Journal of
Water, Sanitation & Hygiene for Development

 Journal of Water, Sanitation and Hygiene for Development Vol 14 No 3, 229 doi: 10.2166/washdev.2024.267

Research Paper

Chemical recovery of magnesium from the Dead Sea and its use in wastewater treatment

Mousa Almousa[a,*], Tomomewo Olusegun[b], Yeo Lim[a], Kamel Al-Zboon[c], Islam Khraisat[d], Ali Alshami[e] and Bashaar Ammary[c]

[a] Civil and Environmental Engineering Department, University of North Dakota, Grand Forks, ND 58203, USA
[b] Energy and Petroleum Department, University of North Dakota, Grand Forks, ND 58203, USA
[c] Water and Environmental Engineering Department, Al-Balqa Applied University, Huson University College, Irbid 21510, Jordan
[d] Department of Civil Engineering, Yarmouk University, Irbid 21163, Jordan
[e] Chemical Engineering Department, University of North Dakota, Grand Forks, ND 58203, USA
*Corresponding author. E-mail: mousa.almousa@und.edu

ABSTRACT

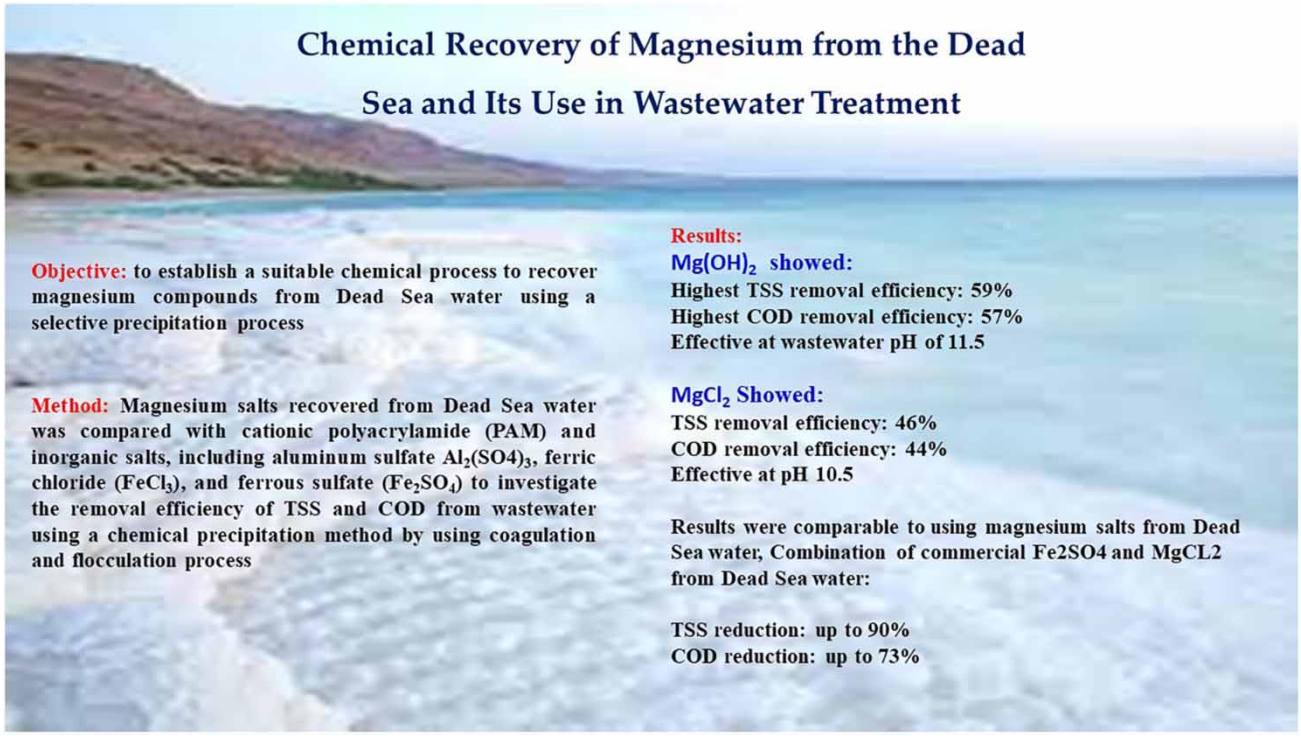
The objective of this study was to establish a suitable chemical process to recover magnesium compounds from Dead Sea water using a selective precipitation process. The recovered magnesium hydroxide ($Mg(OH)_2$) and magnesium chloride ($MgCl_2$) are applicable for wastewater treatment processes since they can effectively remove total suspended solids (TSS) and chemical oxygen demand (COD). Magnesium salts recovered from Dead Sea water were compared with cationic polyacrylamide (PAM) and inorganic salts, including aluminum sulfate $Al_2(SO_4)_3$, ferric chloride ($FeCl_3$), and ferrous sulfate (Fe_2SO_4) to investigate the removal efficiency of TSS and COD from wastewater using a chemical precipitation method by using coagulation and flocculation process. Results show that $Mg(OH)_2$ yielded the highest TSS and COD removal efficiencies of 59 and 57%, respectively, with a wastewater pH of 11.5. $MgCl_2$ yielded lower removal efficiencies of 46 and 44%, respectively; at pH 10.5, lower magnesium concentration doses were needed. The most effective chemical precipitation method for removal involved cationic PAM coagulants, resulting in an 86% reduction in TSS and a 65% reduction in COD. Combining commercial Fe_2SO_4 and $MgCL_2$ recovered from Dead Sea water reduced up to 90 and 73% of TSS and COD, respectively.

Key words: adsorption, COD, dead sea, magnesium salts, precipitation, wastewater treatment

HIGHLIGHTS

- Suitable chemical process recovers Mg compounds from Dead Sea (DS).
- $Mg(OH)_2$ and $MgCl_2$ effectively remove total suspended solids (TSS) and chemical oxygen demand (COD).
- Mg salts were compared with polyacrylamide, $Al_2(So4)_3$, $FeCl_3$, and Fe_2SO_4 to investigate the removal efficiency of TSS and COD.
- Mg recovery from DS is a new and novel contribution to this research.
- This research tackles the unique opportunity to leverage the high concentration of Mg compounds available from DS.

GRAPHICAL ABSTRACT



1. INTRODUCTION

$Mg(OH)_2$ and $MgCl_2$ are important and valuable commercial resources because they can be used in many applications, including products used to reduce dust, materials used for drilling, ion exchange resins, cements containing oxy-chlorine, coagulants, and fertilizers. Seawater is one of the primary sources of magnesium, particularly $MgCl_2$ and $Mg(OH)_2$. There are significant $MgCl_2$ reserves in the Dead Sea (DS), approximately 52,000 mg/l, while seawater concentrations in other areas are approximately 1,400 mg/l (Weber *et al.* 2022). Magnesium is an alkaline earth metal and the eighth most abundant element in the Earth's crust; however, it is formed in combination with other elements making it difficult and expensive to extract (Kim 2011).

One of the environmental challenges is waste brines, which were generated from seawater desalination, and the potential of using rejected brines as a valuable source for mineral recovery. Specifically, it emphasizes the significance of magnesium, classified as an essential raw material, found in these brines, and the need for a pretreatment method to optimize salt production (Morillo *et al.* 2014; Loganathan *et al.* 2017).

Various methods have been developed for magnesium recovery, such as cationic selectrodialysis (Ghyselbrecht *et al.* 2019) and precipitation processes using ammonium to react with $MgCO_3$ (Mohammad *et al.* 2019). Selective precipitation, crystallization, and electrodialysis technologies have demonstrated efficiency in magnesium recovery, aligning with zero liquid discharge initiatives and environmental pollution reduction goals (Zhang *et al.* 2021).

Magnesium is precipitated as $Mg(OH)_2$ from seawater using the chemical separation method as follows:

$$Mg + 2 + 2OH- \rightarrow Mg(OH)_2 \downarrow \quad (1)$$

The chemical separation method for precipitating $Mg(OH)_2$ from seawater is outlined, followed by the challenges associated with impurities in the precipitate. Various techniques, including the use of $Ca(OH)_2$ and sulfuric acid (H_2SO_4), have been explored to enhance purity, with notable successes reported in the literature, which are discussed here.

