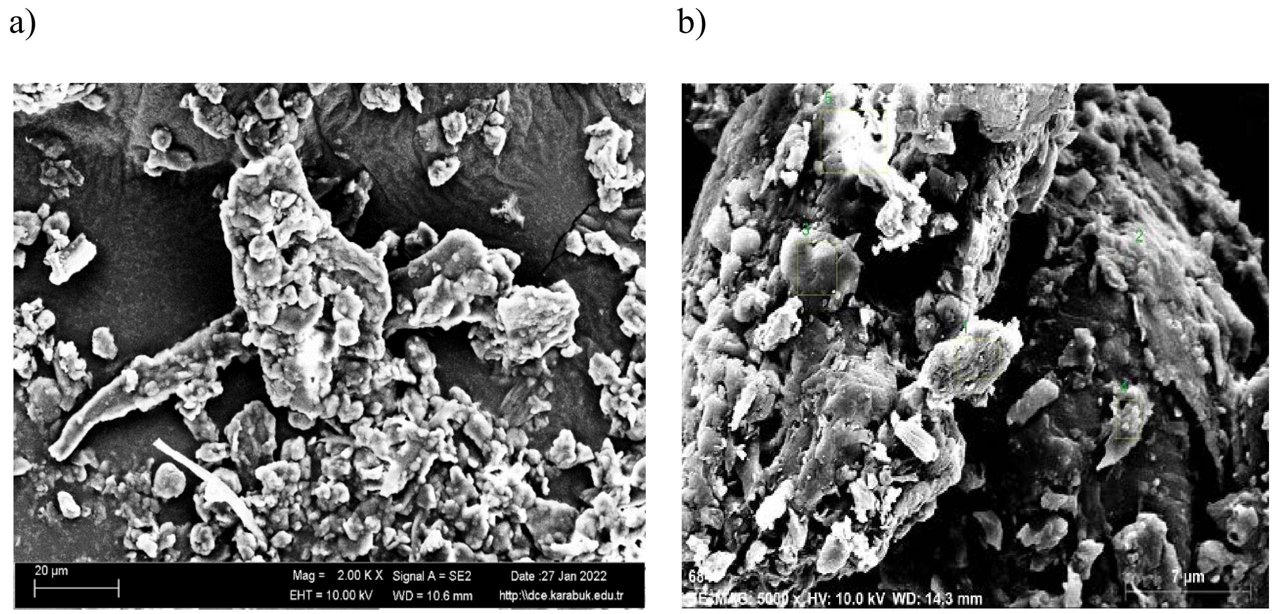

Fig. 2. Microscopic image (2 μm) for rosehip seeds powder (a) before (b) after coagulation process observed by scanning electron microscopy.

3.3. *Effect of rosehip seeds powder dosage*

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

The effect of coagulant dosages on COD, ammonia-nitrogen NH_3–N and heavy metals (manganese Mn, iron Fe, zinc Zn, aluminum Al 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 dosage, a series of tests were carried out by adjusting the quantities of rosehip seeds powder from 1 to 10 g and mixing them with 200 mL of iron and steel industrial effluent and agitating them with an orbital shaker under the conditions described in section 2.2. Surface charge, according to Ramavandi and Farjadfard [42], might have a significant influence on coagulation efficacy due to the mass of the coagulant. Economical optimization of coagulant dose and most-needed coagulant mass for scale-up, as well as the design of large-scale equipment, are needed. As a result, the effect of rosehip seeds powder dosage on COD and Ammonia-nitrogen NH_3–N removal at an original iron and steel industrial effluent pH of 8 was tested, and the results are illustrated in Fig. 4.

Rosehip seed powder coagulant demonstrated efficacy when used as a coagulant at the optimum dosage of 1 g/L. The most effective removal efficiency COD removal efficiencies were 86.1%, as indicated in Fig. 4.

As seen in Fig. 1, increasing the dosage of rosehip seeds powder (up to 10 g/L) leads in a decrease in COD removal. This is because coagulant overcrowding reduces the number of possible adsorption portions for colloidal particle bridging by covering the natural coagulant's surface [42,43].

The batch test results, revealed in Fig. 4, illustrate the effect of rosehip seeds powder coagulant dose on the effectiveness of ammonia-nitrogen NH_3–N removal. The most highest two removal treatment efficiency was found at dosage of 1 and 5 g/L with 79% and 79.9% at 1 g/L, respectively; however, from an economic standpoint, and to reduce the volume of sludge formed by the treatment process, the optimal dosage could be 1 g/L as no considerable difference in removal efficiency between both dosages. Furthermore, no significant removal was found in this experiment when the dose increased was larger than 1 g/L.

TSS removal efficacy, on the other hand, was found to be stable at 99% when pH ranged from 5 to 10. Because of the neutral electric charge, the particles have a high coagulation capacity at pH levels ranging from 7–9 [44], meaning that the particles have a high adsorption capability for COD and ammonia-nitrogen NH_3–N.

