

## Article

# Application of Different Coagulants and Cost Evaluation for the Treatment of Oil and Gas Produced Water

Namita Das <sup>1</sup>, Himadri Rajput <sup>2,3</sup>, Ashraf Aly Hassan <sup>2,3,\*</sup> and Sandeep Kumar <sup>4</sup><sup>1</sup> General Education Department, City University College of Ajman, Ajman 18484, United Arab Emirates<sup>2</sup> Civil and Environmental Engineering Department, United Arab Emirates University, Al-Ain 15551, United Arab Emirates<sup>3</sup> National Water and Energy Center, United Arab Emirates University, Al-Ain 15551, United Arab Emirates<sup>4</sup> Department of Bio and Nano Technology, Guru Jambheshwar University of Science and Technology, Hisar 125001, India

\* Correspondence: alyhassan@uaeu.ac.ae; Tel.: +971-(03)713-5334

**Abstract:** A coagulation treatment is a separation technology widely used in industries as a pre-treatment step to remove the dissolved organic matter in wastewater. However, the type of coagulant, the optimized dose, and the treatment cost associated with various commercially employed coagulants must be investigated for the treatment of oil and gas produced water. In this study, five widely employed coagulants—ferric chloride, aluminum potassium sulphate, chitosan, sodium sulfide, and magnesium oxide—were tested for the treatment of actual complex oilfield-generated produced water. Water quality parameters such as the total suspended solids (TSS), total dissolved solids (TDS), turbidity, salinity, and pH were assessed for a better understanding of different coagulant activities against the produced water treatment. All the coagulants were efficient for the treatment of produced water. The findings of this study showed that ferric chloride led to the best removal of total solids (74.25%) of all water quality parameters, with treatment costs of USD 4 per m<sup>3</sup> of produced water. The results from this study contribute to the environmentally friendly, broader, and cost-effective application of a coagulation treatment to produced water.

**Keywords:** produced water; coagulation; treatment cost; ferric chloride; aluminum potassium sulphate; chitosan; sodium sulfide; magnesium oxide

**Citation:** Das, N.; Rajput, H.; Aly Hassan, A.; Kumar, S. Application of Different Coagulants and Cost Evaluation for the Treatment of Oil and Gas Produced Water.

*Water* **2023**, *15*, 464.

<https://doi.org/10.3390/w15030464>

Academic Editor: P. V. Nidheesh

Received: 15 November 2022

Revised: 17 January 2023

Accepted: 18 January 2023

Published: 23 January 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Produced water (PW) is a by-product of the natural gas and crude oil recovery process at onshore and offshore operations [1]. Worldwide, approximately 250 million barrels of PW is generated per day to produce 80 million barrels of oil [2]. The composition of PW varies from location to location and with the type of production facility. A producing field throughout its economic life can generate 10 times more volume of PW compared with the volume of produced hydrocarbons. This volume can further increase based on the maturity of the producing oil and gas fields. PW is considered to be toxic as it is a complex mixture of various organic and inorganic components such as aliphatic dispersed oils and hydrocarbons, including benzene, toluene, and polycyclic aromatic hydrocarbons, as well as metal ions, hardness, and phenols [3,4]. The oil and grease content present in PW can pose serious side effects such as the fouling of sewer systems and the generation of foul odors if it does not meet the discharge standards [5]. The impact of PW discharge on the environment is summarized in Table 1. The threat of PW to the environment can be understood by the fact that its discharge in coastal estuarine and marine waters is not permitted in the United States; however, the offshore discharge limit of treated PW in Australia is 30 mg L<sup>−1</sup> (daily average) and the limit for the total oil and grease content in the Arabian Gulf and Asia is 40 mg L<sup>−1</sup> [6].

**Table 1.** Impact of PW discharge.

Location	Impact of PW discharge	Reference
United Kingdom	Elevated level of radium ( $^{226}\text{Ra}$ ) up to 97% was detected in marine sediment samples at sites downstream of the point of PW discharge.	[7]
Nigeria	Even after treatment, the PW discharged in the Niger Delta exceeded the discharge limits for the oil and grease content ( $60 \pm 20$ ), TDS ( $6200 \pm 700$ ), and chloride ions ( $4100 \pm 500$ ).	[8]
Texas	PW discharged in Nueces Bay made the sediments in the vicinity of the discharge toxic, with $\text{EC}_{50}$ values ranging between 7.3 and 24.6%.	[9]
Canada	After the release of PW in the Grand Banks, selected health bioindicators of fish (cell count, visible skin and organ lesions, cellular alteration, etc.) were absent or similar to the reference site.	[10]
Mexico	Long-term PW discharge into the ocean at the Gulf of Mexico could cause an increase in ecological and human risks over time and space due to high concentrations of PAHs (up to 2324 ng/g).	[11]
Norway	PW discharge may have toxic effects on organisms close to the outlet and severe cumulative effects.	[2]
Italy	PW discharged in Adriatic Sea led to the toxicity of water ( $\text{EC}_{50}$ value of 20.73% for <i>P. lividus</i> ); however, no significant effect was observed on marine sediment.	[12]

The presence of calcium chloride and magnesium chloride is also very common in PW. These compounds can generate scaling issues in the American Petroleum Institute (API) oil–water separators used in oilfields, with further generating issues in the oil–water separation process. The discharge of toxic PW can have a detrimental effect on fresh and brackish marine life, and its treatment in an economical way can be challenging because of the presence of high salinity and a large oil content. Therefore, efficient treatment methods are needed for PW before its disposal. An efficient treatment enables the beneficial recycling and reuse of a huge volume of PW, which can lead to a reduction in the water disposal cost along with the mitigation of the potential adverse effects of PW on the environment. Several treatment methods such as adsorption, membrane processes, coagulation, gas flotation, biological processes, and advanced oxidation have been explored for the remediation of PW [5,13]. Among these, membrane processes such as a reverse osmosis (RO) treatment are usually used in combination with other pre-treatment methods for the efficient remediation and reuse of PW. RO is considered to be a good choice for treating PW as it possesses properties such as a high rejection rate of colloids and salts [14]. However, before being subjected to the RO process, the pre-treatment of PW is needed due to membrane fouling and scaling problems. Oil, fine organic compounds, and other pore-blocking colloids present in PW cause the issue of membrane fouling [15]. The problem of scaling is caused by the deposition of  $\text{CaCO}_3$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , which are mostly responsible for scaling in membranes. Complications such as a hindrance to the permeate flow, irreversible pore plugging, an increased pressure drop, and physical damage to the membrane are the consequences of scaling [16]. It has also been observed that the membrane surface charge was decreased due to calcium ions, which led to a reduction in the solute rejection [17]. Therefore, attention to the scaling issue is needed as it significantly affects the operation of the RO process. To solve these issues, a pre-treatment by coagulation prior to the RO process has been recommended to enhance the treatment of PW and the life span of the used membrane [18].