Mohammadesmaeili *et al.* (2010) used 95% sulfuric acid (H_2SO_4) solution to lower the pH value to less than 4.3 and convert the acid to carbonic acid, which could then be released as carbon dioxide to improve magnesium and calcium removal

efficiency (Equation (2)).

$$H + HCO_3 \rightarrow CO_2 \uparrow + H_2O \quad (2)$$

$MgCl_2$ can be recovered by adding HCl until the pH value reaches 4. $Mg(OH)_2$ is dissolved and converted to dissolved ($MgCl_2$), which is then converted to dry bittern by placing it in an oven (Abdel-Aal 2018). Equation (3) describes dissolved $MgCl_2$ production:

$$Mg(OH)_2 + 2HCL \rightarrow MgCl_2 + 2H_2O \quad (3)$$

Continuing the exploration of magnesium recovery methods, Bevacqua *et al.* (2015) have used a sophisticated method to improve $Mg(OH)_2$ purity, achieving 99.5% $Mg(OH)_2$ purity using inexpensive reactants such as $Ca(OH)_2$. In addition, Quist-Jensen *et al.* (2016) discovered that the magnesium salts recovered from bittern of seawater were feasible low-cost and effective coagulants for removing both organic and inorganic substances from wastewater.

Transitioning to applications, Young *et al.* (2021) demonstrated the effectiveness of $Mg(OH)_2$ and $MgCl_2$ in the flocculation process for wastewater treatment, removing various organic contaminants, inorganic compounds such as ammonia and phosphorous, and chemical oxygen demand (COD) from wastewater by adjusting the pH value. The recovery of $MgCl_2$ from $Mg(OH)_2$, another detailed study by Peeva *et al.* (2022), presented its cost-effectiveness compared to traditional coagulants, particularly in removing organic and inorganic contents from wastewater sludge.

The objective of this research was to develop a comprehensive process for recovering $MgCl_2$ and $Mg(OH)_2$ from DS water by adding NaOH and HCl. The recovered materials were used to remove total suspended solids (TSS) and COD from domestic wastewater. DS water has a very high concentration of magnesium ions; therefore, it is vital to evaluate recovering magnesium for use in industrial applications and the coagulation process, which is more efficient than recovering magnesium from regular seawater due to higher concentrations as investigated by Reiss *et al.* (2020). Chemically recovering salts, such as magnesium, reduces the load on other desalination technologies, allowing stakeholders to mitigate rejected brines through reverse osmosis, which is becoming popular for water desalination in Jordan and elsewhere since it conserves natural resources and protects the environment. Chemical treatments also reduce a large amount of TSS and COD during the pretreatment process, which makes the secondary treatment process more economically viable (Walschot *et al.* 2020).

2. METHODOLOGY

2.1. Sampling

Thirty DS water samples with a pH of 7.2, total dissolved solids (TDS) concentration of 358.4 g/l, total alkalinity ($(HCO_3)^-$, $(CO_3)^{-2}$, and $(OH)^-$) of 182 mg/l, and an approximate magnesium ion concentration of 38 g/l were collected. Samples were obtained from the DS beach during Spring – April 2020 and contained high-density polyethylene (1,000 ml). Also, more than 30 l of municipal wastewater samples were collected from the Jordan University of Science and Technology's treatment plant primary sedimentation tank effluent and filled in high-density polyethylene bottles with an initial magnesium ion concentration of approximately 8 mg/l and a calcium ion concentration of approximately 21 mg/l. The municipal water's pH value was 7.3, and the TSS and TDS concentrations were 450 and 680 mg/l, respectively. The phosphorus concentration was 9.2 mg/l, nitrate nitrogen was 35 mg/l, and the COD was 620 mg/l. The samples were used for the purpose of magnesium recovered from DS water and used for wastewater treatment experiments using the magnesium recovered from DS water.

In order to examine the adsorption capabilities of $MgCl_2$ obtained from DS water as well as various commercial coagulants, another raw wastewater sample, with high levels of TSS at 1,150 mg/l and COD at 950 mg/l, was taken from the same source for analysis.

For robust environmental data, we implement stringent quality control measures during sample transportation and storage. This includes using clean, inert containers, maintaining temperature control, establishing a clear chain of custody, and taking duplicate samples. We carefully choose transportation conditions and controlled storage environments. Regular instrument calibration, meticulous documentation, and periodic quality control checks ensure the reliability of our laboratory measurements for parameters such as pH, temperature, TDS, magnesium ion concentration, total alkalinity, phosphorus concentration, nitrate, COD, Biochemical Oxygen Demand (BOD), and TSS. Table 1 shows all measured parameters.

Table 1 | Dead Sea water sample parameters

Parameter	Dead Sea	Municipal water	Laboratory measurement methods
pH (acidity/alkalinity)	7.2	7.3	pH meters
Temperature	19.5 °C	12.3 °C	Digital thermometers
TDS	358.4 g/l	680 g/l	TDS meters, Gravimetric methods
Magnesium ion concentration	38 g/l.	8 mg/l	
COD	Not applicable	620 mg/l	Titration methods
TSS	–	450 mg/l	Gravimetric methods (filtration and weighing)

2.2. $Mg(OH)_2$ and $MgCl_2$ recovery from Dead Sea water

$Mg(OH)_2$ was recovered from DS water using an alkali solution (NaOH) at different dosages. The recovered $Mg(OH)_2$ was separated and then dissolved in distilled water to convert it to $MgCl_2$ by adding HCL. The recovered $MgCl_2$ and $Mg(OH)_2$ salts were assumed to be mostly pure. The recovery procedure of $Mg(OH)_2$ from DS water was carried out in a jar tester, six beakers of 1 l at 25 °C to obtain magnesium precipitation after rapid mixing and followed by slowing mixing. Each dose of caustic soda was added to the beaker, after which the stirrer immediately began mixing for a minute rapid mixing and then slowing mixing at 40 rpm for 20 min (Bagastyo *et al.* 2021). The following recovery plan was implemented:

- $Mg(OH)_2$ was precipitated by adding NaOH to 250 ml of DS water to increase pH value from 7.2 to 9.5, 10.5, and 11. The precipitated $Mg(OH)_2$ was removed using filter paper 45 μm and purified with distilled water to obtain high purity. The recovered $Mg(OH)_2$ is called liquid bittern. Different doses of NaOH were added, from 8 to 35 ml, to increase the pH values to 8.5–11 and precipitate $Mg(OH)_2$.
- A stock solution was prepared for magnesium measurement after the $Mg(OH)_2$ was precipitated. The extracted liquid bittern was placed in 1 l of distilled water, and then the amount of magnesium present was examined and measured. $Mg(OH)_2$ samples with known magnesium concentrations were dissolved by adding HCL to convert it to $MgCL_2$. pH was adjusted to 4 for each $Mg(OH)_2$ sample, and then the dissolved $MgCl_2$ was placed inside an oven at 104 °C for 24 h to produce the dry $MgCL_2$ bittern. The dry bittern was added to 1 l of distilled water for sedimentation experiments.

Figure 1 depicts a schematic overview of the sequential recovery of $Mg(OH)_2$ and chloride (Figure 3(a)) and the evaluation of the magnesium salt's ability to efficiently remove TSS and COD from wastewater at pH values ranging from 9.0 to 11.5 (Figure 2(b)).

2.3. Coagulation/flocculation experiments

Chemical coagulation experiments were performed by adding pure Mg solution from the recovered $MgCL_2$ and $Mg(OH)_2$. Commercial coagulants, including $Al_2(SO_4)_3$, Fe_3Cl_3, Fe_2SO_4, and polyacrylamide (PAM), were used to compare their effectiveness when removing TSS and COD from wastewater. The jar test apparatus was used to investigate the optimal removal of TSS and COD using the magnesium recovered from the DS water. The conventional jar test apparatus consisted of six beakers of wastewater, where 1 l at room temperature was used to mix the samples for each experiment. A known dose of magnesium was then added to the six jars of wastewater. The samples were mixed rapidly at 250 rpm for 1 min. The rapid mixing was followed by gentle mixing at 20 rpm. TSS and COD were measured in the bulk after the settling period. The experiments were performed with prior pH adjustments and at a fixed dose of 0.4 g/l for each coagulant, Al^{+3}, Fe^{+3}, Fe^{+2}, and Mg^{+2}, to compare the performance of the magnesium recovered from the DS water and the other coagulants. Each sample was promptly stirred at a speed of 180 rpm for 3 min after the dose was added to the solution, and then the solution was mixed at a slow speed of 50 rpm for 15 min. Stirring was then stopped to obtain the sludge that was precipitated after 1 h.