The potential of rosehip seeds powder's natural polyphenols to adsorb organics and metal ions facilitated organic contamination removal [45]. The increase in organic and ammonia elimination may be attributed to the action of electric double layers generated by carboxylic, phenolic, and amino groups [46]. When greater doses of rosehip seeds powder (>1 g) were used, the removal effectiveness of the target parameters decreased. The positively charged primary amino groups in rosehip seeds powder increased the bridging mechanism of the particles and colloids in the wastewater, hence enhancing flocculation [47]. The rosehip seeds powder has a high molecular weight and has not been hydrolyzed in wastewater. A greater dose of rosehip seeds powder causes a substantial amount of powder to precipitate quickly, which may restrict flocculation efficiency [48].

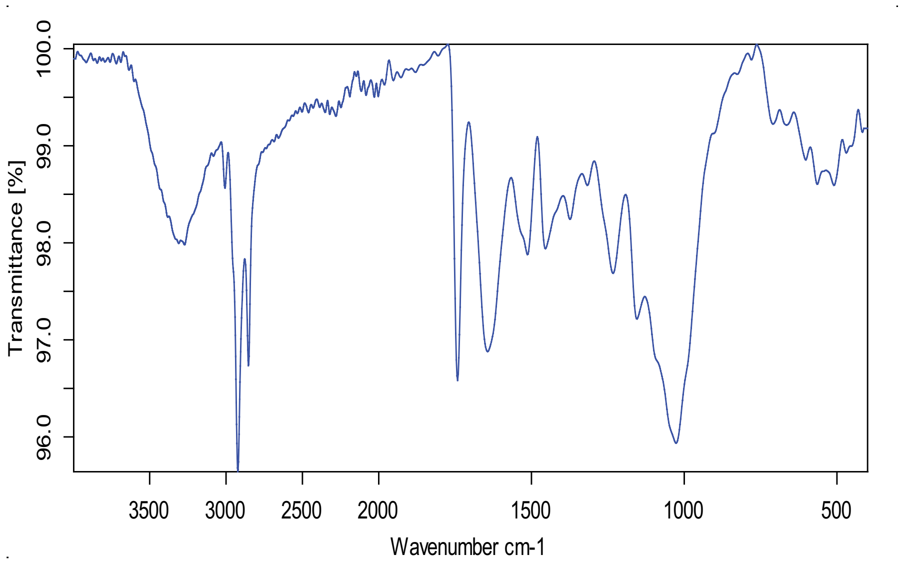

Fig. 3. Fourier transformed infrared (FTIR) spectroscopy curve for rosehip seeds powder.

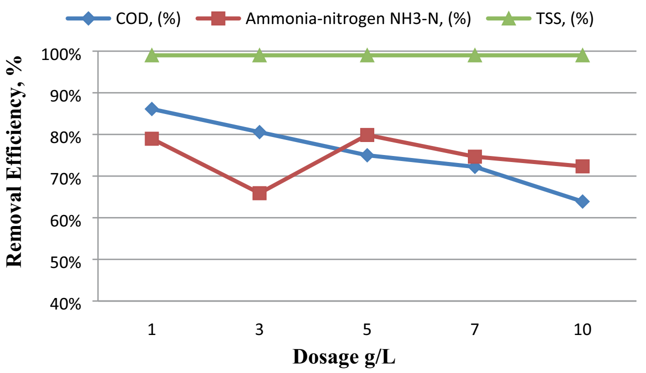

Fig. 4. Effects of rosehip seeds powder dose on COD, TSS and NH_3–N removal (pH 8).

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

In coagulation-flocculation experiments, the optimal dosage of rosehip seeds powder for heavy metals (Mn, Fe, Zn, Al, and Ni) in the iron and steel industry wastewater was obtained at 1g/L dose with highest removal efficiency (85.7%, 91.7%, 90.6%, 73.7% and 100%) for Mn, Fe, Zn, Al, and Ni, respectively. Furthermore, when the dosage used was larger than the suggested value of 1 g/L, no significant removal was found in this experiment.

Because of their neutral electric charge, the particles exhibit a good coagulation capacity at pH values ranging from 7 to 9 [44]. By interacting with rosehip seed powder particles, cations in wastewater can increase coagulation by neutralizing and reducing the negative charges of the coagulant functional group residue [49]. 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 [50–52], who found that multivalent cations such as Ca^{2+}, Mn^{2+}, and Al^{3+} enhanced flocculation activity. As the presence of Ca^{2+}, Mg^{2+} and Mn^{2+} enhanced flocculating activity [52,53].

3.4. *Effect of variance pH at industrial wastewater treatment*

The pH of the wastewater was adjusted from 5–10, 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 1 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 5–10 on COD and NH_3–N removal using 1 g/L rosehip seed powder are shown in Fig. 6. At pH 8.0, the maximum coagulation efficiency was reached, with 83.9% COD removal and 78.8% NH_3–N removal. The removal of COD and NH_3–N increased steadily as pH climbed until the maximum value was reached. When the pH climbed slightly above optimum, the percentage removal of COD and NH_3–N decreased.