Coagulation is one of the most conventional pre-treatment methods used for the purification of PW. Many recent studies have shown the effectiveness of coagulation technology for the treatment of wastewater [19]. The presence of a chemical agent destabilizes the colloidal particles, causing them to be suspended in water. Later, these individual colloids aggregate and grow in size, followed by their settlement at the bottom. The coagulant can be synthetic or natural and has a positive charge that combines with the

negatively charged impurities in the water, ultimately causing their settlement and removal [20]. Various studies have been carried out on the treatment of PW using different coagulants such as lime [21], polynuclear polymers [22], calcite [23], and ferric ions [24]. Coagulation has been shown to successfully remove suspended solids and turbidity; however, its efficiency depended on the colloids, pH, temperature, dose, and type of coagulants [25]. Coagulation is a preferred method because of its easy operation, economic viability, low energy demand, reduced environmental impacts, and high removal efficiency [26,27]. Coagulation can be employed as a pre-treatment technology in combination with other advanced treatment methods for the efficient treatment of complex PW.

In this study, we explored the effectiveness of different coagulants and compared them in terms of the treatment efficiency and cost. We used real PW from the Gulf region and explored the effectiveness of commercially available coagulants for its pre-treatment. As PW is highly complex and generated in huge quantities, we investigated a cost-effective coagulant for the pre-treatment of PW. The pre-treatment PW could be further subjected to a secondary treatment to minimize the organic load and its complexity. A total of five different coagulants—namely, ferric chloride ( $\text{FeCl}_3$ ), sodium sulfide ( $\text{Na}_2\text{S}$ ), chitosan, aluminum potassium sulphate ( $\text{AlKSO}_4$ ), and magnesium oxide ( $\text{MgO}$ )—were tested and analyzed for their efficiency in the remediation of PW. The effect of the coagulant dose on the removal of solids has been studied for its potential application as a pre-treatment method on a large scale. The cost of the treatment of the produced water using the five coagulants was evaluated to understand the potential practical implementation. The outcomes gave an insight into the activity and convenience of different coagulant materials for PW treatments.

## 2. Materials and Methods

### 2.1. Chemicals and Materials

The real produced water sample was provided from an undisclosed oilfield located in the Middle East. The sample was collected and stored in a refrigerator throughout this study. Ferric chloride (98.5%) and magnesium oxide (97%) were provided by Alpha Chemika, India. Sodium sulfide (60%) was purchased from S.D. Fine-Chem Limited, India. Aluminum potassium sulphate (99%) was obtained from Loba Chemie, India. Chitosan powder, a natural fiber derived from the ocean, was purchased online (Mystic Moments). All the coagulants used in the present study were not further modified and used as received.

### 2.2. Coagulation Experiments and Analytical Methods

A glass reactor ( $9 \times 7$  cm) was used to perform the batch-scale coagulation experiments. Different coagulants were added to the PW (50 mL) and kept for rapid mixing using a magnetic stirrer (ST10, 220 V, Didactic Systems and Technology, Al Ain, UAE) for 30 min. After mixing, the flocs were allowed to settle for a few hours; the supernatant sample was then carefully separated using a pipette and characterized. A similar procedure was followed for all the coagulants used in this study. The influence of the coagulant dose variation was studied for the treatment of PW. All the experiments were performed in triplicate and an average value was reported. An analysis of the PW samples before and after their coagulation treatment was performed for their electrical conductivity (EC), salinity, and total dissolved solids (TDS) using a conductivity meter (Laqua Horiba, PC 1500). The pH was measured using a pH meter (Extech, China). The turbidity of the samples was measured by using a turbidity meter (Lutron TU-2016). The total suspended solids (TSS) were estimated using Hach Lange DR 3900 equipment.

### 3. Results and Discussions

#### 3.1. Characterization of PW

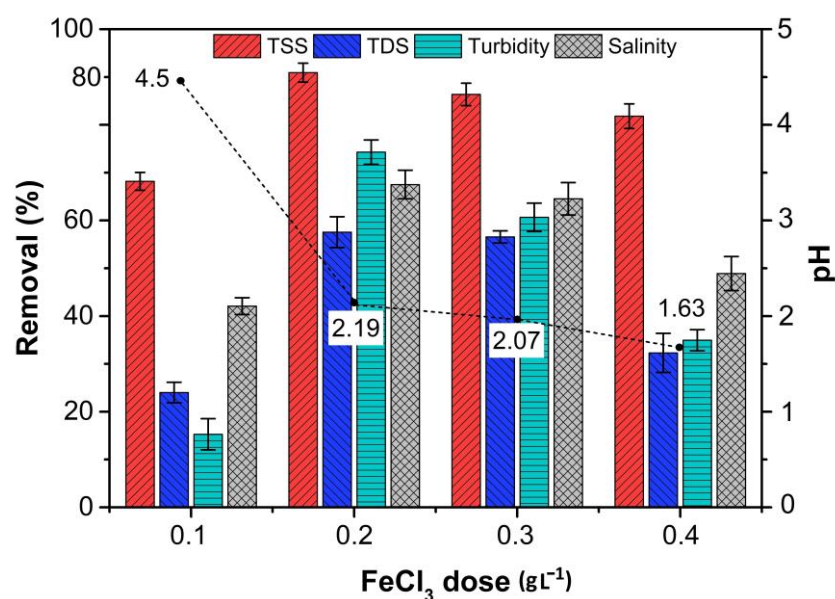
The PW obtained from the oilfield site was characterized for its properties so that a comparison could be made after its coagulation treatment. The results of the PW characterization are summarized in Table 2.