2.4. Adsorption experiments

All adsorption trials were performed in beakers, where 1 l of the sample was mixed with varying coagulant doses, from 0.1 to 1 g/l of the Fe_2SO_4 and $MgCl_2$ as Mg and Fe combinations, and then shaken for a period until mixed well. All experiments were conducted at a pH of 8.5, a settling duration of 60 min, and a temperature of 24 °C or room temperature. The supernatant for all samples was analyzed with regard to TSS and COD content. TSS and COD removal coagulation adsorption

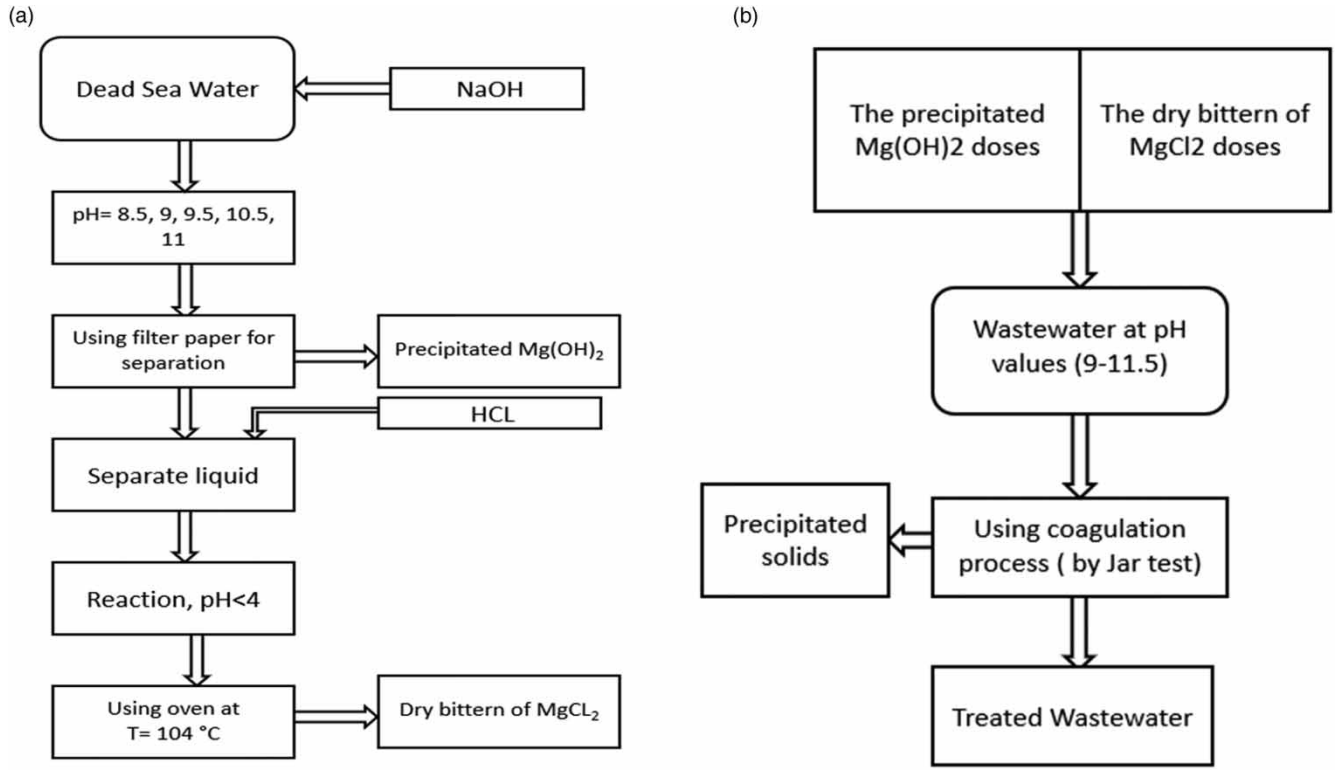


Figure 1 | Precipitation of magnesium salts from Dead Sea water. (a) $MgCl_2$ and hydroxide recovery. (b) The recovered magnesium use in the treatment of wastewater.

mechanisms were investigated at various Fe_2SO_4 and $MgCl_2$ doses using a Freundlich isotherm model, a mathematical technique used to explain the coagulation process (Hussain *et al.* 2013). The coagulation adsorption capability was determined according to the following equation:

$$q_e = \frac{C_i - C_e}{W} \times V \tag{4}$$

where the coagulation adsorption capacity (in mg/g) denoted by q_e, is determined by the volume of the wastewater sample in ml (V) and the coagulant dosage in grams per liter (W).

3. RESULTS AND DISCUSSION

3.1. Mg $(OH)_2$ and $MgCl_2$ recovery from Dead Sea water

Table 1 lists the concentration of the magnesium extracted from the DS water at different pH values.

Table 2 lists Mg concentration in the solution recovered from 250 ml DS water at different pH values. Table 3 includes the mass of $Mg(OH)_2$ and $MgCl_2$ in solids after performing calculation.

The quantity of $MgCl_2$ and $Mg(OH)_2$ present in the solids was determined using Equations (5) and (6):

$$\text{Amount of } Mg(OH)_2 \text{ in dry solids} = 3100 \frac{\text{mg}}{250\text{L}} \text{Mg} \times \frac{58.33}{24.31} = 7,438 \text{mg}/250\,\text{ml} \tag{5}$$

$$\text{Amount of } MgCl_2 \text{ in dry solids} = 3100 \frac{\text{mg}}{250\text{L}} \text{Mg} \times \frac{95.2}{24.31} = 12,140 \text{mg}/250\,\text{ml} \tag{6}$$

3.2. Wastewater characteristics

The results demonstrated that the magnesium salts recovered from DS water were effective coagulants for the two main treatment objectives, a decrease in both TSS and COD. The precipitation of the colloidal particles after 10 min of coagulation using $MgCl_2$ in wastewater is depicted in Figure 2(a). Another interesting result was the residual color change (Figure 2(b) and 2(c)); the coagulation process resulted in increasingly clearer water after 2 and 10 min; however, color clarity was not a part of our study.

The characterization of $MgCl_2$ was performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Figure 4 displays the products, which were verified as $MgCl_2.4H_2O$ through XRD analysis as shown in Figure 3. This finding corresponds to the distinctive XRD pattern observed in aqueous $MgCl_2$ examined at various temperatures, and the diffraction intensity range (2-theta) was about from 20°to 40° at a temperature of 100 °C (Rioyo *et al.* 2018).

The presence of a small amount of calcite in the sample has been identified at a 2-theta value with a peak at 29.4°, which matched with the XRD pattern of calcite studied by investigators (Rioyo *et al.* 2018). Although $Mg(OH)_2$ presence inhibits the precipitation of calcite, a small quantity of calcite is shown in the SEM-energy-dispersive X-ray spectroscopy analysis as

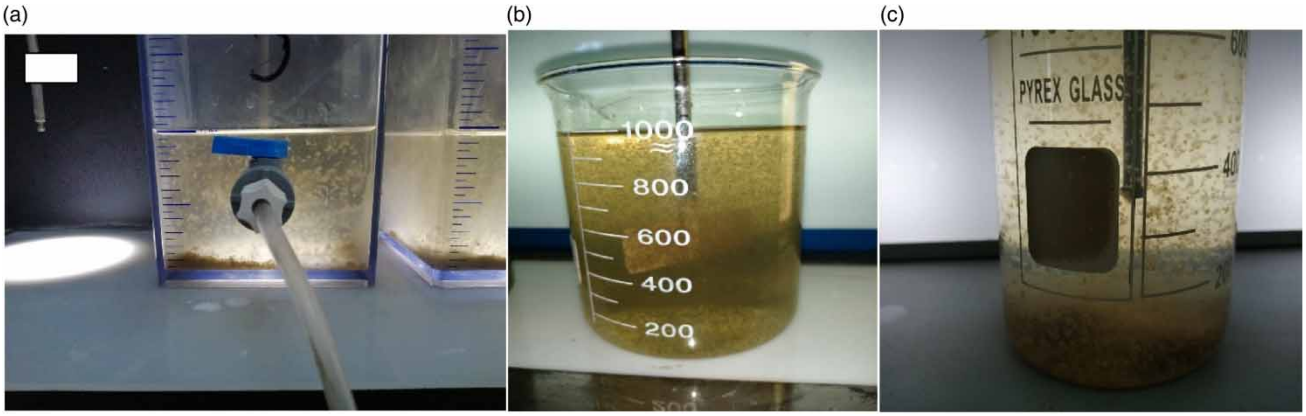


Figure 2 | Coagulation/flocculation experiments: (a) TSS and COD removal from wastewater using $MgCl_2$. (b) TSS removal at 1 min of coagulation process using $MgCl_2$ recovered from Dead Sea water. (c) TSS removal at 10 min of coagulation process using $MgCl_2$ recovered from Dead Sea water.

