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ORIGINAL ARTICLE

A techno-economic analysis of marine algae for dye-sensitized solar cells: process optimization and scale-up

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Abstract
Currently, there is a global interest in the production of marine natural products. Naturally occurring macroalgae can be a potentially viable source of generating various products such as dyes and carbohydrates. Hence, in this study, the potential of extracting natural solvent-based dyes of *Sargassum* sp., *Gracilaria* sp., and *Enteromorpha* sp. was evaluated using the microwave-assisted extraction technique by applying the response surface methodology. In comparison with the conventional solvent extraction method, the microwave-assisted method enhanced the dye extraction by 70.37%, 64.31%, and 20.71% in *Sargassum* sp., *Gracilaria* sp., and *Enteromorpha* sp, respectively. Based on the results, increasing temperature, extraction time, and ethanol/water solvent ratio increased the dye extraction yield significantly for the microwave-assisted technique. Moreover, the effect of pH on the dye extraction was species-specific. In the second step, characterization techniques were used to examine the concentration and the optical activity of the extracted dyes by employing the UV–vis spectrophotometer and the circular dichroism, which showed them as promising candidates for sensitizers in dye-sensitized solar cells. Finally, a comprehensive economic and profitability analysis was conducted for both extraction methods. The results showed that the return on investment (ROI) for the conventional and microwave-assisted extraction methods was more than 358% and 268% for a production capacity of 10000 L, which corresponded to the payback period (PBP) of less than 4 and 5 months, respectively. In addition, it was found that increasing the production capacity would significantly decrease the PBP and the total production cost (TPC) of both extraction methods. Estimated income and return cost (EIRC) for both processes also showed that the ROI for the microwave-assisted extraction method was less than the conventional solvent extraction method; however, the efficacy of the microwave-assisted extraction method was significantly higher than the conventional solvent method. By utilizing low-cost natural dyes, the production cost of DSSCs can be reduced, making them more competitive with conventional solar cell technologies.

Keywords Algae · Microwave-assisted extraction · Natural dye · Economic analysis · RSM · CAPEX · OPEX

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Nomenclatures

ADC	Administrative cost
BEP	Breakeven point
BEPC	Breakeven point capacity
C	Dye concentration
CAPEX	Operating expenditure
CCD	Central composite design
CD	Circular dichroism
CE	Conventional solvent extraction
CI	Capital investment
CONT	Contingency costs
D&SC	Distribution and selling cost
DC	Direct costs
DEP	Depreciation
DF	Degree of freedom
DPC	Direct production cost
DS&CL	Direct supervisory and clerical labor

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EIRC	Estimated income and return cost
ELEC	Electrical costs
ENG	Engineering and supervision costs
Ent	*Enteromorpha* Sp.
ERR	Error
FC	Fixed charge
FCI	Fixed capital investment
Gra	*Gracilaria* Sp.
GE	General expenses
GP	Gross profit
IDC	Indirect costs
INS	Insurance
INST	Installation costs
LC	Laboratory charges
LTX	Local taxes
M&R	Maintenance and repairs
MC	Manufacturing cost
ME	Microwave-assisted extraction
MS	Mean square
N	Percentage
NP	Net profit
OPEX	Operating expenditure
OL	Operating labor
OS	Operating supplies
P&R	Patents and royalties
PBP	Payback period
PC	Production capacity per year
PCP	Product cost for the plant
PEC	Purchased equipment costs
POC	Plant overhead cost
PT	Pigment types
R^2	Coefficient of determination
R_a^2	The adjusted coefficient of determination
R&DC	Research and development cost
REN	Rent
RM	Raw materials
ROI	Return on investment
RSM	Response surface methodology
Sar	*Sargassum* Sp.
SP	Selling price
SR	Solvent ratio
SS	Sum of squares
TCI	Total capital investment
TPC	Total product cost
TYI	Total yearly income
UT	Utilities
WC	Working capital
Y	Response values for the extracted dye concentration
YIBEPC	Yearly income in BEPC
3-D	Three-dimensional

Greek letter

Φ	The fixed income tax rate

Subscript

A	Adjusted
Optimal	Optimum condition

1 Introduction

Along with the growing public awareness of environmental safety and health issues, non-toxic and environment-friendly bioresource products have regained popularity in various areas of our lives. Natural dyes, which are extracted from plants, are renewable, biodegradable, eco-friendly, and sustainable bioresource products that can serve as a practical alternative or co-partner to synthetic dyes [1, 2]. Synthetic dyes have some limitations, including adverse effects on the environment and associated allergic, toxic, carcinogenic, and harmful responses [3, 4]. Hence, extensive studies have been conducted on new natural dye resources along with environment-friendly, efficient, and cost-effective technologies for their processing and application [5–8]. Due to their biochemical, pharmacological, and biological properties, the application of natural dyes is continuously extending. These applications include natural textile dyeing [9, 10], food and health supplements [11, 12], dye-sensitized solar cells [13–16], ultra-violet (UV) protective clothing [17], pH indicators [18], and various other application disciplines [1, 19]. Extracting natural dyes from plants is the first essential step toward utilizing them. Therefore, it is crucial to select an appropriate technique for the extraction of dyes under optimized conditions to achieve the maximum extraction yield [20]. The traditional methods of extraction, i.e., conventional solvent extraction [13] and Soxhlet extraction [21], are very time- and solvent-consuming [22, 23]. Novel extraction techniques such as ultrasound-assisted extraction [24, 25], microwave-assisted extraction [13, 26], supercritical fluid extraction [27], pressurized liquid extraction [28], enzyme-assisted extraction [29, 30], and accelerated solvent extraction [31] require less solvent and processing time and provide a higher yield and quality of the extracted dye [32]. Microwave technology can significantly improve the extraction efficiency of the natural dyes from plants. In this regard, Krishnan et al. showed that microwave-assisted extraction is superior to conventional solvent extraction for the extraction yield of flavonoids [33]. Also, they found no loss of antioxidant activity due to the microwave exposure. Dahmoune et al. achieved an enhanced extraction yield of phytochemicals. They decreased their extraction time by using the microwave-assisted extraction 14, 15-fold compared to the ultrasound-assisted and conventional solvent extraction methods [34]. There are influential factors in the extraction of dye from plants, including plant type, extraction time, process temperature, solvent type, solvent concentration, and solution pH [13, 35]. Hence, from an industrial point of view, it is important to employ an appropriate extraction method and operating conditions to develop the statistical model for optimizing and predicting the process.

Economic evaluation plays a crucial role in selecting optimum dye extraction techniques. Techno-economic analysis provides a link between laboratory research and industrial applications. Techno-economic analysis for plant design enables evaluating and comparing many types of feedstocks, products, and possible process configurations [36]. An acceptable plant design must present a profitable process under its operating conditions. Moreover, the profitability analysis provides information for selecting different process techniques and pathways. Hence, to determine the necessary investment and net profit, design engineers must be aware of the different types of costs involved in the manufacturing processes. The total capital investment for any process consists of fixed capital investment, known as capital expenditure (CAPEX), and working capital, known as operating expenditure (OPEX). Working capital management affects the liquidity and profitability of the plant. Thus, in any economic analysis of the industrial processes, capital-investment costs, manufacturing costs, and general expenses must be considered [37].

