Immobilized Algae for Produced Water Treatment and Desalination

Shibin Nadersha and Ashraf Aly Hassan

***Abstract*—Produced water (PW) is the effluent generated during oil mining and extraction. On average, for every barrel of oil, 4-5 barrels of PW are generated worldwide. The presence of various contaminants in PW makes it toxic. Disposal of untreated PW into oceans and water bodies can cause adverse effects on human health and the environment. Taking into account the large volumes of it being generated, and its effects on the environment, proper treatment is required before reuse or disposal. Microalgal treatment is an effective method for the bioremediation and biodesalination of produced water when acclimatized algal biomass is used for the treatment. However, harvesting this acclimatized high-value algal biomass for reuse and recycling, and the reuse or disposal of produced water is challenging. Thus, the immobilization of microalgae into polymer matrices will be beneficial in solving both problems. Different polymers, both natural and synthetic are used as matrices for immobilizing cells. In this study, experiments were done with alginate and chitosan matrices to immobilize algae. Microalgae enriched and grown in wastewater were acclimatized to three different produced water samples by progressive adaptation in a steadily increasing ratio of produced water. The algae which could adapt and grow in the highest ratio in minimum time were immobilized and used for bioremediation of produced water. The study also evaluated the stability of the matrix in produced water and the treatment efficiency. The results of the study led to the conclusion that produced water is highly toxic for the stability of alginate and chitosan matrices. A more stable matrix has to be determined and experimented with for immobilizing algae and treatment of produced water.**

***Index Terms*—Produced water, algae, immobilization, bioremediation.**

I. Introduction

The oil and gas industry generate more polluted water than the desirable products. This polluted water is called the produced water (PW). The produced water contains varying levels of impurities, such as inorganic salts, aliphatic and aromatic hydrocarbons, phenols, metals, radioactive elements, and chemical additives used in the extraction line separating water and oil [1]. The disposal of PW is a concerning environmental problem because of the massive volume of it to be discharged, its complex and hazardous nature, and the lack of information on their potential long-term and ecological effects. Therefore, extensive treatment of PW is an important requirement before discharge in several locations worldwide. Due to limited freshwater resources and high treatment costs before PW discharge, beneficial reuse of PW is an attractive option in water-scarce regions. PW can be recycled and used in a variety of applications, including crop irrigation, wildlife and livestock consumption, aquaculture, hydroponic vegetable culture, dust control, vehicle and equipment washing, and power generation. However, reusing PW poses similar challenges to reusing other types of wastewaters. In addition to the high treatment costs, chronic water toxicity, and high salinity is also a concern. Treatment costs for PW are strongly influenced by the physical and chemical characteristics of the produced water, which change over time in a field, which can differ greatly between the geologic nature of oil wells, and the regulatory environment. Moreover, the hyper salinity of produced water adds to the treatment challenge, as it limits the efficiency of treatment.

Microalgal treatment is an effective method for the bioremediation and desalination of produced water when acclimatized algal biomass is used for the treatment [2]. However, harvesting this acclimatized high-value algal biomass for reuse and recycling, and the reuse or disposal of produced water is challenging. Thus, the immobilization of microalgae into polymer matrices enables the harvesting and reuse of algal biomass. Algal cells in an immobilized state occupy less space and are easier to handle [3]. Immobilized algal cells have been used in water purification processes and pollutant removal for decades [4], [5]. However, the use of immobilized algae for the treatment of produced water has not been reported in the open literature.

Different polymers, both natural and synthetic are used as matrices for immobilizing cells, however, they must meet a number of criteria, including photo-transparency, nontoxicity, cellular viability retention, and stability in the culture medium [4], [6]. The most common and widely used polymer matrix for the immobilization of algae is alginate. It is transparent and nontoxic, both of which allow photosynthesis and growth of autotrophic organisms like microalgae [4]. Several studies have utilized immobilized algal cells to remove nutrients from wastewater [7]–[9]. Immobilized algae typically possess increased nutrient-removal efficiencies due to both their enhanced photosynthetic rate and their ionic exchange with the immobilization matrix [10].