**Table 2.** Characteristics of PW.

S. No.	Parameter	PW Composition
1	pH	7.8
2	Electrical conductivity (mS cm <sup>-1</sup> )	151.2
3	Salinity (parts per thousand)	90.8
4	TDS (g L <sup>-1</sup> )	80.8
5	Turbidity (NTU)	6.6
6	TSS (mg L <sup>-1</sup> )	22

#### 3.2. Treatment of PW Using Ferric Chloride

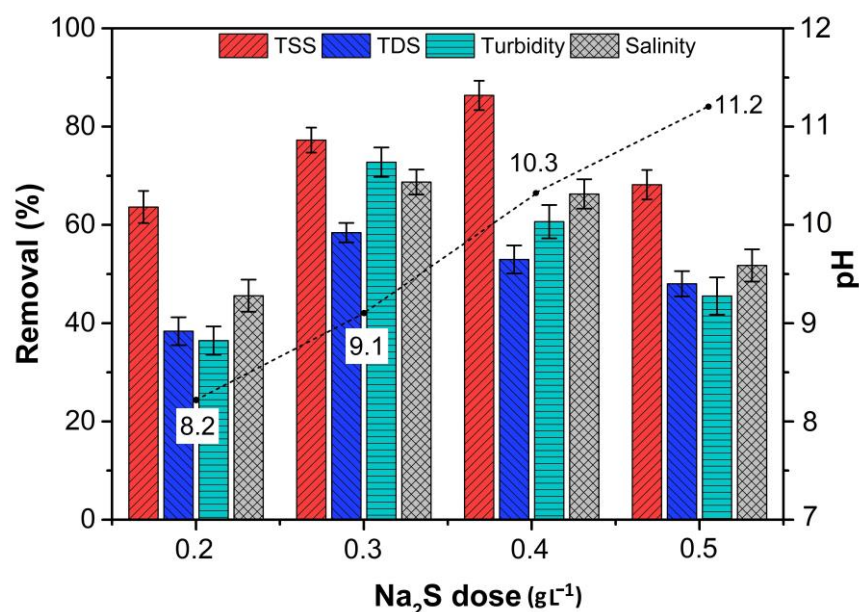
Upon addition to water, a dissociation of iron salts takes place and reacts to generate hydrolysis products. These hydrolysis products form coagulant species, which are responsible for the removal of turbidity and color from wastewater [28]. The hydrolysis of ferric chloride leads to the formation of monomers, dimers, trimers, and polycations with 24 Fe atoms in a  $\beta$ -FeOOH structure [29]. In this study, a raw PW sample was subjected to a coagulation treatment using the most common coagulant, i.e., ferric chloride. Different concentrations of FeCl<sub>3</sub> (0.1, 0.2, 0.3, and 0.4 g L<sup>-1</sup>) were added to the PW. The effects are represented in Figure 1. With an increase in the concentration, a drop in the pH of the solution was observed. At 0.1, 0.2, 0.3, and 0.4 g L<sup>-1</sup> FeCl<sub>3</sub>, the pH of the PW solution was observed to be 4.5, 2.19, 2.07, and 1.63, respectively. Once the coagulant was added, a sudden drop in the pH was observed, i.e., from 7.8 to 4.5, with a further reduction upon an increase in the coagulant dose. A similar reducing trend of pH was also observed with an increase in the FeCl<sub>3</sub> concentration as the coagulant hydrolysis exceeded the buffer capacity of the solution [30]. No attempt was made to alter the pH of the solution as, on an industrial scale, a pH adjustment for a large volume would require additional care and cost. The effect of the FeCl<sub>3</sub> dosage on turbidity, TSS, TDS, and salinity reduction was studied. The maximum treatment was observed at a FeCl<sub>3</sub> dose of 0.2 g L<sup>-1</sup> (74.3% removal of turbidity, 91% removal of TSS, 57.5% removal of TDS, and 67.5% removal of salinity). A further increase in the FeCl<sub>3</sub> dosage did not lead to a better degradation efficiency. The concentration of the coagulant must be proportional to the present colloidal quantity. If the coagulant dose exceeds the required quantity, the restabilization of particles occurs due to a charge reversal on the colloids [31]. At the optimum coagulant dose (0.2 g L<sup>-1</sup>), lower residual turbidity and better removal efficiency were observed, as also previously reported in [32].



**Figure 1.** Effect of ferric chloride on the treatment of produced water.

### 3.3. Treatment of PW Using Sodium Sulfide

The utilization of Na<sub>2</sub>S is an option for wastewater remediation due to its non-toxic nature and excellent chemical properties [33]. The wide application of Na<sub>2</sub>S as a reducing agent [34], surface cleaning agent [35], depressant for rutile and zircon [36], sulfurizing agent [37], and chemical coagulant [38] has been extensively explored. When Na<sub>2</sub>S is added to wastewater, it neutralizes the negative charge present on the suspended solids. After this reaction, the suspended particles aggregate and form slightly larger particles, which can easily be separated [39]. In the present study, different concentrations of sodium sulfide (0.2, 0.3, 0.4, and 0.5 g L<sup>-1</sup>) were added as a coagulant for the treatment of PW, which led to a significant reduction in the solids (Figure 2). Even though PW is a very complex mixture, 0.4 g L<sup>-1</sup> Na<sub>2</sub>S resulted in an 86%, 53%, 60.6%, and 66% removal of TSS, TDS, turbidity, and salinity, respectively. The highest turbidity removal (86.3%) was observed at 0.4 g L<sup>-1</sup> Na<sub>2</sub>S. However, 0.3 g L<sup>-1</sup> Na<sub>2</sub>S also showed a comparable removal of TSS (77.2%), TDS (58.4%), turbidity (72.7%), and salinity (68.7%). As the highest TSS removal was achieved at 0.4 g L<sup>-1</sup>, it was considered to be the optimum coagulant dose. Na<sub>2</sub>S was previously reported to be efficient for removing heavy metals [40] and nickel from pickling and electropolishing processes [41]. A slight increase in the pH was observed with an increase in the concentration of sodium sulfide, which might have been due to the hydrolysis of a strong base salt. A similar pH rising trend was seen upon the addition of Na<sub>2</sub>S in a previous study [41]. However, a major concern associated with Na<sub>2</sub>S is its cost, and, at a low pH, it might lead to the formation of H<sub>2</sub>S. However, if the solution pH is adjusted to 8 with the existence of Na<sub>2</sub>S, the generation of H<sub>2</sub>S can be prevented [42]. In our study, the pH of the reaction solution was above 8 after adding the coagulant; hence, the chances of toxic gas formation were very low.