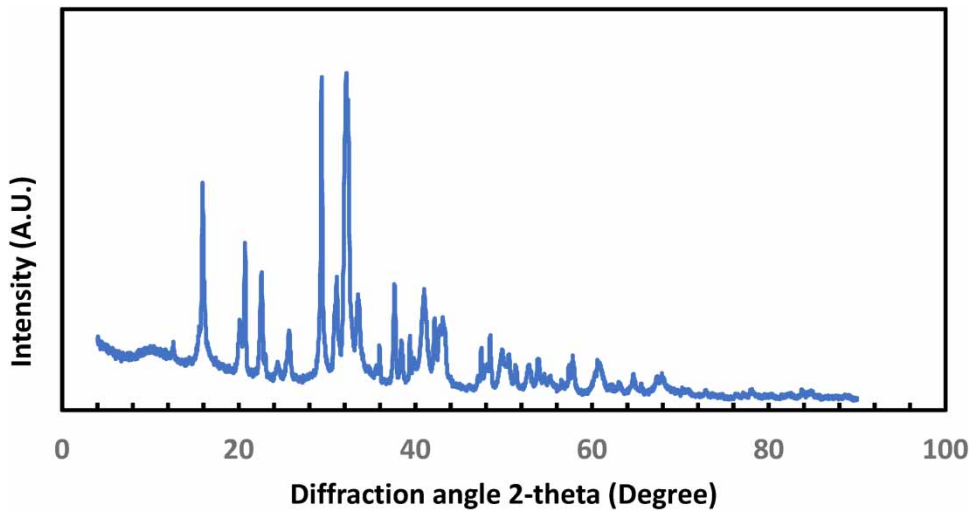


Figure 3 | XRD pattern of $MgCl_2$ recovered from Dead Sea water at a pH of 11.5.

Table 2 | Magnesium concentration was obtained from Dead Sea water by the recovery process

pH value	Mg concentration (g/250 ml)
8.5	3.1
9	4.15
9.5	6.83
10.5	8.83
11	9.89

Table 3 | Mg concentration and Mg compounds concentration at different pH values

pH	Mg (g/250 ml)	$Mg(OH)_2$ (g/250 ml)	$MgCl_2$ (g/250 ml)
8.5	3.1	7.438	12.14
9.0	4.15	9.95	16.25
9.5	6.89	16.50	26.96
10.5	8.83	21.18	34.57
11.0	9.89	23.73	38.73

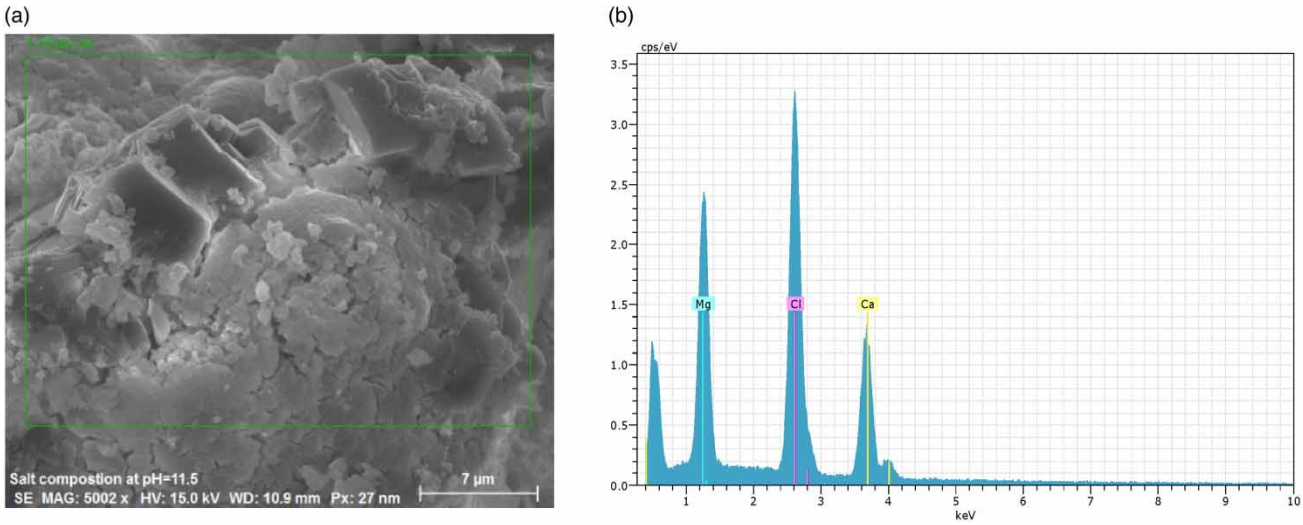


Figure 4 | SEM image showing (a) $MgCl_2$ recovered from Dead Sea water with the presence of other precipitated salts and (b) SEM graph showing that most of the Ca, Cl, and Mg ions present along with some minor precipitated salts.

shown in Figure 4. The main reason for the impure magnesium and presence of calcite is due to not using H_2SO_4 to release CO_2 from solution; thereafter, $CaCO_3$ was precipitated (Yoo *et al.* 2022).

3.3. Coagulation/flocculation in wastewater treatment

The coagulation and flocculation process is one of the most effective choices for treating wastewater sludge parameters such as TSS and COD, $Mg(OH)_2$, and $MgCl_2$ recovered from DS water, which were used as coagulants at different doses, as reported (Karam *et al.* 2021): Kwon *et al.* (2018) showed that the system of treatment with enough Mg^{2+} ions could achieve good coagulation. A schematic illustration of the magnesium dosages is shown in Figure 5, and this figure explains how TSS and COD were removed from wastewater by adding the recovered $MgCL_2$ and $Mg(OH)_2$ from DS water. In addition, different coagulants were used in TSS and COD removal and compared with the magnesium coagulant in wastewater.

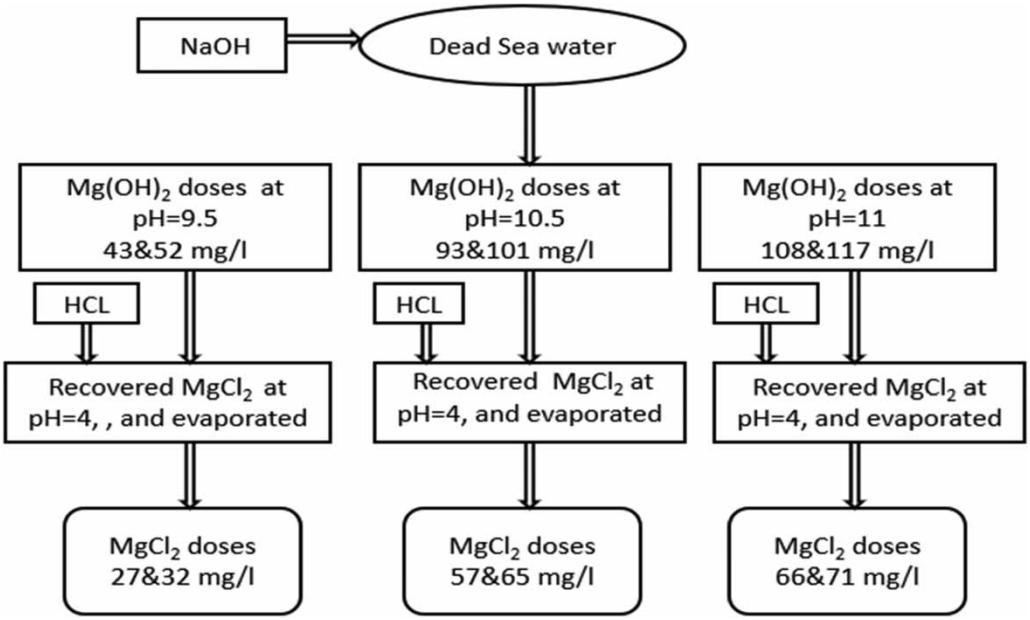


Figure 5 | The explanation of using different recovered $MgCl_2$ and $Mg(OH)_2$ dosages in wastewater.