Alginate is the most commonly used natural polysaccharide gel for entrapping live cells. Alginates constitute a family of unbranched binary copolymers of 1–4-linked-b-D-mannuronic acid and a-L-guluronic acid. Permeability, low toxicity, and transparency of the produced

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matrix indicate that immobilized cells will be in a relatively mild environment. Eleven marine microalgal species were used to study immobilized cell development and Ca-alginate bead stability by [11] and it was discovered that the stability of the beads can be affected by the immobilized species. Since the widest application of immobilized algae is in wastewater treatment, a large number of studies have been conducted about using alginate immobilized algae for tertiary wastewater treatment. [12] co-immobilized microalgae with sludge bacteria in alginate beads for treatment of real meat processing wastewater and designed an annular photobioreactor for facilitation of photo transmission. Results indicated that A mixture of 1.25% and 2.00% (w/v) alginate increased the beads' stability in real wastewater from three to seven days. Algal growth was almost doubled in the improved annular photobioreactor, and removal of COD and TN were improved from 78.5 to 82.9% and from 68.5% to 84.4%. A study was conducted by [13] to investigate the effect of alginate concentration on the removal of wastewater nutrients by alginate-immobilized microalgae bead systems of *Chlorella vulgaris*. Results showed that a concentration of 3% alginate is found to be optimal both for the removal of nutrients in immobilized algal beads as well as for the adsorption of nutrients in blank beads.

Chitosan is a polysaccharide coagulant and is a linear copolymer of D-glucosamine and N-acetyl-D-glucosamine. With its unique physicochemical properties, it can interact with a wide range of contaminants, including particulate matter and dissolved substances. This compound is obtained mainly from chitin, one of the most abundant organic compounds in nature, which is found in crustaceans and other organisms as an exoskeleton [14]. A novel application involving cross-linked chitosan-based polymers for microalgae immobilization and nutrient capturing is described for the first time by [15]. These polymers showed to be environmentally friendly materials capable of improving nutrient bio removal by immobilized microalgae cells.

In this study, experiments were done with both alginate and chitosan matrices to immobilize preadapted microalgae for the treatment of produced water and evaluate the stability of the matrix in produced water and the treatment efficiency. The algae stock culture used was enriched from wastewater and was acclimatized to PW in several steps using the progressive adaptation method by progressively increasing the PW concentration in which algae grew. The treatment was analyzed by measuring and comparing water quality such as pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), salinity, Chemical Oxygen Demand (COD), and Total Organic Carbon (TOC) before and after treatment.

II. Materials and Methods

A. Preparation of Immobilized Algae Beads

The algae acclimatized to the three produced water served as the stock culture for the preparation of immobilized algal beads, the details of which are presented in [2]. The produced water samples were collected from three different undisclosed onshore and offshore oilfields in the Middle East (PW1, PW2, and PW3). The samples were characterized and analyzed before and after treatment. The immobilized algae treatment experiments were conducted with two different matrices namely alginate and chitosan.

B. Separation of Biomass

The stock culture algae were centrifuged at 7500 rpm for 7 minutes. The supernatant was discarded, and the algal biomass was resuspended using a minimum amount of BG11 media.

C. Alginate Bead Preparation

Sodium alginate (5%) solution was prepared by dissolving 25g of sodium alginate in 500 ml of deionized water. The resuspended algal biomass was mixed with the alginate solution in the ratio of 4:1 alginate: algae. 500 ml of 2% calcium chloride solution was prepared separately for producing algae-alginate beads and blank alginate beads. The algae-alginate mixture was dropped into calcium chloride solution using a syringe manually. Blank beads were prepared similarly using alginate without algae. This was left overnight for bead formation. The beads were then rinsed thoroughly and stored in DI water for further use in experiments. Fig. 1 shows the bead formation in calcium chloride solution.

Fig. 1. Preparation of immobilized algae beads with alginate.