**Figure 2.** Effect of sodium sulfide on the treatment of produced water.

### 3.4. Treatment of PW Using Chitosan

Chitin is one of the most abundant biopolymers worldwide and comes in second place after cellulose. The raw material chitin is extracted from shellfish sources (shrimps and crabs) [43]. The alkaline deacetylation of chitin produces chitosan, which is a partially deacetylated polymer. Chitosan is a linear chain copolymer of d-glucosamine and N-acetyl-d-glucosamine. Chitosan possesses unique properties when compared with other biopolymers such as the presence of primary amino groups. It is a compound of commercial interest due to the presence of a high nitrogen content in comparison with cellulose [44]. Chitosan has gained attention due to its coagulation properties in the field of wastewater treatments [45]. Chitosan is capable of performing coagulation as well as flocculation and has properties such as a long polymer chain and a high cationic charge density. It is also capable of bridging aggregates in neutral or alkaline pH conditions. These properties of chitosan can be advantageous for the removal of organic and inorganic suspensions and even for the removal of dissolved organics. The advantages chitosan has over chemical coagulants are its eco-friendly behavior, biodegradability, non-toxic nature, efficient chelation behavior, and low cost [46].

In the present investigation, an optimum chitosan dose of 0.2 g L<sup>-1</sup> led to the 86%, 79%, 82%, and 66% removal of TSS, TDS, turbidity, and salinity, respectively (Figure 3). When the chitosan dose was increased above the optimum concentration, a decrease in the TSS value (73% at 0.3 g L<sup>-1</sup> and 59% at 0.4 g L<sup>-1</sup>) was observed, which could be attributed to the reversal of the surface charge and the restabilization mechanism [47]. It was observed that adding chitosan did not significantly alter the original pH of the reaction solution. The results obtained under an optimum concentration showed that chitosan could be used as a coagulant for the efficient treatment of PW, resulting in an effective TSS removal from palm oil mill wastewater [48].



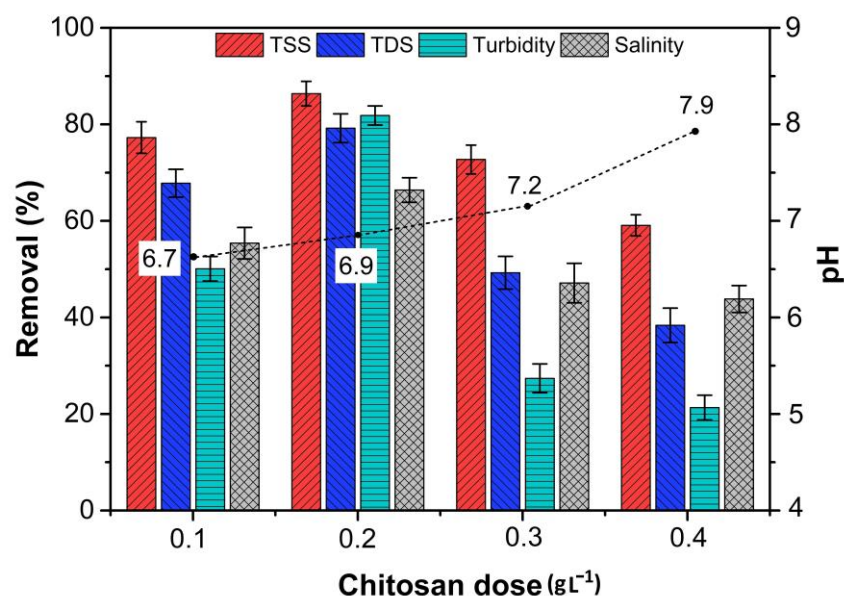


Figure 3. Effect of chitosan on the treatment of produced water.

### 3.5. Treatment of PW Using Aluminum Potassium Sulphate

Aluminum potassium sulphate, commonly known as potash alum, was used to treat PW at different concentrations. Potash alum is a very common coagulant used widely due to its relatively low cost and ready availability. A  $0.1 \text{ g L}^{-1}$  optimum dose of potash alum resulted in the 77%, 70%, 88%, and 54% removal of TSS, TDS, turbidity, and salinity, respectively (Figure 4). When this coagulant is added to PW, Al ions rapidly hydrolyze to form different metal hydrolysis species. These cationic species are adsorbed onto negatively charged particles and neutralize the charge, which results in the destabilization of the particles and aggregation occurs [49,50]. The pH of the reaction solution after the addition of the coagulant at different doses was observed to be in the range of 5 to 5.5. If the pH increases from 8, aluminum exists in the form of  $\text{Al}(\text{OH})_4^-$  ions. These ions can reduce the treatment efficiency due to electrostatic repulsion between the negatively charged impurities present in the wastewater and  $\text{Al}(\text{OH})_4^-$  ions [31].