The use of natural dyes in industrial processes has been a major challenge due to the significant current demand for dyestuffs [5, 38]. Moreover, agricultural land and water are necessary to feed the world's growing population. In addition, biodiversity should not be compromised due to overextraction [39]. Extraction of dyes from abundant marine algae and renewable resources, with minimal or no environmental impact, mitigates these challenges. Given that dyes account for a significant portion of the cost of fabricating dye-sensitized solar cells (DSSCs) [13], using marine macroalgae for the natural dye production can significantly lower costs and improve the performance/cost ratio of DSSCs. Considering the above, the present study aims to utilize all the dyes derived from the locally isolated abundant macroalgae for the efficient sensitization of DSSCs [12–14]. Recently, Armendáriz-Mireles et al. conducted an investigation into the world of algae pigments, their significance as natural sensitizers and exploring their unique properties [8]. The study delves into the complex mechanisms that govern the interaction between these pigments and photoelectrodes, offering a comprehensive analysis of their impact on light absorption efficiency, electron transport, and the structural, morphological, optical, and electrochemical impedance aspects of algae pigments. It provides insights into the potential applications of natural dyes, derived from algae, in energy technologies, with a specific focus on DSSCs [8, 12]. Ignoring the dye purification process not only greatly reduces the economic load of the process, but also combines two or more dyes to achieve panchromatic light-harvesting, thereby enhancing the performance of DSSC. In this study, the potential of natural dye production (i.e., fucoxanthin, chlorophyll, phycoerythrin, and phycocyanin) from three marine-macroalgae (*Sargassum* sp. (*Sar*), *Enteromorpha* sp. (*Ent*), and *Gracilaria* sp. (*Gra*)) was evaluated to sensitize DSSCs. Apart from chlorophyll a, the major dyes extracted from *Gracilaria* sp. are phycoerythrin and phycocyanin, which serve as the accessory dye for the photosynthesis[40]. A typical dominant carotenoid of *Sargassum* sp. is fucoxanthin, and the most dominant dye extracted from *Enteromorpha* sp. is chlorophyll [41–43]. The selected macroalgae grow naturally in non-agricultural lands of the Persian Gulf tidal areas and do not conflict with the agro-food sector [44]. To achieve this goal, the response surface methodology based on the central composite design (RSM-CCD) was employed to optimize the dye extraction parameters using the microwave-assisted extraction method [45, 46]. In this approach, the influence of four parameters of extraction time, process temperature, solution pH, and ethanol/water solvent ratio (*SR*), as well as their interactions on the extraction yield, was examined. Based on a comprehensive review of prior research and careful initial screening, we identified these key parameters that stand out as crucial for our study. In the next step, the effect of microwave exposure on the optical activity of the extracted dyes was examined using the circular dichroism (CD). The amount of the extracted dye was measured using the UV–vis spectrophotometer in all the experiments. Finally, a comprehensive economic evaluation was performed for the two studied extraction methods. In terms of the cost, the base year of the study was 2024. One of the main objectives of the present work was to study the scale-up and to add value to the indigenous raw materials as promising candidates for DSSC applications using a cost-effective and environment-friendly technology. For the dye production scale-up, the production processes should be efficient and economically attractive. This study conducted an economic and profitability analysis on both studied extraction methods, targeting production scales ranging from 2000 to 10,000 L.

2 Materials and method

2.1 Materials

Sargassum sp. (*Sar* Phaeophyceae), *Gracilaria* sp. (*Gra* Rhodophyceae), and *Enteromorpha* sp. (*Ent* Ulvaceae) were collected along the northern bank of the Persian Gulf in Bushehr coastal area (Fig. 1). Technical grade (96%) ethanol provided by a local supplier was used throughout the study.

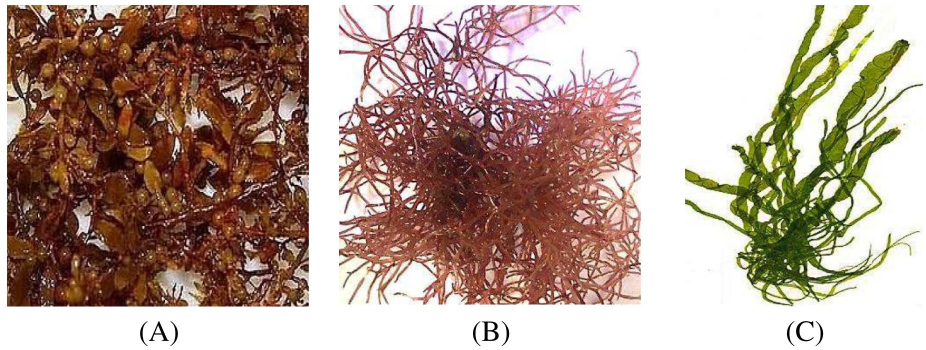


Fig. 1 (***I***) Macroalgae and dominant chemical structures of **A** *Gracilaria* sp. (*Gra* Rhodophyceae), **B** *Sargassum* sp. (*Sar* Phaeophyceae), *Gracilaria* sp. (*Gra* Rhodophyceae), and **C** *Enteromorpha* sp. (*Ent* Ulvaceae). (***II***) Macroalgae collection location: the northern bank of the Persian Gulf in Bushehr coastal area

Table 1 Coded levels of the studied variables for the dye extraction

Parameters	Codes				
	−2	−1	0	+1	+2
Temperature (°C)	30	35	40	45	50
Extraction time (min)	15	23	30	38	45
pH of the solution	5	6	7	8	9
Solvent ratio	0	0.25	0.5	0.75	1

Analytical grades HCl and NaOH were used to adjust the pH of the solutions when required.

2.2 Methods

2.2.1 Optimization using RSM-CCD

To optimize the dye extraction process, an experimental design was conducted applying RSM-CCD to evaluate the combined effect of four effective parameters, including extraction time, process temperature, ethanol/water solvent ratio, and solution pH, on the dye extraction. RSM-CCD is a reliable statistical optimization method based on the multivariate nonlinear model that offers valuable insights with minimal experimental runs. It also helps identify the most effective parameters, analyzes the simultaneous interaction of variables, and determines a regression model equation. This approach provides a reasonable amount of information for testing lack-of-fit. The designed experiments were conducted for dye extraction from the selected macroalgae using microwave-assisted extraction. The experimental design included 31 samples for each alga, with six samples at the center point to evaluate the method's repeatability. The different levels of the employed variables in the present study and the corresponding codes are listed in Table 1. Minitab software was used to carry out the RSM-CCD. The experimental design based on RSM-CCD for the microwave-assisted extraction is summarized in Table S1. An estimate of the total dye concentration based on the spectral measurements and the equations presented in the Supplementary Information is shown in Table S2 as the "Estimated dye concentration" term.

2.2.2 Dye extraction procedure

The dye extraction procedure from each type of algae was previously described [13]. The fresh marine macroalgae were washed immediately after collection, oven-dried at 42 °C, powdered, and then stored in a dark and dry place. The average dry material recovery was 0.243 g per 1 g of raw material (fresh algae). Then, 1 g of the dried powdered sample was dissolved in 20 ml of the solvent for the dye extraction. The conventional solvent extraction and microwave-assisted extraction techniques were performed in an incubator shaker apparatus (FTSKT-801L, Korea) and a microwave apparatus (Anton Paar, Multiwave 3000) at the desired conditions, respectively. Afterward, to obtain impurity-free dye, the solid fibers were filtered out from the dye extract by filter papers and followed by centrifuged at 2500 rpm for 5 min. The UV–vis spectrophotometer (UviLine9600, SECOMAN) was used for the determination of the extracted dye concentration. In the next step, the circular dichroism (CD, Aviv-215) experiments were carried out to investigate the influence of the extraction procedures on the optical activity of the dyes for samples with maximum dye extraction [13, 47, 48]. The CD signals only appear at wavelengths where the dyes absorb light. Since CD records the differential absorption of the dye molecules excited by the right- and left-handed circularly polarized light, these signals may be positive or negative.