D. Chitosan Bead Preparation

Chitosan solution was prepared by mixing 4gm chitosan powder in 100 ml of 0.5% acetic acid. The resuspended algae were mixed with the chitosan solution in a 4:1 ratio Chitosan: algae. This mixture was dropped into 0.1N NaOH solution manually using a syringe. Chitosan- cell mixture was allowed to drip for 2 minutes, followed by 3 minutes of agitation and then picking them up with a mesh. The beads were then washed several times to clear off NaOH. This method of dripping-agitating-washing was done to reduce the contact time of the algae with NaOH. The process was repeated until the chitosan-algae mixture was completed. Blank beads were prepared without algae for control (Fig. 2).

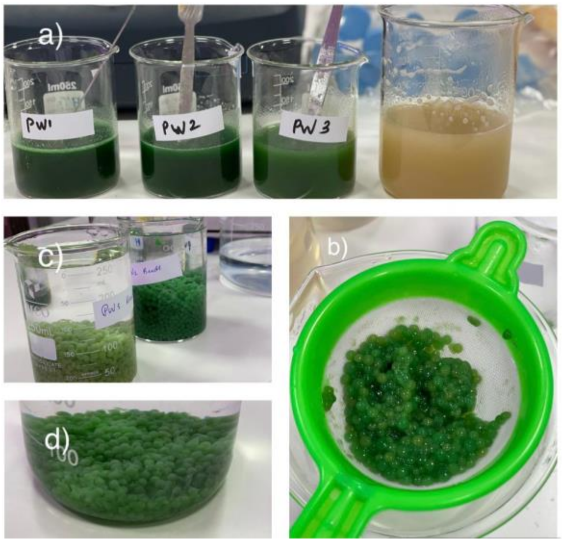

Fig. 2: a) Chitosan solution with and without algae b), c), d) algae immobilized in chitosan beads.

E. *Treatment Using Immobilized Algae*

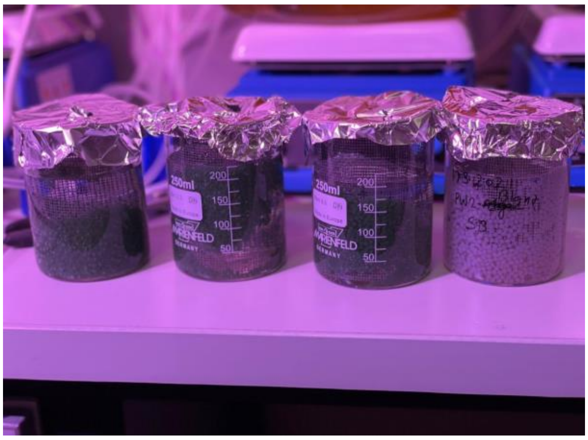

Fig. 3. Treatment of PW2 with algae immobilized in alginate beads.

The immobilized algae treatment using chitosan was done with all three PW samples. However, using alginate was done only with one PW sample (PW2). All treatment experiments were done in 250ml beakers. Cylindrical wire mesh was placed inside the reactors to keep the beads to the sides of the beakers so that every bead gets exposed to light and the whole bead surface is in contact with produced water.

In each reactor, 25 mL of the beads were mixed with produced water to a volume of 200mL. A control for each produced water was prepared with blank beads. Light intensity was maintained at 1500 – 1700 LUX with 12 hours of light and dark cycles. The beakers were covered with perforated aluminum foil to enable air passage from and to the reactor. The treatment was done for seven days. Parameters such as optical density, pH, electrical conductivity, total dissolved solids, salinity, COD, TOC, alkalinity, and anions were monitored before and after one, two, three, five, and seven days of treatments. Fig. 3 and 4 show the reactors and the experimental setup using alginate and chitosan beads.