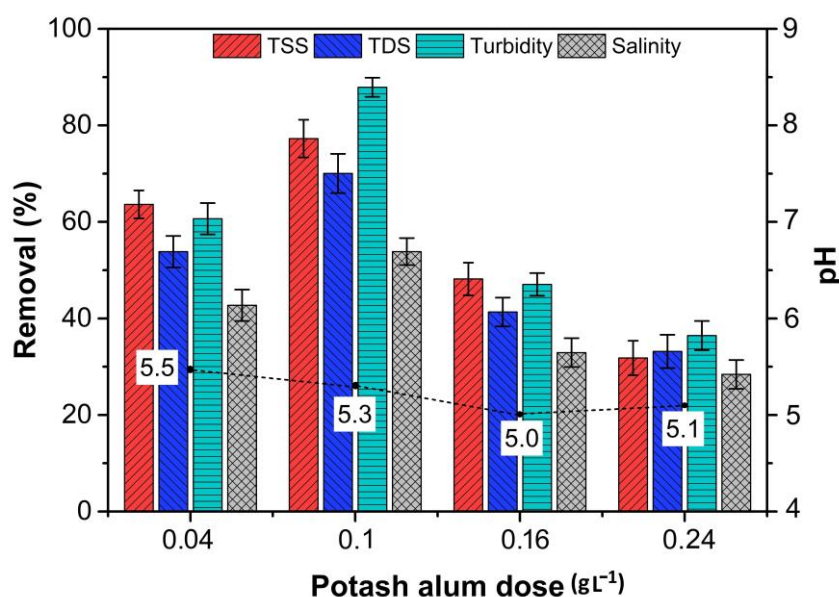
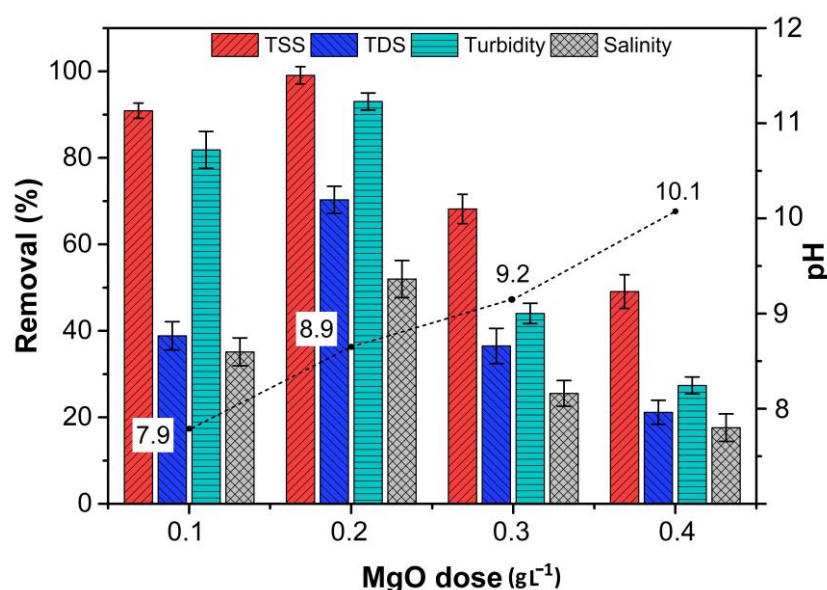


Figure 4. Effect of potash alum on the treatment of produced water.

### 3.6. Treatment of PW Using Magnesium Oxide

MgO is widely used in the remediation of wastewater due to properties such as its strong adsorption potential and large activate surface. When MgO was used as a coagulant for the treatment of PW, an almost complete removal of turbidity was achieved. At a  $0.2 \text{ g L}^{-1}$  MgO concentration, a 99%, 70%, 93%, and 52% removal of TSS, TDS, turbidity, and salinity was observed (Figure 5). It was previously reported that, under alkaline conditions, MgO generates a complex molecular structure of MgO and  $\text{Mg}(\text{OH})_2$  [51].  $\text{Mg}(\text{OH})_2$  can dissociate and form colloid particles of positive electrons surrounded by  $\text{OH}^-$  ions, which can aggregate with the PW impurities [52]. The pH increased from 7.8 to 10 when MgO was added to the reaction mixture. A similar rising trend of pH was also previously reported when MgO was used as a coagulation treatment [53].



**Figure 5.** Effect of magnesium oxide on the treatment of produced water.

### 3.7. Cost Comparison of Different Coagulants

The cost is a critical factor in determining the practical consideration of any existing or innovative technologies. For the successful commercialization of a process, the coagulation process must significantly reduce the cost of the treatment to remove the dissolved organics from the produced industrial water. In the case of a coagulation treatment, the overall expense of the treatment includes the cost of the catalyst required to achieve the desired removal of the dissolved organics in the produced water. However, it does not include the cost of the light source, start-up of the process, electricity, labor, and maintenance. The cost of the treatments of the produced water using the five coagulants was evaluated. The results are summarized in Table 3.



**Table 3.** Summary of cost assessment for the treatment of produced water using the various coagulants.

	Coagulants				
	FeCl <sub>3</sub>	Na <sub>2</sub> S	Chitosan	AlKSO <sub>4</sub>	MgO
Coagulant dose used (mg L <sup>-1</sup> )	200	400	200	100	200
Coagulant dose used (kg 10 <sup>-3</sup> m <sup>-3</sup> )	200	400	200	100	200
Commercial cost of coagulants (USD kg <sup>-1</sup> )	0.02	0.09	0.2	0.19	0.6
Cost of treatment (USD m <sup>-3</sup> )	4	36	40	19	120
Removal efficiency (%) *	74.25	69.5	82.5	73.5	84.5
Treatment cost efficiency (USD m <sup>-3</sup> % <sup>-1</sup> ) **	(1)	(4)	(3)	(2)	(5)

Note: \* Total solids (TS) removal efficiency was used as a water quality parameter. TS was calculated by taking the average of TSS and TDS removal efficiencies. \*\* Values in brackets signify the ranking score by the cheapest treatment per unit TS removal efficiency (%).