2.2.3 Economic evaluation

An economic feasibility analysis was performed on both studied extraction methods for the base year 2024. The total capital investment (TCI) and total production costs (TPC) of the natural dye extracted from algae using the conventional extraction (CE) and microwave-assisted extraction (ME) methods were estimated using Excel software, following the methodology proposed by Peters and Timmerhaus [37]. The profitability of each process was determined based on the return on investment (ROI) and internal rate of return (IRR) on the total capital investment of each procedure. Figure 2 shows the process flow diagram (PFD) for the dye extraction process using the conventional and microwave-assisted extraction methods. For both of the extraction methods studied, the cost of raw materials and the required equipment was considered based on the information presented in the extraction procedures section. Table 2 summarizes the operating costs used in cost estimates. The scale-up criteria were developed based on the laboratory experiments and chlorophyll extracted from *Enteromorpha* sp., which can be also applied to various other pigments. The operating conditions to scale-up the dye extraction from the algae species using the conventional and microwave-assisted procedures were considered as the optimal conditions obtained in the cases of the microwave-assisted technique (Table S4). Also, the operating mode for the dye extraction process using both the studied methods was batch. The production capacity was a parameter that had a non-linear effect on the equipment costs. The purchased equipment costs for the particular operational capacity were estimated based on the equipment costs available in the laboratory. A detailed explanation of the scale-up criteria and procedure is presented in the Supplementary Information. Also, the instruction about how to get industrial-scale equipment costs based on the equipment costs available in different capacities is reported in the Supplementary Information. The detailed specifications to scale-up the dye extraction process and the industrial-scale equipment costs for different production capacities are shown in Table 3.

TCI includes expenses associated with both fixed capital investment (FCI) and working capital (WC) for dye production processes. The capital required for physical equipment and facilities at the plant is classified as FCI, whereas the capital needed for the operational expenses of the process is referred to as WC.

$$TCI = FCI + WC \tag{1}$$

The FCI for any process consists of direct costs (DC) for the purchased equipment costs (PEC), Installation costs (INST), and electrical costs (ELEC) plus indirect costs (IDC), which must be allocated for the engineering and supervision costs (ENG) and the contingency costs (CONT). The purchased equipment costs are the basis of the predesign method, which is employed for the estimation of TCI. The WC for an industrial plant includes the total capital invested in several key areas. This encompasses costs related to raw materials, labor, wastewater management, utilities, product distribution, and the value of products in stock or semi-finished products in the manufacturing process. Additionally, it accounts for payables such as accounts and taxes, as well as cash reserves set aside for salary payments and the purchase of raw materials. Plant commissioning costs include the FCI, along with one-time expenses for raw materials and ancillary start-up costs.

$$FCI = DC + IDC \tag{2}$$

$$DC = PEC + INST + ELEC \tag{3}$$

$$IDC = ENG + CONT \tag{4}$$

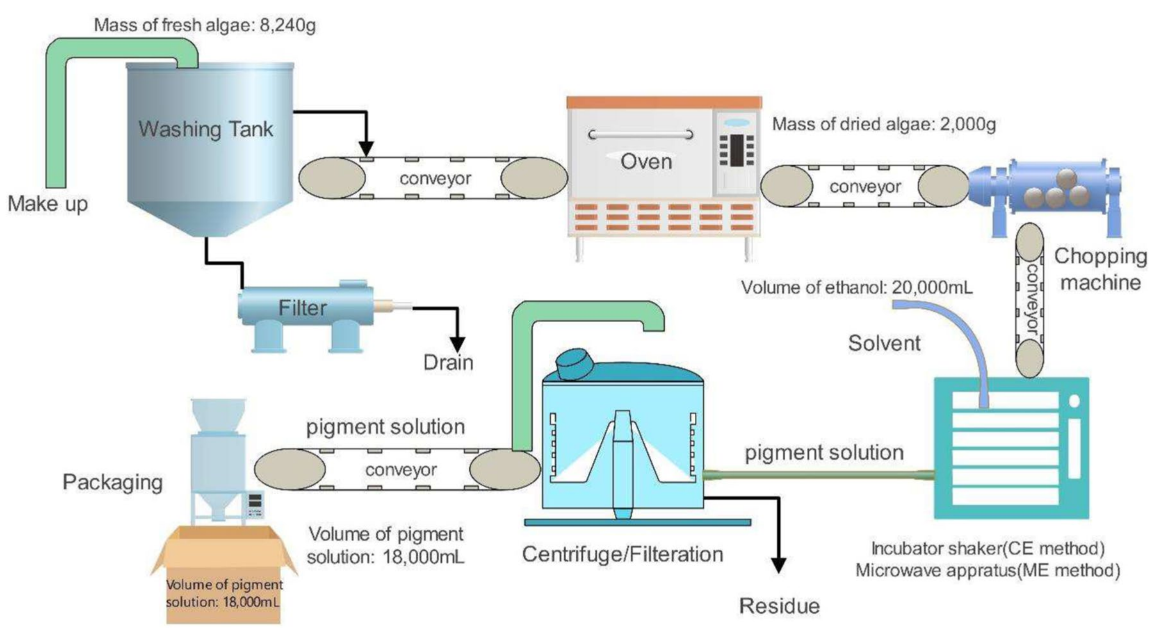


Fig. 2 Process flow diagram (PFD) for the dye extraction process using the conventional and microwave-assisted extraction methods

Table 2 Summary of experimental data used in cost estimations

Items	Cost	Unit	Observations
Raw material (fresh algae)	1190	\$/ton	Average dry material recovery was 0.243 g per 1 g of raw material (fresh algae)
Selling price of the dye solutions	60	\$/L	
Utilities			
Process water	0.14 [49]	$\$/m^3$	
Electricity	20 [49]	\$/MWh	
Chemicals			
Ethanol	14,286	$\$/m^3$	
Base case equipment			
Microwave apparatus	14,750 [50]	\$	Used in ME method
Incubator shaker apparatus	9995 [51]	\$	Used in CE method
Oven	1890 [52]	\$	Used in both extraction methods
Centrifuge machine	2600 [53]	\$	Used in both extraction methods
Grain mill grinder	175 [54]	\$	Used in both extraction methods
Laboratory glassware	100	\$	Used in both extraction methods
Other costs			
Operating labor	36,000 [55]	\$/employee year	
Installation	0.15 × PEC [37]	\$	
Electrical	0.1 × PEC [37]	\$	
Engineering and supervision	0.05 × DC [37]	\$	
Contingency	0.05 × FCI [37]	\$	
Working capital	0.25 × TCI [37]	\$	
Plant overhead cost	0.01 × TPC [37]	\$	
Utilities	0.01 × TPC [37]	\$	
Maintenance and repairs	0.1 × FCI [37]	\$	
Operating supplies	0.15 × M&R [37]	\$	
Laboratory charges	0.02 × OL [37]	\$	
Patents and royalties	0.02 × TPC [37]	\$	
Depreciation	0.02 × FCI [37]	\$	
Local tax	0.02 × FCI [37]	\$	
Insurance	0.01 × FCI [37]	\$	
Administrative cost	0.01 × MC [37]	\$	
Distribution and selling cost	0.01 × TPC [37]	\$	
Research and development cost	0.01 × TPC [37]	\$	

*Based on local costs in 2024

The estimated capital investment and the operating costs for the conventional and microwave-assisted extraction processes in the production capacities of 2000 and 10000 L are given in Table 4.

The percentages (N) of the cost items constituting the TCI are the approximations applicable to ordinary chemical plants. These values can be modified depending on such factors as plant location, equipment, and the type of process. The purchased equipment cost was the major contributor to the capital investment and operating costs for both extraction methods.