During the studies, pH of the samples in the beakers were adjusted to the wanted pH before any further coagulation procedure using rosehip seed powder. At pH 8, the removal efficiencies for COD and NH_3–N were 83.9% and 78.79%, respectively, as shown in Fig. 6, the removal efficiency improves from 5 to 10 and then drops takes place. The organic nature of rosehip seeds 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 rosehip seeds powder was utilized as a coagulant.

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

Experiments were then carried out at different pH levels with the optimal dosage of rosehip seed powder (1 g/L) to

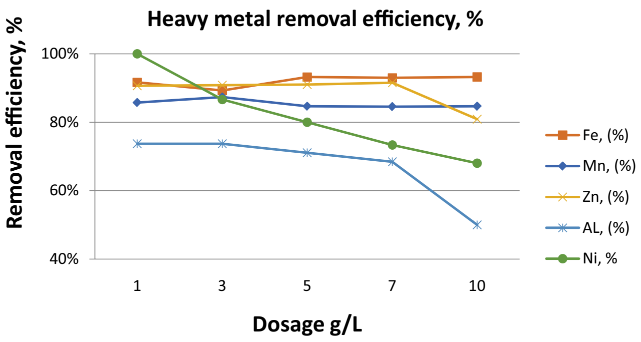

Fig. 5. Effects of rosehip seeds powder dose on heavy metals removal (pH: 8).

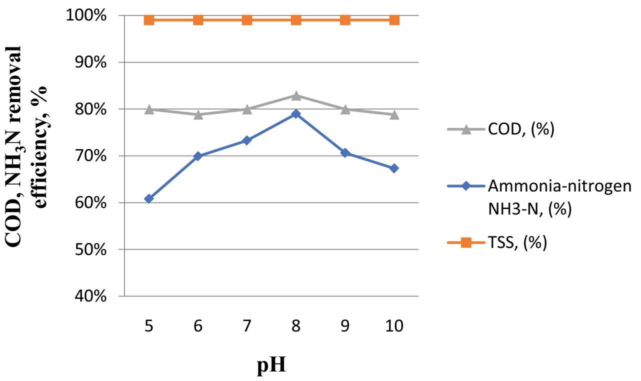

Fig. 6. Effects of pH on COD, TSS and ammonia-nitrogen NH_3–N removal.

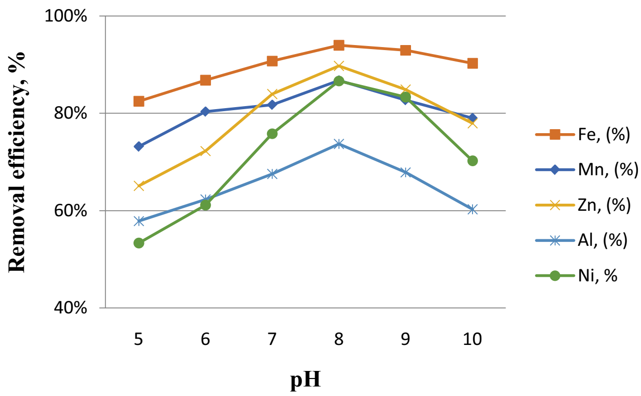

Fig. 7. Effects of pH on heavy metals removal.

determine the best pH range. The optimal pH was identified to be 8 and the use of the coagulant resulted in improved removals. At pH 8, the reductions of Mn, Fe, Zn, Al, and Ni by rosehip seed powder were 85.4%, 91.7%, 90.6%, 73.7%, and 100%, respectively (Fig. 7) rosehip seeds powder's organic nature maintained the pH of industrial effluent after its addition.

As a consequence, when rosehip seed powder was used as a coagulant, no pH adjustment was necessary during the treatment operation.

4. Conclusion

In general, the efficiency of rosehip powder in removing COD, TSS, NH_3–N, Mn, Fe, Zn, Al, and Ni as a plant-based natural coagulant in iron and steel mill treatment has shown substantial promise. The experiment demonstrated that rosehip powder had substantial coagulation properties.

The rosehip powder remove a large amount of COD, TSS, NH_3–N, Mn, Fe, Zn, Al, and Ni from effluent at pH 8 with percentages of 86.1%, 99%, 79%, 86%, 91.7%, 90.6%, 73.7%, and 100%, respectively, at 1 g/L. The effects of pH ranges ranging from (5–10) reveal that the natural pH of the wastewater sample demonstrates the maximum practicable removal effectiveness. The addition of rosehip seeds powder had no influence on the pH of industrial effluent since it is organic. As a result, when rosehip seeds powder was utilized as a coagulant, no pH modification was required during the treatment period.

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