3.3.1. COD removal using $Mg(OH)_2$

In the coagulation process, the pH level is a crucial factor in the elimination of organic substances in the process of treating wastewater. Figure 6 shows the effect of pH at different coagulation doses for COD removal using $Mg(OH)_2$ as a coagulant. Based on the results, it can be concluded that the efficiency of COD removal from wastewater was enhanced by increasing the concentration of precipitated $Mg(OH)_2$ at a higher pH.

The removal efficiency increased using the same concentration when the wastewater's pH value reached 11, after which the removal rate is constant. $Mg(OH)_2$ precipitates at a pH greater than 10.5 due to the solubility constant. When the concentrations of either Mg ions or hydroxide ion increase, the $Mg(OH)_2$ are formed. Thus, $Mg(OH)_2$ particles, which have a strong affinity for pollutants attract and bind with the organic compounds in the water, form larger particles that are easier to remove through sedimentation. Raising the magnesium concentrations in wastewater was found to be an effective coagulant and in an alkaline state, which increases the precipitation of $Mg(OH)_2$.

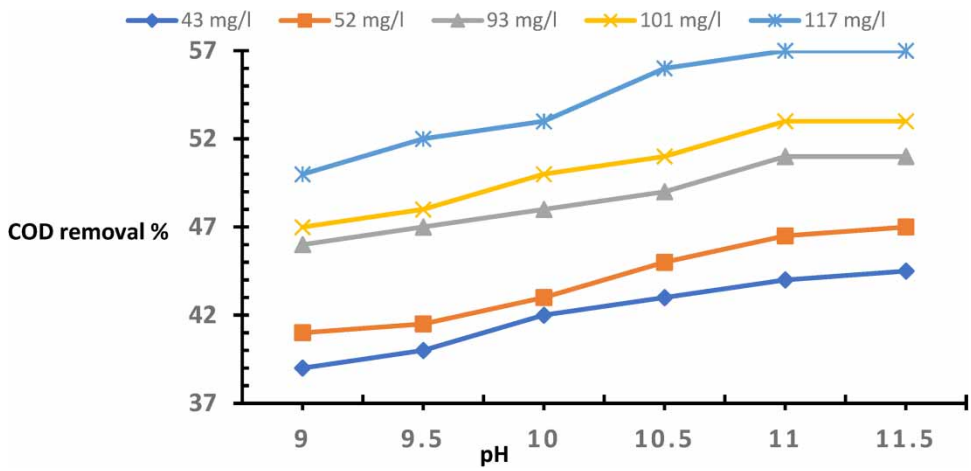


Figure 6 | COD reduction after treatment using the precipitated $Mg(OH)_2$ as Mg at pH = 9, 10.5, 11, and 11.5.

The highest COD removal of about 57% was achieved at pH 11.5 and 117 mg/l dose at 30 min coagulation time. Therefore, pH 11.5 is deemed to be the most suitable for wastewater treatment using $Mg(OH)_2$ recovered from DS water.

Efficient coagulation can be achieved by increasing the dosage of magnesium concentration, as it can neutralize the negative charge of organic particles and flocs (Zhao *et al.* 2015). Due to the rise in precipitated $Mg(OH)_2$, which has a large absorbent and positive surface that attracts negative particles, thus reducing colloidal particles from wastewater (Stumm & Morgan 2012). Magnesium began to precipitate in the form of $Mg(OH)_2$ when the wastewater had a pH of 8.5 by inducing the adsorption and agglomeration process. Thus, COD removal efficiency increased with an increase in $Mg(OH)_2$ dosage. The presence of $Mg(OH)_2$ in wastewater with a high pH value of less than or equal to 10.5 aids the coagulation process, which leads to better removal efficiency.

3.3.2. COD removal using $MgCl_2$

Similar experiments were conducted using $Mg(OH)_2$ and the same wastewater pH values. The effectiveness of the wastewater coagulation and flocculation process improved as $MgCl_2$ concentration increased. The removal efficiency increased as the pH increased until it reached 10.5, at which point the rate of removal began to slow down. The results indicated that higher doses of $MgCl_2$ led to improved efficiency in removing COD and enhancing the flocculation process, particularly at pH levels that were higher but still below 10.5 as shown in Figure 7. The removal efficiency decreasing after pH 11 was probably due to precipitate of $Mg(OH)_2$, which tends to form at pH values above 10.5 due to their solubility constant as discussed by Romano *et al.* (2023).

The greatest COD removal about 44% was achieved at pH 10.5 and 71 mg/l dose at 30 min coagulation time. In addition, the solution's alkalinity increases by adding NaOH containing $MgCl_2$, leading to the formation of precipitates of $Mg(OH)_2$. However, as the pH level goes beyond 11, the rate of precipitation slows down (Kajjumba *et al.* 2021).

3.3.3. TSS removal using $Mg(OH)_2$

TSS was removed from wastewater with different pH values using different doses of $Mg(OH)_2$ and $MgCl_2$, as COD removal. The original TSS value was 450 mg/l. The removal of TSS was highly efficient in wastewater at higher dosages of $Mg(OH)_2$. The results indicated that the flocculation process in wastewater was effective with 59% removal at pH 11.5, and there is no TSS that can be removed until a pH 8 by $Mg(OH)_2$. The removal increased due to reaction of $Mg(OH)_2$ with colloidal particles, which forms large flocs that are then precipitated at the bottom as shown in Figure 8.

The rate of precipitation of TSS reduction, after treatment using precipitated $Mg(OH)_2$ as Mg, slows down with the increasing pH above 11 due to the solubility equilibrium of magnesium hydroxide ($Mg(OH)_2$) in water.

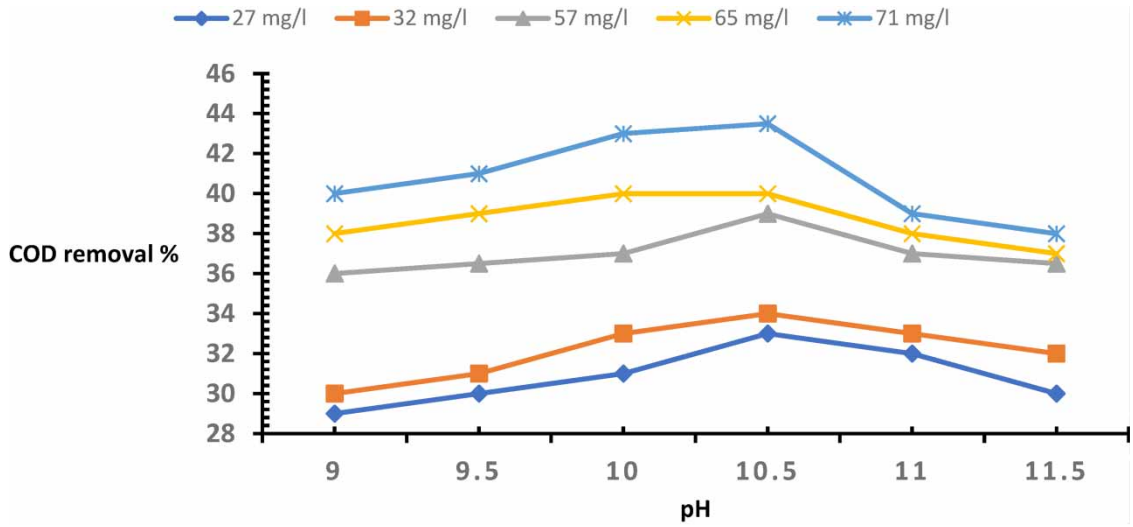


Figure 7 | COD reduction after treatment using the precipitated $MgCl_2$ at pH = 9.0, 10.5, 11.0, and 11.5.