The determination of the necessary TCI is only one part of a complete cost estimate. The other important part is the estimation of the TPC, which is estimated by the sum of two main components, i.e., manufacturing cost (MC) and general expenses (GE), according to the methodology proposed by Peters and Timmerhaus [37]. The procedures implemented for the estimation of TPC on an annual cost basis are further decomposed and detailed by the following equations.

$$TPC = MC + GE \tag{5}$$

Table 3 The detailed specifications to scale-up the dye extraction process and industrial-scale equipment costs for different production capacities

Items	Base case	Medium scale (2000 L)	Large scale (10000 L)
Production capacity (L/day)	0.2	8	40
No. of operating days/year	-	250	250
Production capacity (L/year)	-	2000	10000
Raw material (Fresh algae) (g)	41.1	411522.6	2057613.2
Dried algae powder (g)	10	100000	500000
Process temperature	50	50	50
Extraction time (min)	45	45	45
Ethanol/water solvent ratio	1	1	1
Selling price of the dye solutions ($/L)	60	60	60
Equipment costs			
Microwave apparatus ($)	14750	18812.5	41021.3
Incubator shaker apparatus ($)	9995	12747	27797.2
Oven ($)	1890	2410.5	5256.3
Centrifuge machine ($)	2600	3316.1	7230.9
Grain mill grinder ($)	175	223.2	486.7
Laboratory glassware ($)	100	127.5	278.1

*Based on local costs in 2024

Table 4 Estimated capital investment and the operating costs for the two studied extraction methods in different production capacities

Items	*N*	Costs for CE ($/year)		Costs for ME ($/year)	
Production capacity (L/year)		2000	10000	2000	10000
Purchased equipment cost		18825.0	41049.0	24890.0	54273.0
Installation	0.15 × PEC [37]	2823.8	6157.4	3733.5	8141.0
Electrical	0.1 × PEC [37]	1882.5	4104.9	2489.0	5427.3
Direct cost		23531.3	51311.3	31112.5	67841.3
Engineering	0.05 × DC [37]	1176.6	2565.6	1555.6	3392.1
Contingency	0.05 × FCI [37]	1300.4	2835.6	1719.4	3749.1
Indirect cost		2477.0	5401.2	3275.0	7141.2
Fixed capital investment ($)		26008.2	56712.4	34387.5	74982.4
Working capital investment ($)	0.25 × TCI [37]	8669.4	18904.1	11462.5	24994.1
Total capital investment ($)		34677.6	75616.6	45850.0	99976.6

N, the percentage of the various costs constituting the TCI; *CE*, conventional extraction method; *ME*, microwave-assisted extraction method

MC includes all the expenses directly associated with the manufacturing operation or the physical equipment of the plant. MC considers the expenses related to the direct production cost (DPC), fixed charge (FC), and plant overhead cost (POC).

$$MC = DPC + FC + POC \tag{6}$$

GE consists of the administrative cost (ADC), distribution and selling cost (D&SC), and research and development cost (R&DC).

$$GE = ADC + D\&SC + R\&DC \tag{7}$$

Expenses directly connected with the manufacturing operation are included in the DPC. DPC involves the expenses used for raw materials (RM), operating labor (OL), direct supervisory and clerical labor (DS&CL), utilities (UT), maintenance and repairs (M&R), operating supplies (OS), laboratory charges (LC), and patents and royalties (P&R). The cost of RM involves the expenses related to the costs of raw materials and solvents. It is also assumed to be constant over the production period.

$$DPC = RM + OL + DS\&CL + UT + M\&R + OS + LC + P\&R \tag{8}$$

FC considers the expenses that remain virtually constant over the years and do not vary widely by the changes in the production rate. FC includes the expenses of depreciation (DEP), local taxes (LTX), insurance (INS), and rent (REN). DEP is defined as the gradual decline in the financial value. It is assumed to occur over the usual life of the material assets. In this study, the cost estimates are based on the application of a linear depreciation pattern. The amount of LTX depends on the specific location of the plant and the regional laws.

$$FC = DEP + LTX + INS + REN \tag{9}$$

Table 5 provides important information about the TPC calculation of the two studied extraction processes for the production capacities of 2000 and 10,000 L based on the methodology proposed by Peters and Timmerhaus [37].

Production cost for plant (PCP), breakeven point capacity (BEPC), yearly income in BEPC (YIBEPC), total yearly income (TYI), gross profit (GP), net profit (NP), ROI, and payback period (PBP) are determined by the following equations. The BEPC defines the production level at which the total product cost equals the total sales. The total annual product cost is the sum of the fixed charge, overhead, general expenses, and the direct production costs for *n* units per year. Total annual sales are equal to the production capacity per year multiplied by the corresponding selling price per unit of production.

$$SP \times BEPC = PCP \times BEPC + FC + POC + GE \tag{10}$$

$$PCP = \frac{DPC}{PC} \tag{11}$$

$$YIBEPC = BEPC \times SP \tag{12}$$

$$TYI = PC \times SP \tag{13}$$

where SP is the selling price, and PC is the production capacity per year.

The total yearly income minus the total product cost gives the gross profit. Gross profit is expressed as follows:

$$GP = TYI - TPC \tag{14}$$

The net profit equals the amount that remained of profit after the income taxes have been paid. The income tax expense is deducted in the amount $GP \times \Phi$, where Φ is the fixed income tax rate determined as a fraction of the annual gross profits. If the income tax rate is 25% of the gross profit, net profit is determined as follows:

Table 5 Estimation of the total product cost for the two studied extraction methods in different production capacities

Items	N	Costs for CE ($/year)		Costs for ME ($/year)	
Production capacity (L/year)		2000	10000	2000	10000
Fixed capital investment		26008.2	56712.4	34387.5	74982.4
Manufacturing cost		84321.8	226595.8	85763.6	229739.6
Direct production cost		80152.7	219425.6	81160.8	221623.6
Fixed charges		3300.4	4835.6	3719.4	5749.1
Plant overhead cost	0.01 × TPC [37]	868.6	2334.6	883.4	2366.9
Raw materials		32836.0	164179.9	32836.0	164179.9
Operating labor		36000.0	36000.0	36000.0	36000.0
Direct supervisory and clerical labor		5000.0	5000.0	5000.0	5000.0
Utilities	0.01 × TPC [37]	868.6	2334.6	883.4	2366.9
Maintenance and repairs	0.1 × FCI [37]	2600.8	5671.2	3438.8	7498.2
Operating supplies	0.15 × M&R [37]	390.1	850.7	515.8	1124.7
Laboratory charges	0.02 × OL [37]	720.0	720.0	720.0	720.0
Patents and royalties	0.02 × TPC [37]	1737.2	4669.2	1766.8	4733.8
Depreciation	0.02 × FCI [37]	520.2	1134.3	687.8	1499.7
Local taxes	0.02 × FCI [37]	520.2	1134.3	687.8	1499.7
Insurance	0.01 × FCI [37]	260.1	567.1	343.9	749.8
Rent		2000.0	2000.0	2000.0	2000.0
General expenses		2538.7	6863.4	2578.5	6950.0
Administrative cost	0.01 × MC [37]	801.5	2194.3	811.6	2216.2
Distribution and selling cost	0.01 × TPC [37]	868.6	2334.6	883.4	2366.9
Research and development cost	0.01 × TPC [37]	868.6	2334.6	883.4	2366.9
Total product cost		86860.5	233459.3	88342.1	236689.6

N, the percentage of the various costs constituting the TPC; *CE*, conventional extraction method; *ME*, microwave-assisted extraction method

$$NP = GP(1 - \Phi) = 0.75 \times GP \tag{15}$$

The ROI and IRR on invested capital are profitability measures in the financial analysis. The purpose of calculating the ROI on the invested capital is to monitor the economic performance and evaluate the desirability of a project. The ROI is defined as the net profit after taxes being divided by the total capital investment. The calculated ROI on investment does not consider the time value of money. The ROI on investment is given as follows:

$$ROI = 100 \times \frac{NP}{TCI} \tag{16}$$

The payback period (PBP) is defined as the time needed to return all the investments from the net profit. The PBP is expressed as follows:

$$PBP = \left(\frac{100}{ROI}\right) \times 12 \tag{17}$$

Unlike the PBP and ROI on invested capital, which ignore the time value of money and the entire project lifetime, IRR incorporates both factors. If the IRR exceeds the cost of capital (the minimum rate of return required by the investor), the investment project is considered financially efficient. The IRR is defined as follows:

$$\frac{(1 + IRR)^T - 1}{(1 + IRR)^T.IRR} = \frac{C_0}{C_T} \tag{18}$$

where IRR represents the internal rate of return, T denotes the lifetime of natural dyes, C_0 is the initial investment, and C_T signifies the annual net cash flows, which are assumed to be constant throughout the entire period T.

