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Use of response surface method for modeling and optimization of harvesting of Chlorella sorokiniana pa.91 with Fe3O4/PACl from municipal wastewater

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ABSTRACT: Microalgae have the potential to produce valuable substances for pharmaceutical purposes as well as serve as a food source, providing bioactive compounds and ingredients for cosmetics. However, harvesting microalgae is a crucial step in the mass production of various high-value products derived from microalgae. This process often becomes a major bottleneck in downstream processing. It is essential to find effective and cost-effective harvesting methods for industrial applications. Among several harvesting methods, magnetic flocculation offers the benefits of modest operation, energy savings, and quick separation. This study investigates the harvesting process of Chlorella sorokiniana pa.91 microalgae using a novel flocculation process involving nano-Fe3O4 coated with PACl. In this research, we have used the chemical co-precipitation method to prepare nanoparticles. Using the response surface method to optimize the most important parameters of the magnetic flocculation harvesting process to check the microalgae removal efficiency, three variables of time, concentration of nanomaterials, and pH in the culture medium obtained from municipal wastewater have been investigated. The results demonstrated that the highest harvesting efficiency, nearly 90%, was achieved under the conditions of 3.5 g/L Fe3O4, a constant concentration of 0.075 g/L PACl, a harvesting duration of 40 minutes, and a pH level of 4. On the other hand, the lowest microalgae harvesting efficiency was observed under specific conditions: a composite nanoparticle concentration of 0.5 g/L per liter, a harvesting time of 27.5 minutes, and a pH of 6.5 resulting in a mere 22% efficiency. The rate of microalgal removal increased from 53% in the most alkaline condition to 75% in the most acidic environment. The highest harvesting efficiency, reaching 80%, was achieved under neutral pH conditions with a settling time of 53 minutes. Furthermore, the investigated combined method investigated enhances the flocculation effectiveness of microalgae. Based on the findings, it can be inferred that the efficiency of microalgae harvesting rises with longer duration, higher nanoparticle concentrations, and lower pH levels

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1- Introduction

Due to the growth of the world population and rising living standards in developing nations, microalgae have emerged as a novel biomass source. Microalgae are currently being cultured to produce high-value compounds in various industries, including fuel, nutraceuticals, pharmaceuticals, and wastewater treatment [1]. The basic steps of microalgal production include cultivation and harvesting [2]. It is estimated that the microalgae harvesting step represents 20–30% of the total biomass production cost[3]. In particular, low cell concentrations in cultures (0.5 to 5 g/L), small cell size (<30 µm), and the stability of cell suspension are major economic bottlenecks in microalgal biomass production [4]. Algal cells can be harvested by various methods such as centrifugation, sedimentation, flocculation, filtration, flotation or by a combination of these methods [5]. The current harvesting methods have various disadvantages, including high costs, increased energy usage, and the need for time-intensive procedures [6]. However, magnetic separation is a quick and simple method due to its time-saving nature. And this method is low-energy and economical [7]. Magnetic separation is a simple technique that uses functionalized magnetic particles to adsorb cells and biomolecules from liquid solutions. This process operates through the influence of an external magnetic field [8]. Additionally, surface coating or modification of magnetic nanoparticles with various materials, such as polymers and surfactants, can improve both the stability of the NPs suspension and the harvesting efficiency[9]. Various types of flocculants have been used to harvest microalgal biomass, which can be broadly classified into three groups: inorganic metal salts (such as aluminum and iron salts such as $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, and $FeCl_3$, etc.), synthetic polymers (including polyelectrolyte and polyacrylamide), and natural polymers (such as chitosan

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and starch) [10]. There are four mechanisms of microalgal cell flocculation in which microalgal cells flocculate through charge neutralization, bridging, and sweeping and facilitate the formation of aggregates or larger particles, thereby aiding the harvesting process [11]. A diverse and highly efficient flocculant for microalgae harvesting still needs to be developed, despite the availability of several flocculants and their performance, as well as their energy and operating costs. Additionally, by lowering expenses and promoting more sustainable microalgae production methods, the enhanced flocculants can aid in the growth and implementation of microalgae-based companies.