The coagulants were ranked in terms of their feasibility by considering their commercial cost and treatment performance for PW. According to the removal of total solids and starting with the most desirable coagulant for PW, the coagulants were ranked as follows: FeCl<sub>3</sub>, AlKSO<sub>4</sub>, chitosan, Na<sub>2</sub>S, and MgO. The best removal of all the measured water quality parameters was achieved by FeCl<sub>3</sub> (74.25%), which cost USD 4 per m<sup>-3</sup> of produced water. However, it should be specified that other operating costs (such as the sum of the energy consumption, land requirement, labor, and maintenance costs) were not considered, which do not particularly depend on the initial organics in the produced water, but instead on the specific characteristics of the water quantity and energy/labor prices of each case study.

#### 4. Conclusions

In this study, we utilized widely and commercially employed coagulants for the coagulation treatment of oilfield-generated produced water. Among the utilized coagulants, the most desirable coagulant produced was FeCl<sub>3</sub>, followed by AlKSO<sub>4</sub>, chitosan, Na<sub>2</sub>S, and MgO. The findings of this study demonstrated the advantage of the coagulation treatment of produced water with a high removal efficiency (close to 74% TS removal) and a nominal treatment cost. The treated water could undergo further treatment steps to be reused or recycled for various applications. Considering the treatment cost, current commercial prices were used for the coagulants whereas the energy consumption, labor, and maintenance costs were not considered. The economic and environmental benefits from this study suggest the great potential of coagulation as a pre-treatment technology for oilfield-generated produced water. If a secondary treatment of coagulation for pre-treated PW proves to be highly efficient, it will be helpful for the treatment of the huge volumes of PW being generated. Future studies should focus on the generated sludge and its characterizations as well as the post-treatment methods to polish the produced water. The management of the sludge volume and handling costs could signify the total operational costs associated with the commercial application of coagulation treatments at on-site and industrial facilities.

**Author Contributions:** The conceptualization and preparation of the methodology for this manuscript were undertaken by A.A.H. and H.R. The experimentation and collection of data were performed by N.D. and H.R. The original manuscript draft was prepared by H.R. and N.D. The writing, review, and editing and funding acquisition were undertaken by A.A.H. and S.K. This study was performed under the supervision of A.A.H. and S.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Water and Energy Center at United Arab Emirates University, grant number G00003661.

**Data Availability Statement:** The data supporting reported results can be made available upon request to the authors.

**Acknowledgments:** We thank Salem Hegazy for facilitating the laboratory experiments.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Zhao, S.; Huang, G.; Cheng, G.; Wang, Y.; Fu, H. Hardness, COD and turbidity removals from produced water by electrocoagulation pretreatment prior to Reverse Osmosis membranes. *Desalination* **2014**, *344*, 454–462. <https://doi.org/10.1016/j.desal.2014.04.014>.
2. Bakke, T.; Klungsoyr, J.; Sanni, S. Environmental impacts of produced water and drilling waste discharges from the Norwegian offshore petroleum industry. *Mar. Environ. Res.* **2013**, *92*, 154–169. <https://doi.org/10.1016/j.marenvres.2013.09.012>.
3. Dickhout, J.; Moreno, J.; Biesheuvel, P.; Boels, L.; Lammertink, R.; de Vos, W. Produced water treatment by membranes: A review from a colloidal perspective. *J. Colloid Interface Sci.* **2017**, *487*, 523–534. <https://doi.org/10.1016/j.jcis.2016.10.013>.
4. Nadersha, S.; Hassan, A.A. Biodesalination and treatment of raw hypersaline produced water samples using indigenous wastewater algal consortia. *Desalination* **2022**, *528*, 115638. <https://doi.org/10.1016/j.desal.2022.115638>.
5. Chen, X.; Chen, G.; Yue, P.L. Separation of pollutants from restaurant wastewater by electrocoagulation. *Sep. Purif. Technol.* **2000**, *19*, 65–76. [https://doi.org/10.1016/S1383-5866\(99\)00072-6](https://doi.org/10.1016/S1383-5866(99)00072-6).