The estimated income and return cost (EIRC) provide the key information for the economic evaluation of a dye extraction process. The calculated EIRC for the two studied extraction methods in the production capacities of 2000 and 10000 L is presented in Table 6. The selling price of the extracted dye solutions was considered $60/L based on the prevailing market price [55]. It is assumed that the selling price remains constant within the process cycle.

3 Results and discussion

3.1 Dye extraction and characterization

The detailed results of the RSM approach for optimizing the dye extraction variables are listed in Supplementary Table S2 for all three algae. Moreover, the typical results of the analysis of variance (*ANOVA*) for the predicted model of *Gracilaria* sp. dye are summarized in Supplementary Table S3. Based on the ANOVA results, the high value for the determination coefficient (R^2 = 0.9976) showed the applicability of the proposed model through existing experimental data. The adjusted determination coefficient (R_a^2 = 0.9954) implied that the predicted model was highly significant. Moreover, the calculated p-value for lack of fit was more than tabular values and indicated that the model is compatible with experimental data. The total model is associated with a p-value of less than 0.0001, showing the high significance of the model again. Based on a regression analysis at 95% of the confidence interval, the ANOVA

Table 6 Estimated income and return cost statement for the two studied extraction methods in different production capacities

Extraction method	Costs for CE ($/year)		Costs for ME ($/year)	
Production unit	L	L	L	L
Direct production cost ($/year)	80152.7	219425.6	81160.8	221623.6
Fixed charges ($/year)	3300.4	4835.6	3719.4	5749.1
Plant overhead cost ($/year)	868.6	2334.6	883.4	2366.9
General expenses	2538.7	6863.4	2578.4	6950.0
Capacity of unit per year (plant capacity) (production unit)	2000	10000	2000	10000
Production cost for sale ($/production unit)	59.5	59.5	59.5	59.5
Production cost for plant ($/production unit)	40.1	21.9	40.6	22.2
Breakeven point capacity (production unit/year)	344.9	373.4	379.1	403.3
Yearly income in BEPC ($/year)	20530.8	22227.5	22564.8	24003.0
total yearly income ($)	119047.6	595238.1	119047.6	595238.1
Gross profit ($/year)	32187.1	361778.8	30705.6	358548.5
Tax (%)	25	25	25	25
Net profit ($/year)	24140.3	271334.1	23029.2	268911.4
Return on investment (%)	69.6	358.8	50.2	269.0
Payback period (month)	17.2	3.3	23.9	4.5

illustrated that linear, quadratic, and crossed effects of some parameters did not have a statistically significant effect on the extraction of pigments from these algae, while other factors exerted a significant influence on the extracted pigments. By discarding the insignificant terms, the analysis was carried out again, and the fitted models for the pigment extraction yield, Y_{Algae}, was given by the following equation:

$$Y_{Gar} = 155.92 + 14.87 \times Time + 26.83 \times Temp. + 72.26 \times SR + 5.07 \times Temp.^2 + 2.47 \times SR^2 + 5.59 \times Time \times SR + 19.75 \times Temp.SR \tag{19}$$

$$Y_{Ent} = 208.72 + 9.38 \times Time - 2.21 \times pH + 19.64 \times Temp. + 72.424 \times SR - 7.2 \times SR^2 + 11.04 \times Temp. \times SR \tag{20}$$

$$Y_{Sar} = 181.45 + 14.99 \times Time + 4.39 \times pH + 24.74 \times Temp. + 73.24 \times SR - 4.96 \times Time^2 + 6.234 \times pH^2 + 13.16 \times SR^2 + 12.88 \times Time \times SR4 + 8.05 \times pH \times Temp. + 6.05 \times pH \times SR + 17.75 \times Temp.SR \tag{21}$$

The adequacy of the regression model was verified using a close agreement of the extraction yield estimated by the proposed model with the experimental values, the variance analysis of the model, and the significant value of lack of fit. The analysis of the variance of the suggested model was applied to the other algae, and the same results were obtained for all of them.

To evaluate the interactions between different factors and the optimal condition of pigment extraction, the regression coefficients were used to generate three-dimensional (3-D) plots from the predicted model. Figure 3 shows typical contour and surface 3-dimensional plots for extracted pigments from *Gracilaria* algae. The plots illustrate that the highest pigment extraction was obtained with increasing ethanol concentration, extraction time, and temperature. Because the pigments are heat-sensitive molecules, higher temperatures and longer process time may cause pigment degradation and loss of their optical properties. The optimum extraction conditions, as well as the highest extracted pigments for all algae, are presented in Table 7. The optimum conditions for the dye extraction from algae using the conventional method were considered as those obtained in the cases of the microwave-assisted technique. Also, both processes were operated at batch conditions.

Figure 4a shows the UV–vis results of the extracted dyes from *Enteromorpha* sp., *Gracilaria* sp., and *Sargassum* sp. using the conventional and microwave-assisted extraction methods under optimal conditions. The dye extracted from *Enteromorpha* sp. showed two wide absorption peaks appearing around the 380–480 nm region and at 660 nm, which was in good agreement with the chlorophyll structures. The intense light absorption in the 416 and 666 nm wavelengths was ascribed to the fucoxanthin extracted from *Sargassum*. Also, the presence of chlorophyll, phycoerythrin, and phycocyanin in dye extracted from *Gracilaria* sp. was verified by two strong light absorption around the 400–440 nm region and at 666 nm. According to this figure, microwave-assisted extraction had a higher extraction yield with no dye degradation compared to the conventional method. The highest dye extraction yield was obtained for *Sargassum* sp., followed by *Gracilaria* sp. and *Enteromorpha* sp. by the microwave extraction method. Compared to the conventional solvent extraction, the enhancement of the dye extraction from *Sargassum* sp., *Gracilaria* sp., and *Enteromorpha* sp. using microwave-assisted extraction was 70.37%, 64.31%, and 20.71%, respectively. The microwave-assisted method is more efficient than conventional solvent extraction for the extraction of dyes from *Sargassum* sp. and *Gracilaria* sp. than Enteromorpha sp. because they have a stronger cell wall, and the dye extraction from these species is more difficult when using a conventional solvent extraction method. Microwave electromagnetic radiation destructs cell walls and skin tissues which leads to an increase in solvent penetration into the cell structures and the leaching of the ingredients [56, 57].

The typical UV–vis result of the microwave-assisted extracted dyes from *Enteromorpha* sp. using ethanol and water as the solvent under optimum extraction conditions is presented in Fig. 4b. The results show that the highest concentration, as well as the most variety of the dyes, including fucoxanthin, chlorophyll, phycoerythrin, and phycocyanin, was extracted using pure ethanol for all algae and both extraction methods. In this condition, the order of the extracted dye type from different sources (*PT*) is as follows:

$$PT_{Sar} < PT_{Ent} = PT_{Gar}$$

The CD spectra of the extracted dyes from *Enteromorpha* sp., *Sargassum* sp., and *Gracilaria* sp. using conventional and microwave-assisted extraction under optimal conditions are summarized in Fig. 4c. The CD signal appeared only at wavelengths where the dyes absorbed radiation. Depending on the handedness of the dye molecules, these signals may be positive or negative. Based on the results, all the samples exhibited optical activity in the ultraviolet, visible, and infrared regions (about 300–1000 nm). Based on the results, there was no loss of optical activity and dye degradation due to microwave exposure. The CD results of the extracted dyes from *Sargassum* sp. and *Gracilaria* sp. using the conventional and microwave-assisted extraction methods are shown in Fig. 4c. In comparison to conventional solvent extraction, the enhancement of the optical activity of the extracted