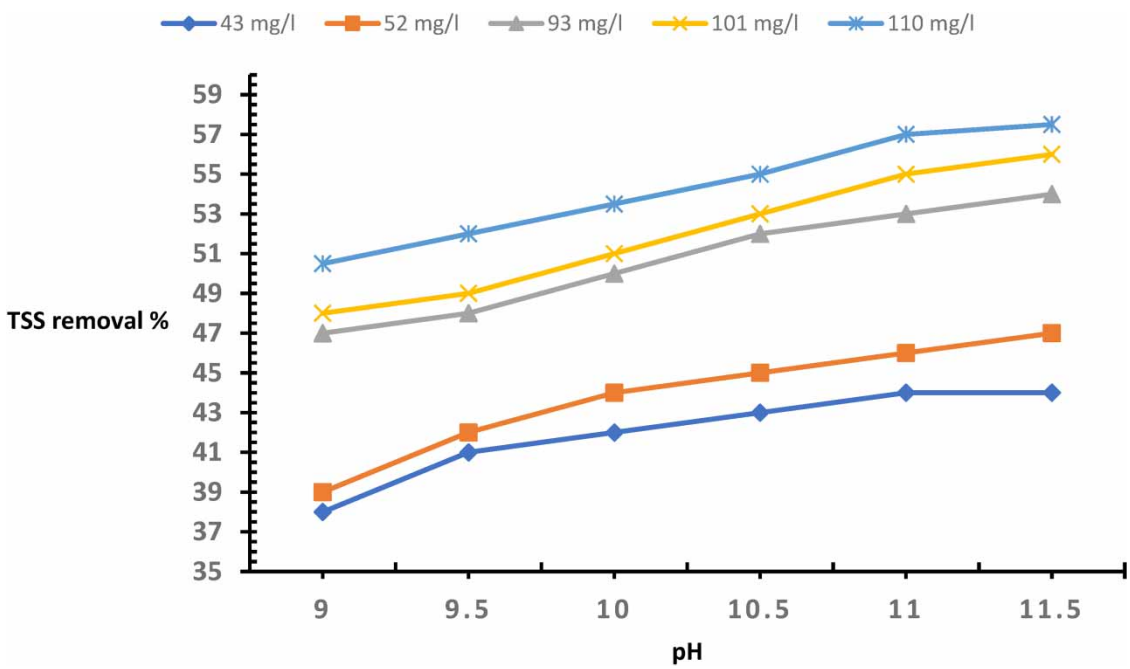


Figure 8 | TSS reduction after treatment using the precipitated $Mg(OH)_2$ as Mg at pH = 9.0, 10.5, 11.0, and 11.5.

When caustic soda (NaOH) is added to water containing magnesium ions (Mg^{2+}), it forms magnesium hydroxide precipitates:

$$Mg^{2+} + 2NaOH \rightarrow Mg(OH)_2 \downarrow + 2Na^{+}$$

The precipitation reaction is favored at lower pH levels because at higher pH, the hydroxide ions (OH-) in solution increase. As the pH rises, the equilibrium shifts toward the dissolved forms of magnesium, i.e., magnesium hydroxide becomes more soluble.

The solubility equilibrium for magnesium hydroxide is represented as follows:

$$Mg(OH)2 \rightleftharpoons Mg^{2+} + 2OH^{-}$$

At pH values above 11, the concentration of hydroxide ions is high, and the equilibrium shifts to the right, leading to the dissolution of $Mg(OH)_2$ back into Mg^{2+} and OH^{-} ions. This means that as you move to a higher pH, the precipitation of magnesium hydroxide becomes less favorable, and the rate of TSS reduction slows down.

3.3.4. TSS removal using $MgCl_2$

Results are observed to be more effective when increasing the dose of $MgCl_2$ as conducted earlier using $Mg(OH)_2$ because the TSS efficient removal increases at the higher magnesium ions when using either $MgCl_2$ or $Mg(OH)_2$. TSS removal increased as the $MgCl_2$ coagulant dose increased, and the removal efficiency decreased slightly with a pH of 11 because adding NaOH increased pH, leading to the formation $Mg(OH)_2$ precipitates (Figure 9). Colloidal particles and suspended solids do not settle under gravity; therefore, the most effective $MgCl_2$ dosage at an appropriate pH yields the greatest floc removal and settling characteristics. The primary reason that suspended solids do not settle under gravity and physical processes is that the charges present on the colloidal surfaces do not allow them to form flocs and agglomerate (Wang *et al.* 2021).

The efficiency of $MgCL_2$ and $Mg(OH)_2$ in the TSS and COD treatment process became more effective when the pH was raised due to a higher precipitation rate, allowing for a higher rate of coagulation and flocculation. The findings suggested that TSS and COD removal was highly efficient when using $MgCL_2$ and $Mg(OH)_2$ at a high pH value due to an increase in

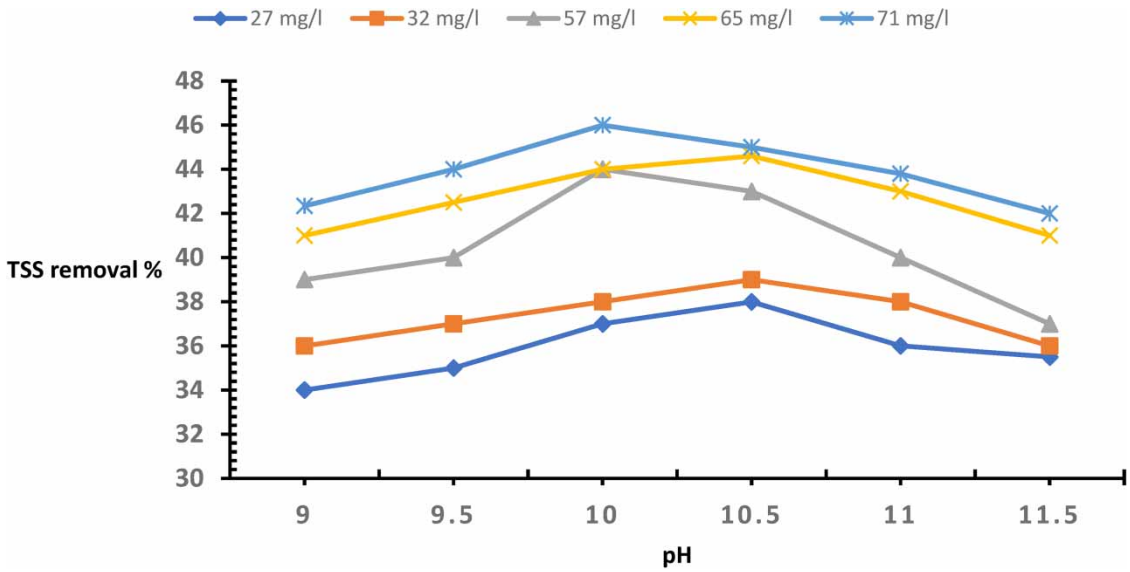


Figure 9 | The effect of different doses of $MgCl_2$, which was precipitated from Dead Sea water at pH of 9, 10.5, 11, and 11.5.

magnesium ions. The removal rate when using $Mg(OH)_2$ was more efficient than $MgCl_2$ at the same pH values and dosages due to the greater quantity of magnesium ions present, which improves the coagulation process.

3.3.5. Other coagulant uses in wastewater

The influence of different coagulants such as $Al_2(SO_4)_3$, $FeCl_3$, Fe SO_4, and cationic PAM on the removal of TSS and COD from wastewater was determined at different pH values. The coagulant doses were chosen based on the optimized doses of $MgCl_2$ and $Mg(OH)_2$ recovered from DS water, which achieved optimal removal of TSS and COD in wastewater, aiming to identify the most effective coagulant.

A prior adjustment of pH for all coagulant trials was performed to determine the pH at optimum removal. The effect of pH on the TSS and COD removal from wastewater was very efficient. Generally, the removal efficiency of COD increased as the pH increased until a pH of 5 was reached, and then the removal decreased until the pH of 7 in all coagulants as shown in Figure 10. For $Al_2(SO)_4$, $FeCl_3$, and Fe_2SO_4 showed optimal removal of COD 21, 22, and 27%, respectively, at pH 5 and at a dosage of 0.4 g/l. However, using PAM, the COD removal was 64% at pH 5.5. The removal of TSS was also studied, and it was found to be 53, 53, and 59% for $Al(SO)_4$, $FeCl_3$, and Fe_2SO_4. Similar to COD removal, cationic PAM achieved excellent removal and higher TSS reduction. TSS and COD removal is almost the same at all pH values except for cationic PAM. The results are shown in Figure 11 that the optimal removal of TSS for all coagulants and optimum removal was 86% by PAM.