6. Neff, J.M. *Bioaccumulation in Marine Organisms: Effect of Contaminants from Oil Well Produced Water*; Elsevier: Amsterdam, The Netherlands, 2002.
7. Ahmad, F.; Morris, K.; Law, G.T.; Taylor, K.G.; Shaw, S. Fate of radium on the discharge of oil and gas produced water to the marine environment. *Chemosphere* **2021**, *273*, 129550. <https://doi.org/10.1016/j.chemosphere.2021.129550>.
8. Isehunwa, S.O.; Onovae, S. *Evaluation of Produced Water Discharge in the Niger-Delta*. Journal of Engineering and Applied Science. **2011**, *6*(8), 66–72.
9. D’Unger, C.; Chapman, D.; Carr, R.S. Discharge of oilfield-produced water in nueces bay, texas: A case study. *Environ. Manag.* **1996**, *20*, 143–150. <https://doi.org/10.1007/p100006697>.
10. Mathieu, A.; Hanlon, J.; Myers, M.; Melvin, W.; French, B.; DeBlois, E.M.; King, T.; Lee, K.; Williams, U.P.; Wight, F.M.; et al. Studies on Fish Health Around the Terra Nova Oil Development Site on the Grand Banks Before and After Discharge of Produced Water. In *Produced Water*; Springer: New York, NY, USA, 2011; pp. 375–399. [https://doi.org/10.1007/978-1-4614-0046-2\\_20](https://doi.org/10.1007/978-1-4614-0046-2_20).
11. Schifter, I.; González-Macías, C.; Salazar-Coria, L.; Sánchez-Reyna, G.; González-Lozano, C. Ecological and human risk assessment of long-term produced water discharge to the ocean at the Sonda de Campeche, Gulf of México. *Environ. Earth Sci.* **2015**, *74*, 5813–5826. <https://doi.org/10.1007/s12665-015-4599-9>.
12. Manfra, L.; Moltedo, G.; Lamberti, C.V.; Maggi, C.; Finoia, M.G.; Giuliani, S.; Onorati, F.; Gabellini, M.; Di Mento, R.; Cicero, A.M. Metal Content and Toxicity of Produced Formation Water (PFW): Study of the Possible Effects of the Discharge on Marine Environment. *Arch. Environ. Contam. Toxicol.* **2007**, *53*, 183–190. <https://doi.org/10.1007/s00244-006-0098-z>.
13. Jiménez, S.; Andreozzi, M.; Micó, M.M.; Alvarez, M.G.; Contreras, S. Produced water treatment by advanced oxidation processes. *Sci. Total. Environ.* **2019**, *666*, 12–21. <https://doi.org/10.1016/j.scitotenv.2019.02.128>.
14. Xu, P.; Drewes, J.E.; Heil, D. Beneficial use of co-produced water through membrane treatment: Technical-economic assessment. *Desalination* **2008**, *225*, 139–155. <https://doi.org/10.1016/j.desal.2007.04.093>.
15. Kumar, M.; Adham, S.S.; Pearce, W.R. Investigation of Seawater Reverse Osmosis Fouling and Its Relationship To Pretreatment Type. *Environ. Sci. Technol.* **2006**, *40*, 2037–2044. <https://doi.org/10.1021/es0512428>.
16. Tzotzi, C.; Pahiadaki, T.; Yiantsios, S.; Karabelas, A.; Andritsos, N. A study of CaCO<sub>3</sub> scale formation and inhibition in RO and NF membrane processes. *J. Membr. Sci.* **2007**, *296*, 171–184. <https://doi.org/10.1016/j.memsci.2007.03.031>.
17. Bellona, C.; Drewes, J.E. The role of membrane surface charge and solute physico-chemical properties in the rejection of organic acids by NF membranes. *J. Membr. Sci.* **2005**, *249*, 227–234. <https://doi.org/10.1016/j.memsci.2004.09.041>.
18. Zhu, B.; Clifford, D.A.; Chellam, S. Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes. *Water Res.* **2005**, *39*, 3098–3108. <https://doi.org/10.1016/j.watres.2005.05.020>.
19. Montaña-Medina, C.U.; López-Martínez, L.M.; Ochoa-Terán, A.; López-Maldonado, E.A.; Salazar-Gastelum, M.I.; Trujillo-Navarrete, B.; Pérez-Sicairos, S.; Cornejo-Bravo, J.M. New pyridyl and aniline-functionalized carbamoylcarboxylic acids for removal of metal ions from water by coagulation-flocculation process. *Chem. Eng. J.* **2023**, *451*, 138396. <https://doi.org/10.1016/j.cej.2022.138396>.
20. Kumar, V.; Othman, N.; Asharuddin, S. Applications of Natural Coagulants to Treat Wastewater — A Review. *MATEC Web Conf.* **2017**, *103*, 06016. <https://doi.org/10.1051/mateconf/201710306016>.
21. Garbutt, C.F. . Water Treatment Process for Reducing the Hardness of an Oilfield Produced Water. U.S. Patent 5879562, 1999-03-09.
22. Zhou, F.S.; Zhao, M.F.; Ni, W.X.; Dang, Y.S.; Pu, C.S.; Lu, F.J. Inorganic polymeric flocculent FMA for purifying oilfield produced water: Preparation and uses. *Oilfield Chemistry*; 2000; Volume 17 (3), pp. 256–259.