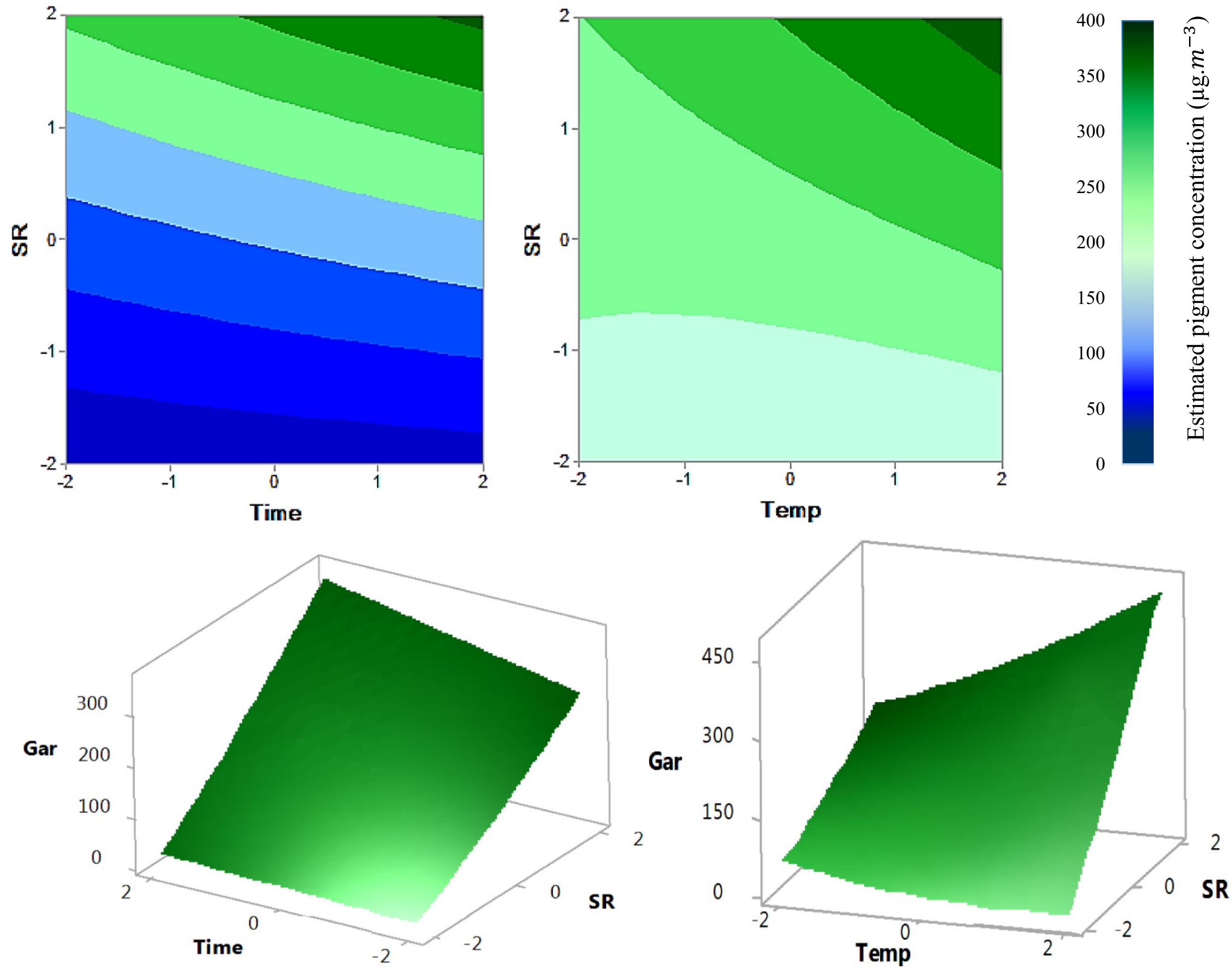


Fig. 3 **a** Contour and **b** surface plots illustrating the interaction effect of extraction time, temperature, and solvent ratio on the extracted pigment concentration from *Gra* using the microwave-assisted extraction method

Table 7 The optimum parameters and response values for the extracted pigment concentration from the algae of Persian Gulf zone using the microwave-assisted extraction method

Algae	Parameter levels				$Y_{optimal}$
	Time (min)	pH	Temp	SR	
Gra	45	-	50	1	515.34
Ent	45	5	50	1	431.22
Sar	45	9	50	1	652.72

dyes from *Sargassum* sp., *Gracilaria* sp., and *Enteromorpha* sp. at wavelength 450 nm using the microwave-assisted extraction was 50.66%, 61.71%, and 37.06%, respectively.

3.2 Economic evaluation of the dye extraction methods

According to the results shown in Table 4, the microwave-assisted extraction method required higher capital investments compared to the conventional solvent extraction method. Figure S1 presents the Pareto graph of the effective parameters on the estimated TCI for the dye extraction using the conventional and microwave-assisted extraction methods in a production capacity of 10,000 L. The purchased equipment cost and working capital fall before the curve breakpoint location, indicating that they had the most influence on the estimated TCI.

As shown in Table 5, the calculated TPC for the microwave-assisted extraction method was slightly higher than that for the conventional solvent extraction method. Also, the results showed that TPC decreased by increasing the

Fig. 4 **a** Comparison of UV–vis absorption spectra of the extracted dyes from *Enteromorpha* sp., *Gracilaria* sp., and *Sargassum* sp. using the conventional and microwave-assisted extraction methods under optimal conditions, **b** comparison of UV–vis absorption spectra of the microwave-assisted extracted dyes from *Enteromorpha* sp. using ethanol and water under optimal conditions, and **c** comparison of circular dichroism spectra of the extracted dyes from *Enteromorpha* sp., *Gracilaria* sp., and *Sargassum* sp. using conventional and microwave-assisted extraction under optimal conditions