The anionic molecules of the dissolved organics interact with cations to form insoluble compounds and settle as sludge at a low pH during coagulation. The coagulation process causes organics to adsorb by metal hydroxides and precipitate out at a higher pH. As the solution has a pH value that is less than 5.5, the TSS and COD are efficiently removed using ferric chloride, probably due to the formation of iron III (Fe^{+3}) with hydroxide (OH^-) in the basic condition to form a polynuclear species. Iron III can react with more colloidal impurities in an acid, including colloidal particles and dissolved organic substances with negative charges (Pan *et al.* 2021). Aluminum salts interact with OH^- ions at higher pH levels than ferric chloride and transfer from species with a greater positive charge to lower positive charges; therefore, TSS and COD removal by $Al_2(SO)_4$, $FeCl_3$, and Fe_2SO_4 are not significantly different. Cationic PAM and magnesium were much more efficient in TSS and COD removal compared to other salt coagulants; however, the polymer was typically more expensive than inorganic coagulants, especially when compared to inorganic salts recovered from DS water, which is a rich source of salts.

The coagulation process using recovered $Mg(OH)_2$ from DS water achieved high removal rates of TSS (60%) and COD (54%) at a dosage of 117 mg/l and a pH of 11. However, the removal efficiency decreased to 46% for TSS and 44% for COD when the pH was lowered to 10.5 and the dosage was reduced to 71 mg/l of $MgCl_2$ recovered from DS water. Beyond pH of 10.5, the removal efficiency of TSS and COD was dropped by $MgCl_2$, while the removal was constant using

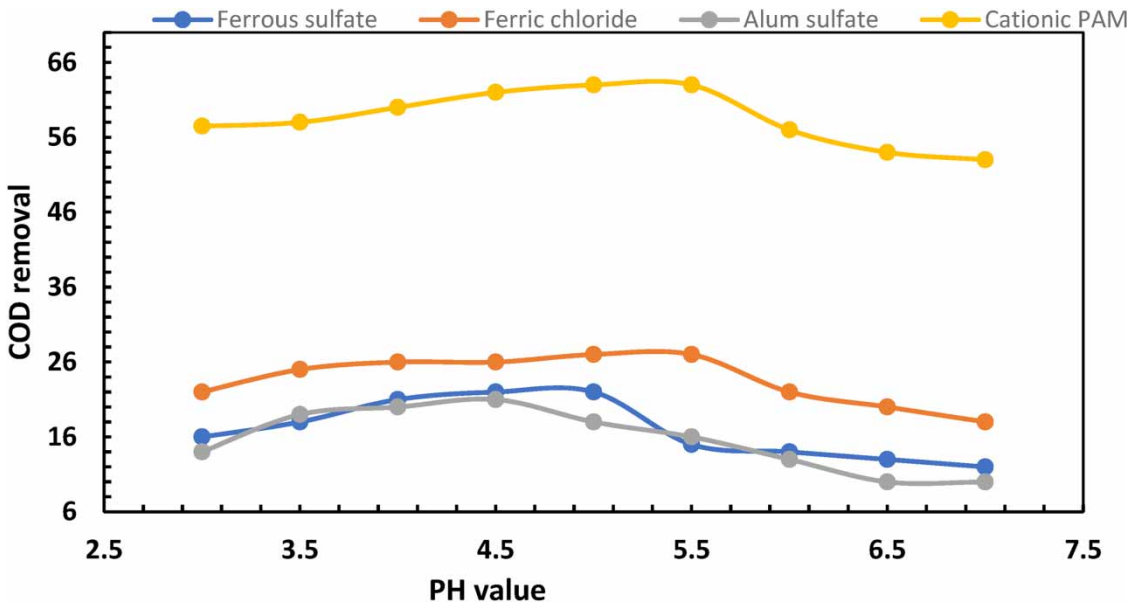


Figure 10 | Removal of COD from wastewater using different coagulants.

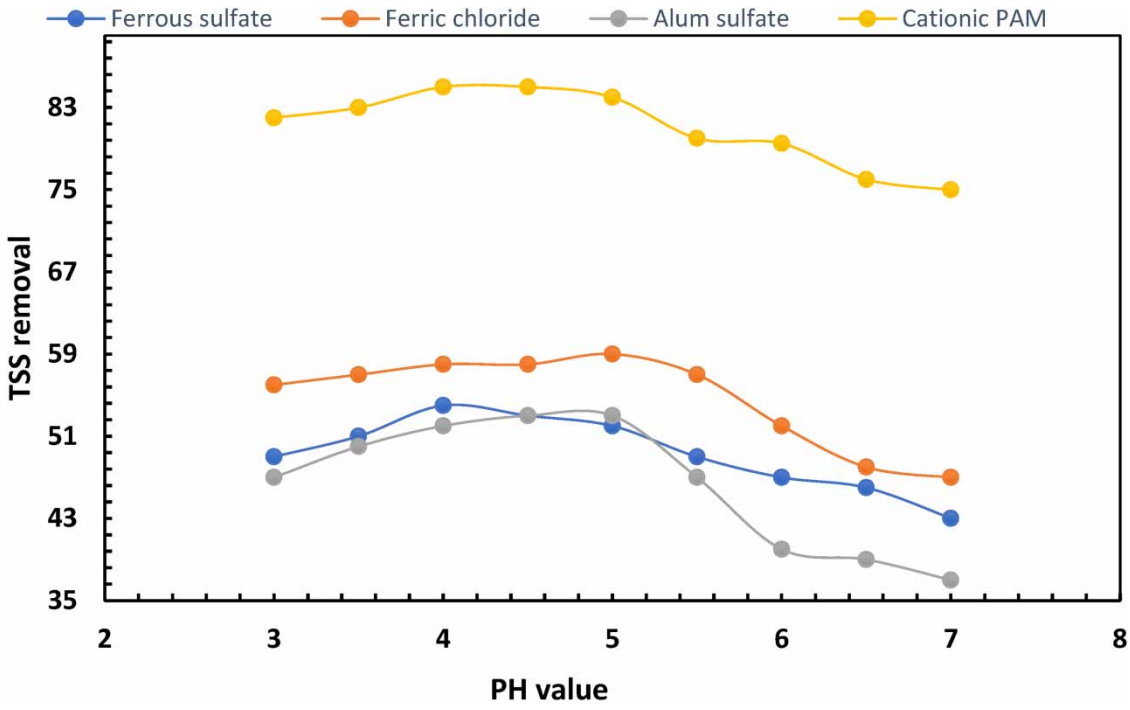


Figure 11 | Removal of TSS from wastewater using different coagulants.

$Mg(OH)_2$. Higher Mg doses yielded better TSS and COD removal efficiencies at all pH values; however, a small improvement in COD or TSS removal required a much higher increase in Mg dose. Reducing pH to 4.0 following magnesium recovery at high pH values did not improve COD or TSS removal efficiency. Therefore, the efficiency of $MgCl_2$ and $Mg(OH)_2$ in the TSS and COD treatment process became more effective when the pH was increased due to a higher precipitation rate, allowing for a higher rate of coagulation and flocculation.

Among the other selected coagulants, the cationic PAM exhibited the greatest effectiveness in removing TSS (with a removal efficiency of 86%) and COD (with a removal efficiency 64%). However, the polymer of PAM was used at a dosage of 0.4 g/l, while $Mg(OH)_2$ recovered from DS water had a great removal with a dosage of 117 mg/l and was more efficient than other commercial inorganic coagulants. In the end, it is recommended to extract $MgCl_2$ from DS water due to its abundance, making it suitable for utilization in the treatment of wastewater.

Verma *et al.* (2012) investigated TSS and COD removal using different coagulants and chemical precipitation techniques. The authors mentioned that the $MgCl_2$ coagulant is the cheapest, and the formed flocs have a shorter settling time than other inorganic salt coagulants. Thereafter, in the case of buying commercial coagulants, magnesium recovered from DS water for wastewater treatment is more effective and crucial.

4. CONCLUSIONS

In this study, magnesium ions from DS water through selective precipitation chemical process were investigated, yielding the highest magnesium ion concentration at a recovery pH of 11.0. The recovered magnesium compounds, ($Mg(OH)_2$) and ($MgCl_2$), demonstrated significant potential for wastewater treatment by effectively removing TSS and COD, especially by adding caustic soda with the increasing pH in enhancing Mg salt recovery; at pH 11.5. $Mg(OH)_2$ exhibits the highest TSS and COD removal efficiencies of 59 and 57%, respectively. In addition, comparative analyses confirmed the competitive performance of magnesium salts versus other precipitation methods, and the combination of commercial Fe_2SO_4 and $MgCl_2$ extracted from DS water showed significant reductions of up to 90 and 73% in TSS and COD, respectively. Overall, the study confirms the efficiency of Mg recovery and emphasizes the potential of the recovered compounds, especially $Mg(OH)_2$, as effective agents for sustainable wastewater treatment.