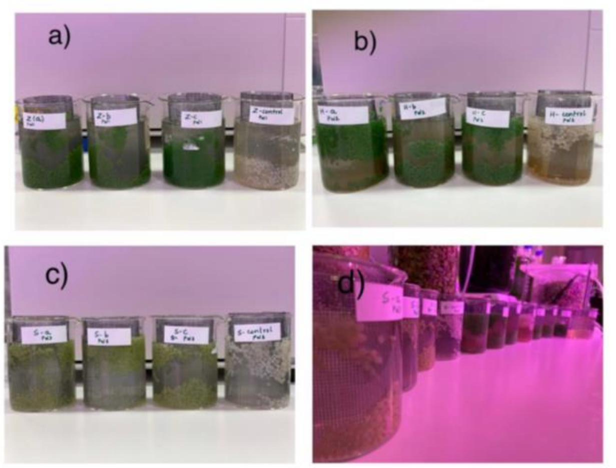

Fig. 4: Immobilized algae in reactors a) PW1, b) PW2, c) PW3 d) experimental setup.

F. *Treatment Using Suspended Algae*

All experiments were performed in triplicate in Schott bottles of 250 ml. The microalgae were centrifuged (SL8 centrifuge, Thermo Scientific) for 10 minutes at 7,500 rpm. Algal biomass was resuspended in a minimum amount of BG11 media after discarding the supernatant. 6.25 percent of algae was found to be the optimum concentration for treatment [10].

A volume of 200mL was thus obtained by mixing 12.5 mL of algae with the produced water. An algae-free control was prepared for each produced water. Mixing was achieved using magnetic stirrer plates, and light intensity was maintained between 1500 and 1700 LUX over 12 hours. A seven-day treatment was conducted and parameters such as organics, salinity, TDS, chloride concentration, and alkalinity were monitored on the first, second, third, fifth, and seventh days of the treatment.

III. Results and Discussions

A. *Treatment of Produced Water with Algae Immobilized in Alginate*

Among other parameters, TOC and TSS were closely observed. The variations in parameters such as pH, EC, TDS, salinity, TOC, and TSS during the first three days are depicted as C/C_0 in Fig. 5.

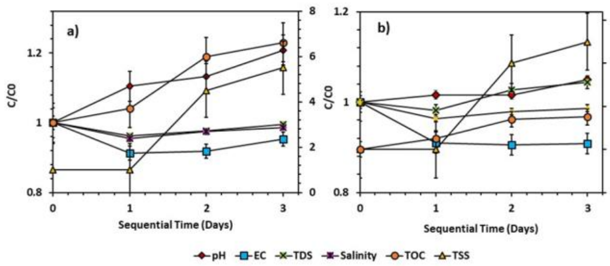

Fig. 5. Variations in parameters during the first three days of treatment: a) Alginate beads with algae b) control beads without algae.

The acidity or alkalinity of a solution is determined by its pH. All the PW samples were mildly acidic. The pH of the samples increased from an initial 6.1 to an average of 6.74 on day one and 7.37 on day 3. During its growth, algae absorb carbon dioxide from the solution for its growth and therefore causes an increase in pH. The parameters such as EC and TDS also indicate the salinity of the solution. In general, TDS is the sum of all dissolved solids in water, including chloride, calcium, magnesium, potassium, sodium, bicarbonates, sulfates, and organic matter [14]. For the algal cells to function properly, they absorb TDS species and use them as nutrients and minerals to support their metabolism, thereby reducing the concentration of TDS in the water [14], [16]. The initial EC, TDS, and salinity of the PW samples were significantly high. The conductivity decreased on day one and then showed an increase on day 3. The decrease in EC was due to the adsorption of ions to the matrix and cell surfaces initially. However, the disintegration and dissolution of alginate in solution caused the increase in EC values thereafter. However, the most important observations were the TSS and TOC which showed a consistent increase on day 1 and day 3, not only in the reactors with algae but also in the control reactor. TOC increased from an initial 2500 mg/L to 2603 mg/L after 24 hours of treatment and to 3076 mg/L on day 3. Algae tend to be mixotrophic in nature, which means that it has the ability to use dissolved carbon present in a solution as a carbon source in presence of light. This causes a reduction in the TOC of the solution due to consumption by the algae. However, an increase in TOC was observed. The reason for this increase in TOC in reactors including the control could be due to the dissolution of alginate in produced water. TSS values also indicate the dissolution of alginate as well as the presence of free cells in the solution. The dissolution of the matrix can also be confirmed from the results of parameters in the control. All the parameters in the control, where no algae were present also showed an increase, hence confirming the dissolution of the matrix in solution.