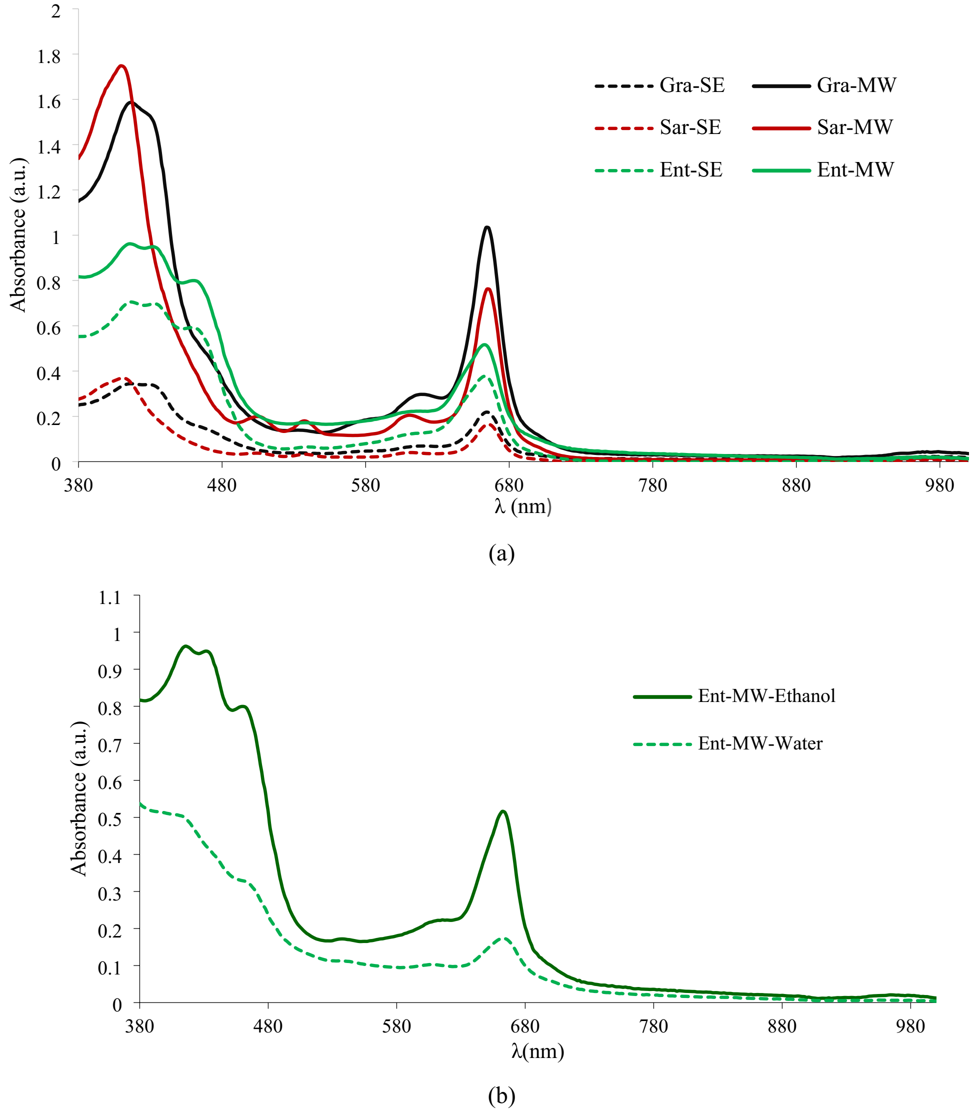
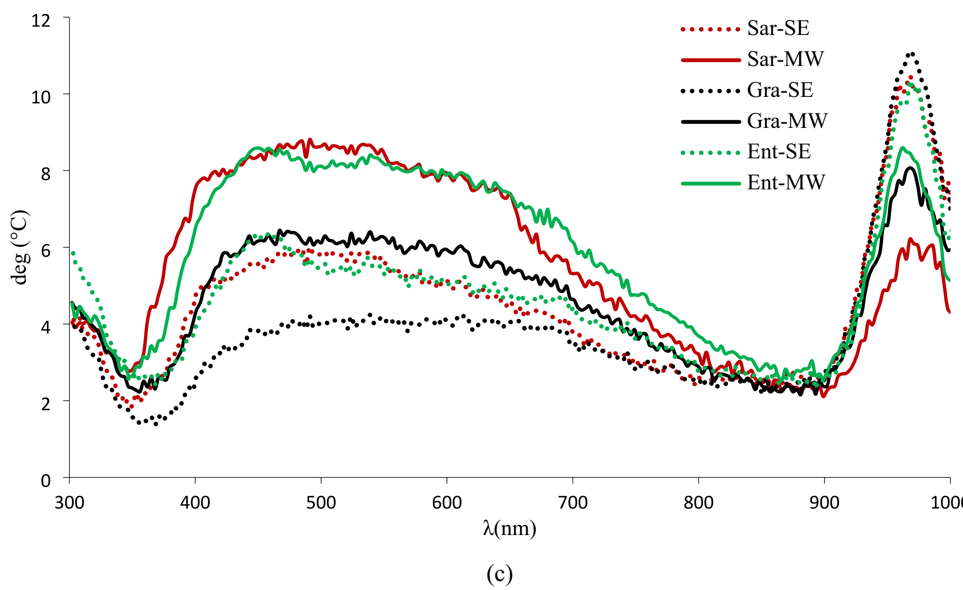


Fig. 4 (continued)



production capacity for all algae and methods. For instance, TPCs were estimated at $44.17/L and $23.67/L for the microwave-assisted extraction method with production capacities of 2000 and 10,000 L, respectively. Moreover, the detailed information for the estimation of TPC at different production capacities using the conventional and microwave-assisted extraction methods are summarized in Supplementary Tables S4 and S5, respectively. Figure S2 exhibits the Pareto graph of the effective factors on the estimated TPC for the dye extraction using the conventional and microwave-assisted extraction methods with a production capacity of 10,000 L. There were two factors before the curve break-point, which indicated that they had the most impact on the estimated TPC.

As shown in Fig. 5, the direct production cost had the most influence on the total product cost for both extraction processes. Also, the results showed that the impact of DPC on the TPC increased by raising the production capacity for all the processes.

Based on the results reported in Table 6, the calculated ROI for the conventional and microwave-assisted extraction methods in a production capacity of 10,000 L was more than 358% and 268%, corresponding to PBP of less than 4 and 5 months, respectively. Also, detailed information on the calculated EIRC in different production capacities using the conventional and microwave-assisted extraction methods are listed in Supplementary Tables S6 and S7, respectively. The influence of production capacity on the PBP and TPC/PC for the conventional and microwave-assisted extraction processes is shown in Fig. 6. The results showed that increasing the production capacity decreased the PBP and TPC for all the processes. Although EIRC for both processes revealed that the ROI for the microwave-assisted extraction method was less than the conventional solvent extraction method, its efficacy is significantly higher in comparison with the conventional method. A few studies have been done on the economic feasibility of various dye extraction methods in the pilot and the industrial scales. Albuquerque and Meireles used the supercritical CO_2 extraction method as a pretreatment for the extraction of bixin from annatto seeds in one pilot and two industrial scales. The economic evaluation for the extracted bixin (22 mg of extract/g of dried seeds) showed the manufacturing cost (MC) of US$ 300.00/kg of extract for the pilot plant with two vessels of 0.005 m^3. Also, the effect of the production capacity on the MC showed that increasing the extraction vessel capacities from 0.1 to 0.5 m^3, decreased the MC from US$ 124.58/kg to US$ 109.24/kg of the extract [58, 59].

The extracted pigments are used as sensitizers to fabricate and analyze the DSSCs. The photovoltaic parameters obtained for the fabricated DSSCs samples are calculated in reference [13]. The I-V curves provided the performance of the fabricated DSSCs, and demonstrated variations in the efficiency, open-circuit voltage, short-circuit current, and filling factor (η, Voc, Isc, and FF) ranging from 350 to 442 mV, 8.05 to 9.43 mA/cm^2, and 0.53 to 0.76%, respectively [13]. Optimization of extraction parameters, such as temperature, time, and solvent ratio, can significantly improve the extraction yield and purity of natural dyes. Efficient dye extraction is crucial for maximizing the yield and quality of natural dyes, which directly impacts the overall cost and performance of DSSCs. Developing

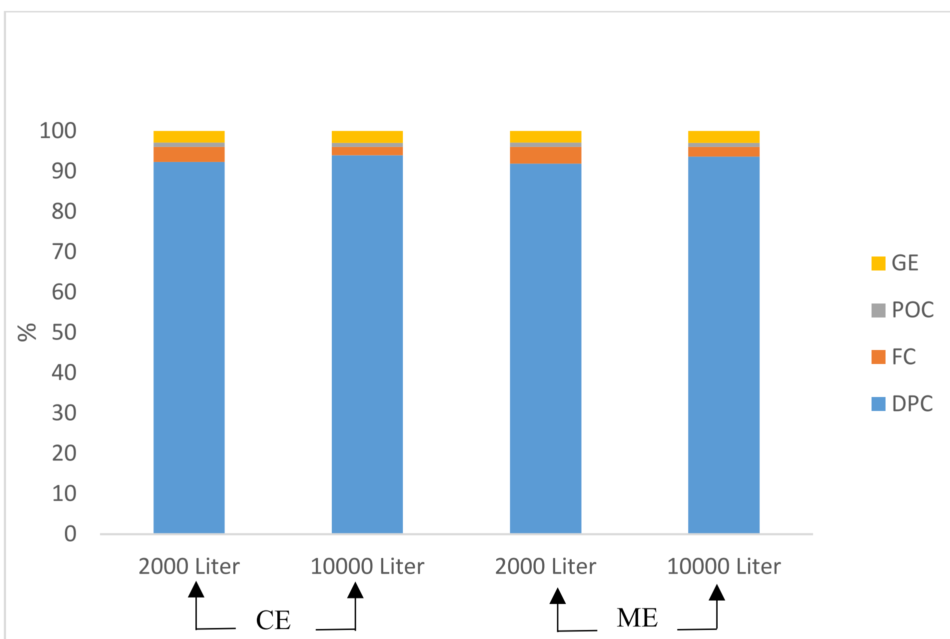


Fig. 5 Influence of the direct production cost (DPC), fixed charge (FC), plant overhead cost (POC), and general expenses (GE) on the total production cost (TPC) for the conventional extraction (CE) and microwave-assisted extraction (ME) processes