AUTHOR CONTRIBUTION

Conceptualization: M.A. and T.O.; methodology: M.A. and K.A.-Z.; software: M.A., Y.L., and I.Kh.; validation: Y.L. and A.A.s.; formal analysis: M.M. and I.Kh.; investigation: T.O. and K.A.-Z.; resources: M.A.; data curation: M.A. and T.O.; writing original draft preparation: M.A.; writing review and editing: Y.L. and I.Kh.; visualization: A.A.s and B.A.; supervision: M.A. and T.O.; project administration: M.A., Y.L., and K.A.-Z.. All authors have read and agreed to the published version of the manuscript.

ETHICAL APPROVAL

The authors declare that this study was not conducted on humans.

FUNDING STATEMENT

This study is supported by Petroleum Engineering Department University of North Dakota.

ACKNOWLEDGEMENTS

The author acknowledges the Deanship of Scientific Research Petroleum Engineering Department University of North Dakota for providing support for the publication of this research project.

CONSENT TO PARTICIPATE

The authors give informed consent to participate in this study

CONSENT TO PUBLISH

The author hereby consents to publication of the work.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

Abdel-Aal, H. K. 2018 *Magnesium: From Resources to Production*. CRC Press. Abingdon, UK.

Bagastyo, A. Y., Sinatria, A. Z., Anggrainy, A. D., Affandi, K. A., Kartika, S. W. T. & Nurhayati, E. 2021 Resource recovery and utilization of bittern wastewater from salt production: A review of recovery technologies and their potential applications. *Environmental Technology Reviews* **10** (1), 295–322.

Bevacqua, M., Cipollina, A., Tamburini, A., Brucato, A. & Micale, G. 2015 Magnesium recovery from exhausted brine. In: *Exchange of Good Practices on Metal by-Products Recovery. Technology and Policy Challenges Book of abstracts* (Herrero, M. G. & Miretti, U., eds.). GRICU Meeting, 12-14 September 2016, Anacapri, Italy, pp. 31–31.

Ghyselbrecht, K., Sansen, B., Monballiu, A., Ye, Z. L., Pinoy, L. & Meesschaert, B. 2019 Cationic selectrodialysis for magnesium recovery from seawater on lab and pilot scale. *Separation and Purification Technology* **221**, 12–22.

Hussain, S., Van Leeuwen, J., Chow, C., Beecham, S., Kamruzzaman, M., Wang, D. & Aryal, R. 2013 Removal of organic contaminants from river and reservoir waters by three different aluminum-based metal salts: Coagulation adsorption and kinetics studies. *Chemical Engineering Journal* **225**, 394–405.

Kajjumba, G. W., Fischer, D., Risso, L. A., Koury, D. & Marti, E. J. 2021 Application of cerium and lanthanum coagulants in wastewater treatment – A comparative assessment to magnesium, aluminum, and iron coagulants. *Chemical Engineering Journal* **426**, 131268.

Karam, A., Bakhoum, E. S. & Zaher, K. 2021 Coagulation/flocculation process for textile mill effluent treatment: Experimental and numerical perspectives. *International Journal of Sustainable Engineering* **14** (5), 983–995.

Kim, D. H. 2011 A review of desalting process techniques and economic analysis of the recovery of salts from retentates. *Desalination* **270** (1–3), 1–8.

Kwon, G., Kang, J., Nam, J. H., Kim, Y. O. & Jahng, D. 2018 Recovery of ammonia through struvite production using anaerobic digestate of piggery wastewater and leachate of sewage sludge ash. *Environmental Technology* **39** (7), 831–842.

Loganathan, P., Naidu, G. & Vigneswaran, S. 2017 Mining valuable minerals from seawater: A critical review. *Environmental Science: Water Research & Technology* **3** (1), 37–53.

Mohammad, A. F., El-Naas, M. H., Al-Marzouqi, A. H., Suleiman, M. I. & Al Musharfy, M. 2019 Optimization of magnesium recovery from reject brine for reuse in desalination post-treatment. *Journal of Water Process Engineering* **31**, 100810.

Mohammadesmaeili, F., Badr, M. K., Abbaszadegan, M. & Fox, P. 2010 Byproduct recovery from reclaimed water reverse osmosis concentrate using lime and soda-ash treatment. *Water Environment Research* **82** (4), 342–350.

Morillo, J., Usero, J., Rosado, D., El Bakouri, H., Riaza, A. & Bernaola, F. J. 2014 Comparative study of brine management technologies for desalination plants. *Desalination* **336**, 32–49.

Pan, C., Jiao, Y., Kersting, A. B. & Zavarin, M. 2021 Plutonium redox transformation in the presence of iron, organic matter, and hydroxyl radicals: Kinetics and mechanistic insights. *Environmental Science & Technology* **55** (3), 1800–1810.

Peeva, G., Yemendzhiev, H. & Nenov, V. 2022 Precipitation of struvite from digested sewage sludge by sea water brine and natural flocculants. *Journal of Chemical Technology & Metallurgy* 57(2), 1–10.

Quist-Jensen, C. A., Jørgensen, M. K. & Christensen, M. L. 2016 Treated seawater as a magnesium source for phosphorus recovery from wastewater – A feasibility and cost analysis. *Membranes (Basel)* **6** (4), 54.

Reiss, A. G., Gavrieli, I. & Ganor, J. 2020 The effect of phosphonate-based antiscalant on gypsum precipitation kinetics and habit in hypersaline solutions: An experimental and modeling approach to the planned Red Sea–Dead Sea Project. *Desalination* **496**, 114638.

Rioyo, J., Aravinthan, V., Bundschuh, J. & Lynch, M. 2018 Research on 'high-pH precipitation treatment' for RO concentrate minimization and salt recovery in a municipal groundwater desalination facility. *Desalination* **439**, 168–178.

Romano, S., Trespi, S., Achermann, R., Battaglia, G., Raponi, A., Marchisio, D. & … Cipollina, A. 2023 The role of operating conditions in the precipitation of magnesium hydroxide hexagonal platelets using NaOH solutions. *Crystal Growth & Design* **23** (9), 6491–6505.

Stumm, W. & Morgan, J. J. 2012 *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. John Wiley and Sons, New York.

Verma, A. K., Bhunia, P. & Dash, R. R. 2012 Supremacy of magnesium chloride for decolourisation of textile wastewater: A comparative study on the use of different coagulants. *International Journal of Environmental Science and Development* **3** (2), 118.

Walschot, M., Luis, P. & Liégeois, M. 2020 The challenges of reverse osmosis desalination: Solutions in Jordan. *Water International* **45** (2), 112–124.

Wang, L. K., Wang, M. H. S., Shammas, N. K. & Hahn, H. H. 2021 Physicochemical treatment consisting of chemical coagulation, precipitation, sedimentation, and flotation. In: *Integrated Natural Resources Research*, (Wang, L. K., Wang, M. H. S. & Hung, Y. T., eds.). Springer, Cham, pp. 265–397.

Weber, N., Antler, G., Lazar, B., Stein, M., Yechieli, Y. & Gavrieli, I. 2022 Hydrological and thermodynamic controls on late holocene gypsum formation by mixing saline groundwater and Dead Sea brine. *Geochimica et Cosmochimica Acta* **316**, 363–383.

Yoo, Y., Kim, I., Lee, D., Choi, W. Y., Choi, J., Jang, K. … & Kang, D. 2022 Review of contemporary research on inorganic CO_2 utilization via CO_2 conversion into metal carbonate-based materials. *Journal of Industrial and Engineering Chemistry* **116**, 60–74.

Young, P., Phasey, J., Wallis, I., Vandamme, D. & Fallowfield, H. 2021 Autoflocculation of microalgae, via magnesium hydroxide precipitation, in a high rate algal pond treating municipal wastewater in the South Australian Riverland. *Algal Research* **59**, 102418.

Zhang, X., Zhao, W., Zhang, Y. & Jegatheesan, V. 2021 A review of resource recovery from seawater desalination brine. *Reviews in Environmental Science and Biotechnology* **20** (2), 333–361.

Zhao, S., Gao, B., Sun, S., Yue, Q., Dong, H. & Song, W. 2015 Coagulation efficiency, floc properties and membrane fouling of polyaluminum chloride in coagulation–ultrafiltration system: The role of magnesium. *Colloids and Surfaces A: Physicochemical and Engineer* **469**, 235–241.

First received 2 November 2023; accepted in revised form 30 January 2024. Available online 12 February 2024