B. Treatment of Produced Water with Algae Immobilized in Chitosan

Since alginate was not stable in produced water, chitosan beads were chosen as the next option for immobilizing algae for the treatment of produced water. chitosan-based polymeric materials have been promising as cost-effective, non-toxic, biocompatible carriers for immobilization of microalgae. Chitosan has been used to immobilize microalgae for the treatment of wastewater and nutrient removal in the recent past. However, no studies are available on the treatment of produced water using chitosan-immobilized algae. The experiments with all three samples of produced water showed results similar to alginate. The variation in parameters in the reactors with algae beads and the control over the first three days of treatment is depicted as C/C_0 in Fig. 6. All the PW samples showed an increase in pH. There was a decrease in salinity during the first 24 hours and thereafter showed an increase in salinity. EC and TDS also showed the same trend, however, the decrease during the first 24 hours was not as much as salinity. The decrease was a result of adsorption of ions initially onto the bead matrix as well as the cell and the subsequent increase was due to the presence of free ions released by the dissolution of the matrix in PW. Overall, it could be assumed that the dissolution of ionic species from the matrix caused an increase in EC, TDS, and salinity values. Similarly, the TSS and COD of the reactors with algae as well as the controls increased drastically over the days indicating the dissolution of chitosan in produced water. The TSS was much higher in reactors with algae than in the controls which can be explained by the presence of free cells in the solution. Therefore, chitosan could not be used as an immobilization matrix for the treatment of produced water. Since chitosan is an organic compound, dissolution of it in solution increased the COD of the solution drastically. PW water is highly complex and toxic in nature and its reaction toward matrices cannot be predicted easily. The data on the treatment of produced water with suspended algae itself is scarce. The treatment of PW with immobilized algae has never been attempted before to the best of our knowledge.

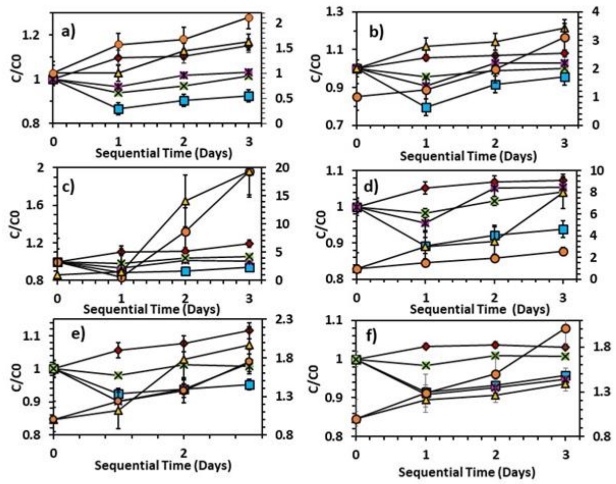

Fig. 6. Variations in parameters during the first three days of treatment with immobilized algae in chitosan: a) PW1, b) PW1 control, c) PW2, d) PW2 control, e) PW3 and, f) PW3 control.

C. Treatment of Produced Water with Suspended Algae

Since the experiments with immobilized algae could not be completed due to stability issues, experiments were run using the acclimatized algal suspension. The 7-day treatment experiments showed excellent treatment and removal efficiencies. A maximum removal rate of 44% for COD and 25% for TOC was achieved. The three produced water samples showed an average reduction of 15% in EC, 16% TDS, 18% salinity, 20% chloride ion concentration, and an increase of 82% alkalinity over the 7-day treatment period. The results of this part of the research have been provided in detail in [2]. Fig. 7 and 8 show the removal efficiencies of organics and chloride concentrations in the three PW samples and their respective controls over the seven-day treatment period. However, if a proper immobilization matrix could be found which is stable in the PW conditions, it could be a breakthrough for the oil and gas industry. The immobilization helps recovery and reuse of acclimatized algal biomass thus enabling economical treatment of PW.