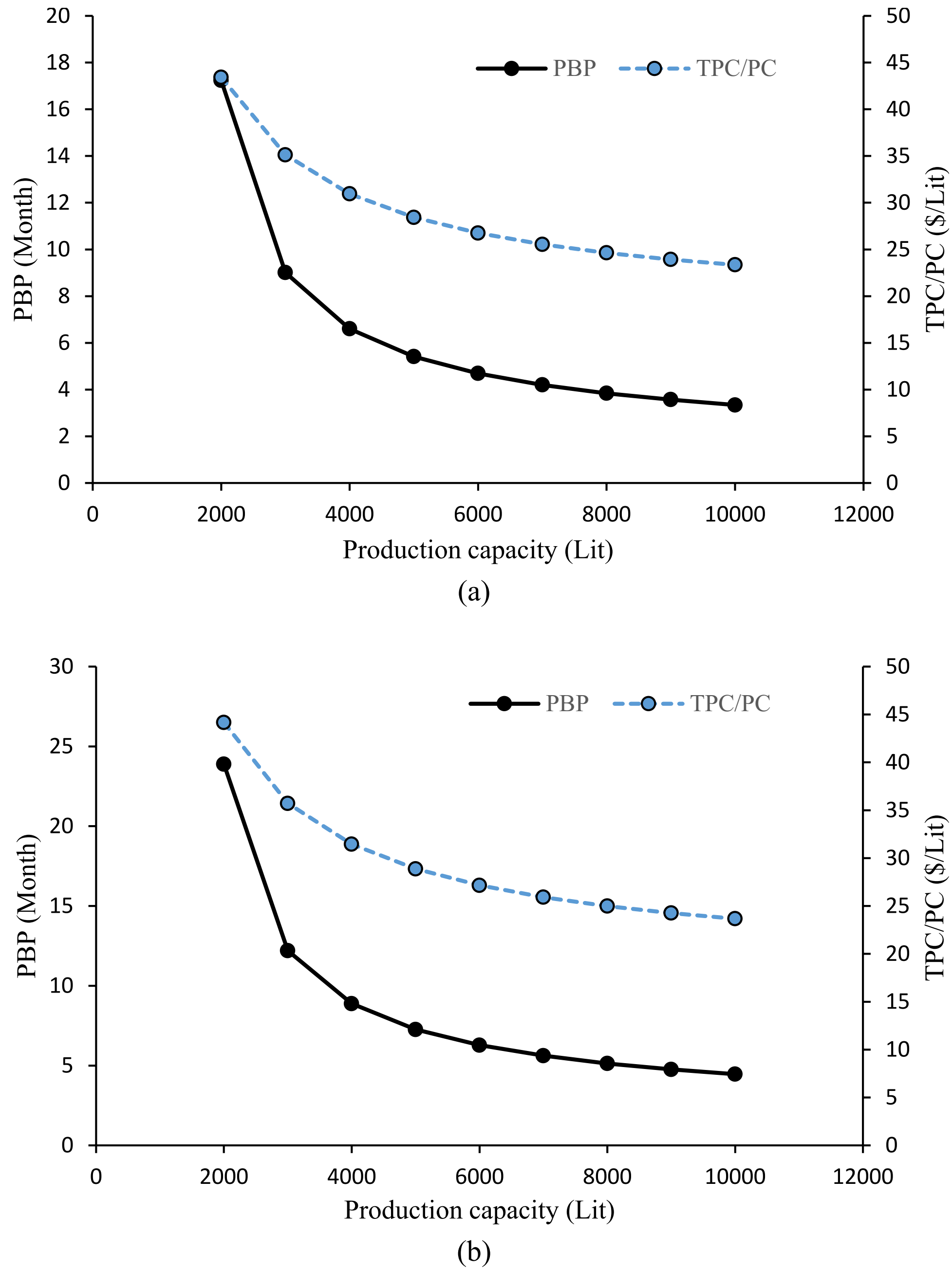


Fig. 6 Influence of production capacity on the payback period (PBP) and TPC/PC for **a** conventional solvent extraction process and **b** microwave-assisted extraction process

efficient and scalable extraction techniques is essential for reducing the cost of natural dye-based DSSCs and promoting their commercial viability. The cost-effective extraction of natural dyes is crucial for the commercial viability of DSSCs. By optimizing extraction techniques and utilizing abundant natural sources, it is possible to significantly reduce the overall cost of DSSC fabrication. Additionally, the efficiency of the extraction process directly impacts the purity and concentration of the extracted dyes, which in turn affects the performance of the DSSCs. Therefore, careful consideration of the extraction method and conditions is essential to maximize the yield and quality of natural dyes.

Overall, the production of natural dyes extracted from the regional algae of the Persian Gulf coastal zone can be considered as a sustainable, environment-friendly, and cost-effective process. These products are valuable bioresources with a promising innovative future. The microwave-assisted extraction method provided a robust and economically feasible technique for the dye extraction from algae that can be a potential substitute for the other extraction methods.

4 Conclusions

In this work, the optimized conditions for the maximum dye extraction yield using microwave-assisted extraction were determined based on RSM-CCD. The results showed that temperature, extraction time, and ethanol/water solvent ratio had a significant influence on the extraction of the dyes, while the pH of the solutions did not exert the same trend effect on it for all algae. In comparison with the conventional solvent extraction method, the microwave-assisted extraction method improved the extraction yield from *Sargassum* sp., *Gracilaria* sp., and *Enteromorpha* sp. 70.37%, 64.31%, and 20.71%, respectively. Moreover, the microwave-assisted extraction method had a higher extraction yield with no dye degradation compared to the conventional method. Also, microwave-assisted extraction enhanced the optical activity of the extracted dye from *Sargassum* sp., *Gracilaria* sp., and *Enteromorpha* sp. at wavelength 450 nm compared to the conventional solvent extraction, 50.66%, 61.71%, and 37.06%, respectively. Finally, the economic and profitability analysis of the two studied extraction methods were conducted. The results revealed that by increasing the production capacity, the PBP and TPC for all processes decreased. In addition, the microwave-assisted extraction method achieved a close PBP and TPC to the conventional solvent extraction method. Besides, due to the low cost and eco-friendly natural dyes extracted from the regional algae of the Persian Gulf zone using microwave-assisted extraction, these algae are excellent candidates for the dye production on an industrial scale. Last, the microwave-assisted extraction method as an efficient technique for dye extraction can be selected for replacement with other extraction methods. The cost of dye materials is a significant factor affecting the overall cost of DSSCs. Natural dyes, especially those derived from abundant and renewable sources, can offer a cost-effective alternative to synthetic dyes. However, the lower cost of natural dyes must be balanced against their potential impact on device performance, such as lower efficiency or shorter device lifetime. The properties of the extracted dyes, such as their absorption spectra, molar extinction coefficients, and electron injection efficiency, play a significant role in determining the overall performance of DSSCs. By selecting appropriate extraction methods and optimizing the extraction conditions, it is possible to obtain dyes with desirable properties that can enhance the power conversion efficiency of DSSCs.

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Data availability The data supporting this study's findings are available from the corresponding author upon reasonable request.

Code availability The code supporting this study's findings is available from the corresponding author upon reasonable request.

Declarations

Ethical approval This paper does not contain any studies with human participants or animals performed by any of the authors.

Consent to participate Not applicable.

Consent for publication Not applicable.

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Declaration of generative AI and AI-assisted technologies This manuscript was written without the use of generative AI or AI-assisted technologies. All text, figures, and tables were created by the author without the assistance of AI.

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