23. Houcine, M. Solution for heavy metals decontamination in produced water/case study in southern Tunisia. In Proceedings of the SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Kuala Lumpur, Malaysia, 20–22 March 2002.
24. Frankiewicz, T.C.; Gerlach, J. Union Oil Co of California. Removal of Hydrocarbons, Mercury, and Arsenic from Oil-Field Produced Water. U.S. Patent 6117333, 2000.
25. Gao, J.-M.; Wang, B.; Li, W.; Cui, L.; Guo, Y.; Cheng, F. High-efficiency leaching of Al and Fe from fly ash for preparation of polymeric aluminum ferric chloride sulfate coagulant for wastewater treatment. *Sep. Purif. Technol.* **2023**, *306*, 122545. <https://doi.org/10.1016/j.seppur.2022.122545>.
26. DePaolis, M.; De Respino, S.; Samineni, L.; Brighton, S.; Kumar, M. Cottonseed extract as a coagulant for water treatment. *Environ. Sci. Adv.* **2022**. <https://doi.org/10.1039/d2va00205a>.
27. Altaher, H.; ElQada, E.; Omar, W. Pretreatment of Wastewater Streams from Petroleum/Petrochemical Industries Using Coagulation. *Adv. Chem. Eng. Sci.* **2011**, *01*, 245–251. <https://doi.org/10.4236/aces.2011.14035>.
28. Otálora, M.C.; Wilches-Torres, A.; Lara, C.R.; Castaño, J.A.G.; Cifuentes, G.R. Evaluation of Turbidity and Color Removal in Water Treatment: A Comparative Study between *Opuntia ficus-indica* Fruit Peel Mucilage and FeCl<sub>3</sub>. *Polymers* **2022**, *15*, 217. <https://doi.org/10.3390/polym15010217>.
29. Bottero, J.Y.; Manceau, A.; Villieras, F.; Tchoubar, D. Structure and mechanisms of formation of iron oxide hydroxide (chloride) polymers. *Langmuir* **1994**, *10*, 316–319.
30. Siéliéchi, J.-M.; Lartiges, B.; Kayem, G.; Hupont, S.; Frochot, C.; Thieme, J.; Ghanbaja, J.; de la Caillerie, J.D.; Barrès, O.; Kamga, R.; et al. Changes in humic acid conformation during coagulation with ferric chloride: Implications for drinking water treatment. *Water Res.* **2008**, *42*, 2111–2123. <https://doi.org/10.1016/j.watres.2007.11.017>.
31. Duan, J.; Gregory, J. Coagulation by hydrolysing metal salts. *Adv. Colloid Interface Sci.* **2003**, *100*, 475–502.
32. Liang, Z.; Wang, Y.; Zhou, Y.; Liu, H. Coagulation removal of melanoidins from biologically treated molasses wastewater using ferric chloride. *Chem. Eng. J.* **2009**, *152*, 88–94. <https://doi.org/10.1016/j.cej.2009.03.036>.
33. Zhao, Q.; Liu, W.; Wei, D.; Wang, W.; Cui, B.; Liu, W. Effect of copper ions on the flotation separation of chalco-pyrite and molybdenite using sodium sulfide as a depressant. *Miner. Eng.* **2018**, *115*, 44–52.
34. Trahar, W. A laboratory study of the influence of sodium sulphide and oxygen on the collectorless flotation of chalcopryrite. *Int. J. Miner. Process.* **1983**, *11*, 57–74. [https://doi.org/10.1016/0301-7516\(83\)90044-3](https://doi.org/10.1016/0301-7516(83)90044-3).
35. Luttrell, G.H.; Yoon, R.-H. The collectorless flotation of chalcopryrite ores using sodium sulfide. *Int. J. Miner. Process.* **1984**, *13*, 271–283. [https://doi.org/10.1016/0301-7516\(84\)90048-6](https://doi.org/10.1016/0301-7516(84)90048-6).
36. Pavez, O.; Peres, A.E.C. Effect of sodium metasilicate and sodium sulphide on the floatability of mona-zite-zircon-rutile with oleate and hydroxamates. *Miner. Eng.* **1993**, *6*, 69–78.
37. Herrera-Urbina, R.; Sotillo, F.; Fuerstenau, D. Effect of sodium sulfide additions on the pulp potential and amyl xanthate flotation of cerussite and galena. *Int. J. Miner. Process.* **1999**, *55*, 157–170. [https://doi.org/10.1016/s0301-7516\(98\)00029-5](https://doi.org/10.1016/s0301-7516(98)00029-5).
38. Wang, K.-J.; Wang, P.-S.; Nguyen, H.-P. A data-driven optimization model for coagulant dosage decision in industrial wastewater treatment. *Comput. Chem. Eng.* **2021**, *152*, 107383. <https://doi.org/10.1016/j.compchemeng.2021.107383>.
39. Bobadilla, M.C.; Lorza, R.L.; García, R.E.; Gómez, F.S.; González, E.P.V. Coagulation: Determination of Key Operating Parameters by Multi-Response Surface Methodology Using Desirability Functions. *Water* **2019**, *11*, 398. <https://doi.org/10.3390/w11020398>.
40. Zainuddin, N.A.; Mamat, T.A.R.; Maarof, H.I.; Puasa, S.W.; Yatim, S.R.M. Removal of nickel, zinc and copper from plating process industrial raw effluent via hydroxide precipitation versus sulfide precipitation. In *Proceedings of the IOP Conference Series: Materials Science and Engineering*; IOP Publishing: Bristol, UK, 2019; Volume 551, p. 012122.
41. Lochyński, P.; Wiercik, P.; Charazińska, S.; Ostrowski, M. Research on neutralization of wastewater from pickling and electropolishing processes. *Arch. Environ. Prot.* **2021**, *47*, 18–29.
42. Blais, J.F.; Djedidi, Z.; Ben Cheikh, R.; Tyagi, R.D.; Mercier, G. Metals Precipitation from Effluents: Review. *Pr. Period. Hazardous, Toxic, Radioact. Waste Manag.* **2008**, *12*, 135–149. [https://doi.org/10.1061/\(asce\)1090-025x\(2008\)12:3\(135\)](https://doi.org/10.1061/(asce)1090-025x(2008)12:3(135)).
43. Renault, F.; Sancey, B.; Badot, P.-M.; Crini, G. Chitosan for coagulation/flocculation processes—An eco-friendly approach. *Eur. Polym. J.* **2009**, *45*, 1337–1348. <https://doi.org/10.1016/j.eurpolymj.2008.12.027>.
44. Roberts, G.A.; Roberts, G.A. *Chitin Chemistry*; Macmillan: London, UK, 1992; pp. 167–172.
45. Castro-Riquelme, C.L.; López-Maldonado, E.A.; Ochoa-Terán, A.; Alcántar-Zavala, E.; Trujillo-Navarrete, B.; Pérez-Sicairos, S.; Miranda-Soto, V.; Zizumbo-López, A. Chitosan-carbamoylcarboxylic acid grafted polymers for removal of metal ions in wastewater. *Chem. Eng. J.* **2023**, *456*, 141034. <https://doi.org/10.1016/j.cej.2022.141034>.
46. Bolto, B.; Gregory, J. Organic polyelectrolytes in water treatment. *Water Res.* **2007**, *41*, 2301–2324. <https://doi.org/10.1016/j.watres.2007.03.012>.
47. Huang, C.; Chen, Y. Coagulation of colloidal particles in water by chitosan. *J. Chem. Technol. Biotechnol. Int. Res. Process Environ. Clean Technol.* **1996**, *66*, 227–232.
48. Ahmad, A.; Sumathi, S.; Hameed, B. Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC. *Chem. Eng. J.* **2006**, *118*, 99–105. <https://doi.org/10.1016/j.cej.2006.02.001>.
49. Yukselen, M.A.; Gregory, J. The effect of rapid mixing on the break-up and re-formation of flocs. *J. Chem. Technol. Biotechnol. Int. Res. Process Environ. Clean Technol.* **2004**, *79*, 782–788.

50. Jiang, J.-Q. The role of coagulation in water treatment. *Curr. Opin. Chem. Eng.* **2015**, *8*, 36–44. <https://doi.org/10.1016/j.co-che.2015.01.008>.
51. Roques, H. *Chemical Water Treatment: Principles and Practice*; VCH Publishers. Inc.: New York, NY, USA, 1996; p. 620.
52. Zeng, Y.; Yang, C.; Pu, W.; Zhang, X. Removal of silica from heavy oil wastewater to be reused in a boiler by combining magnesium and zinc compounds with coagulation. *Desalination* **2007**, *216*, 147–159. <https://doi.org/10.1016/j.desal.2007.01.005>.
53. Bolto, B.; Dixon, D.; Eldridge, R.; King, S. Cationic polymer and clay or metal oxide combinations for natural organic matter removal. *Water Res.* **2001**, *35*, 2669–2676. [https://doi.org/10.1016/s0043-1354\(00\)00552-2](https://doi.org/10.1016/s0043-1354(00)00552-2).

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.