The benefits of this research go beyond cost savings for the oil and gas industry. Properly treated and desalinated PW can be reused for drilling or converted into steam for heavy crude production, greatly improving efficiency by ensuring that water is returned to the system. Integrating produced water into the circular economy promises increased efficiency and value across multiple industries as we are forced to become more inventive to protect our environment. The stringent standards for PW disposal can be met effectively and economically using algal treatment. Large quantities of treated and desalinated PW could be used for various purposes, including potable purposes.

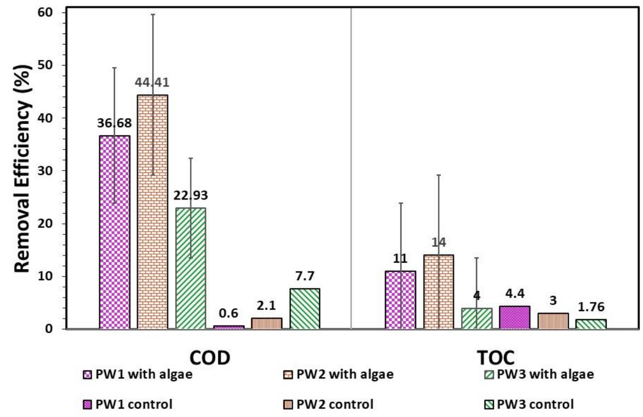

Fig. 7. Organics removal efficiencies using suspended algae in the three PW samples and their respective controls.

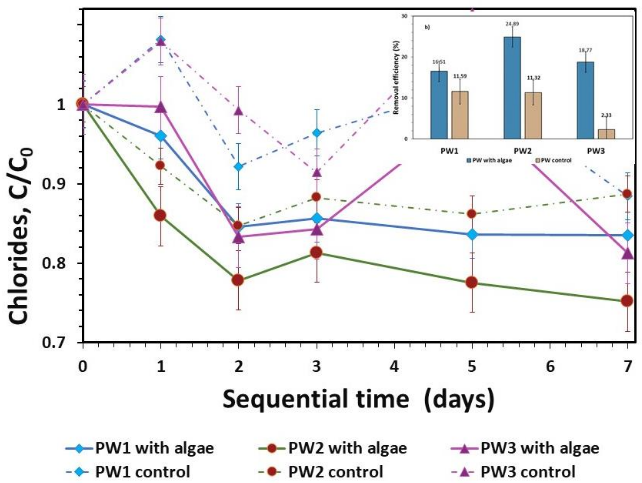

Fig. 8: Chloride concentration and removal efficiencies with suspended algae in the three PW samples and their respective controls.

IV. Conclusions

Using algal treatment, the produced water is cleaned of unwanted contaminants, resulting in freshwater that meets the standards for safe surface discharge established by local and federal regulatory bodies. Treatment and desalination of PW using acclimatized algae suspension have proven to be very efficient. Easy recovery and recycling of algal biomass make the process more sustainable and economical. Immobilization helps in harvesting the biomass for recycling and reuse of both biomass and PW.

From the results of this research, PW is highly toxic for the stability of alginate and chitosan matrices. A more stable matrix has to be determined and experimented with for immobilizing algae and treatment of produced water. Immobilizing the acclimatized algae in a more solvent-tolerant matrix such as graphene oxide could be experimented in the future. Therefore, currently, where research is focusing on treating produced water in ways that go beyond traditional methods, this research can bridge the gap in the literature regarding the biological treatment of PW and can provide insight for future researchers to conduct more elaborate studies in the field.

Conflict of Interest

The authors declare no potential conflict of interest.

Author Contributions

Shibin Nadersha: Conceptualization, Methodology, Data analysis and Investigation, Visualization, Writing – original draft preparation. **Ashraf Aly Hassan**: Supervision, Conceptualization, Investigation, Validation, Funding acquisition, Project administration, Writing – review & editing

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References

[1] M. A. Al-Ghouti, M. A. Al-Kaabi, M. Y. Ashfaq, and D. A. Da'na, "Produced water characteristics, treatment and reuse: A review," *J. Water Process Eng.*, vol. 28, pp. 222–239, 2019.

[2] S. Nadersha and A. A. Hassan, "Biodesalination and treatment of raw hypersaline produced water samples using indigenous wastewater algal consortia," *Desalination*, vol. 528, p. 115638, 2022.

[3] F. Wollmann *et al.*, "Microalgae wastewater treatment: Biological and technological approaches," *Eng. Life Sci.*, vol. 19, no. 12, pp. 860–871, 2019.

[4] Z. B. Bouabidi, M. H. El-Naas, and Z. Zhang, "Immobilization of microbial cells for the biotreatment of wastewater: A review," *Environ. Chem. Lett.*, vol. 17, no. 1, pp. 241–257, 2019.

[5] M. M. El-Sheekh, M. A. Metwally, N. G. Allam, and H. E. Hemdan, "Effect of algal cell immobilization technique on sequencing batch reactors for sewage wastewater treatment," *Int. J. Environ. Res.*, vol. 11, no. 5, pp. 603–611, 2017.

[6] S. A. E. Moghaddam, R. Harun, M. N. Mokhtar, and R. Zakaria, "Potential of zeolite and algae in biomass immobilization," *BioMed Res. Int.*, vol. 2018, 2018.

[7] C.-Y. Chen *et al.*, "Cultivating Chlorella sorokiniana AK-1 with swine wastewater for simultaneous wastewater treatment and algal biomass production," *Bioresour. Technol.*, vol. 302, p. 122814, 2020.

[8] M. Plöhn *et al.*, "Wastewater treatment by microalgae," *Physiol. Plant.*, vol. 173, no. 2, pp. 568–578, 2021.

[9] M. Kube, B. Spedding, L. Gao, L. Fan, and F. Roddick, "Nutrient removal by alginate-immobilized Chlorella vulgaris: Response to different wastewater matrices," *J. Chem. Technol. Biotechnol.*, vol. 95, no. 6, pp. 1790–1799, 2020.

[10] S. Mollamohammada, A. A. Hassan, and M. Dahab, "Nitrate removal from groundwater using immobilized heterotrophic algae," *Water. Air. Soil Pollut.*, vol. 231, no. 1, pp. 1–13, 2020.

[11] O. Murujew *et al.*, "Recovery and reuse of alginate in an immobilized algae reactor," *Environ. Technol.*, vol. 42, no. 10, pp. 1521–1530, 2021.

[12] X. Hu, Y. E. Meneses, A. A. Hassan, J. Stratton, and S. Huo, "Application of alginate immobilized microalgae in treating real food industrial wastewater and design of annular photobioreactor: A proof-of-concept study," *Algal Res.*, vol. 60, p. 102524, 2021.

[13] S. Banerjee, P. B. Tiwade, K. Sambhav, C. Banerjee, and S. K. Bhaumik, "Effect of alginate concentration in wastewater nutrient removal using alginate-immobilized microalgae beads: Uptake kinetics and adsorption studies," *Biochem. Eng. J.*, vol. 149, p. 107241, 2019.

[14] J. Peng, K. Kumar, M. Gross, T. Kunetz, and Z. Wen, "Removal of total dissolved solids from wastewater using a revolving algal biofilm reactor," *Water Environ. Res.*, vol. 92, no. 5, pp. 766–778, 2020.
[15] S. Vasilieva *et al.*, "Bio-inspired materials for nutrient biocapture from wastewater: Microalgal cells immobilized on chitosan-based carriers," *J. Water Process Eng.*, vol. 40, p. 101774, 2021.
[16] L. G. Antonio and T. N. Dunford, "Growing algae in produced water generated during oil and gas production using hydraulic fracturing technique," *Chem. Eng. Trans.*, vol. 74, pp. 1261–1266, May 2019, doi: 10.3303/CET1974211.

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