The objective of this current study is to develop an efficient magnetic separation method for recovering the algal cells of Chlorella sorokiniana pa.91 with Fe_3O_4/PACl composite nanoparticles from municipal wastewater.

2- Methodology

2- 1- Microalgal strain and cultivation

A new strain of Chlorella *sorokiniana pa.91*, which was previously isolated from the Gela dairy wastewater treatment plant (Amol, Iran), was selected and used in this study [12]. In this experiment, the influent from the preliminary settling tank of the wastewater treatment plant (WWTP) in Sari, Iran, was utilized as the microalgae culture medium. Microalgae cultivation experiments were conducted using 1000-mL Erlenmeyer flasks in volumes of 800 mL of culture medium. The flasks were kept at 28°C under 3000 Lx light intensity in a 12/12-h light/dark cycle.

2- 2- Preparation of magnetic nanoparticles

In this study, several substances, including $FeCl_3.6H_2O$, $FeCl_2.4H_2O$, and ammonium hydroxide (25 wt%), were used for the synthesis of nanoparticles. To adjust pH levels, 0.1 M HCl and 0.1 M NaOH were purchased from Merck. Fe_3O_4 magnetite nanoparticles were synthesized using the chemical co-precipitation method. For the synthesis, first, 0.99 g of $FeCl_3.6H_2O$ and 2.7 g of $FeCl_2.4H_2O$ are added to 100 ml of distilled water and mixed in a three-necked flask with a round bottom with a magnetic stirrer. Nitrogen was used to remove oxygen from the solution during the mixing process. When the solution was heated to 80°C, 10 mL of NH_4OH (25 wt%) was added dropwise to obtain a black precipitate, and the reaction was kept at 80°C for 30 minutes under continuous stirring. The black suspension obtained was separated using a permanent magnet, washed three times with distilled water and ethanol, and dried in a vacuum oven at 80 °C [1]. Then Fe_3O_4 nanoparticles were mixed with polyaluminum chloride in 50 ml of distilled water and shaken for 5 minutes in the incubator until they were completely mixed. Then a magnet was placed under the mixture to separate the top layer and the nanoparticle. After that, the separated material was dried at 80°C in an oven.

3- Results and Discussion

The response surface method is a statistical and mathematical approach used to analyze and optimize processes when different factors interact with each other. In this research, the design and modeling of the experiment were done using Design Expert software. Time, the concentration of composite nanoparticles, and pH as three independent parameters in CCD design were determined based on pre-test experiments, and the effects of each of the independent variables, interaction, and simultaneous variables were also investigated. Table 1 based on related literature and preliminary studies, the range of the parameters under examination was selected. The design included 20 experiments, with the best microalgae removal efficiency reaching 88% under specific conditions, such as a 40-minute harvesting period, a pH of 4, and a nanoparticle concentration (g/L) of 3.5. The lowest removal efficiency was obtained in The concentration is 0.5 g, and the pH of 6.5 is displayed for 27.5 minutes Also, the best efficiency is reported at a neutral pH equal to 80%.

Table 1. The results of microalgae harvesting efficiency in Fe3O4/PACl magnetic flocculation process

Run	time min	pH	Fe_3O_4/PACl g/L	HE
1	40	9	3.5	69.386
2	15	9	1.5	32.636
3	27.5	6.5	2.5	53.705
4	27.5	6.5	2.5	58.705
5	27.5	6.5	2.5	56.706
6	27.5	6.5	2.5	50.705
7	40	4	3.5	88.136
8	15	4	3.5	60.886
9	27.5	11.5	2.5	53.364
10	15	4	1.5	35.386
11	27.5	6.5	2.5	55.705
12	27.5	6.5	4.5	69.114
13	27.5	6.5	0.5	22.114
14	27.5	6.5	2.5	50.705
15	15	9	3.5	46.136
16	52.5	6.5	2.5	80.364
17	40	4	1.5	66.636
18	2.5	6.5	2.5	25.864
19	40	9	1.5	49.886
20	27.5	1.5	2.5	75.864

The results of variance analysis show that the modified quadratic model effectively represents the design space and provides a good fit to the data. The results show that the proposed model adequately shows the relationships between the variables and the response. The F model value of 61.89 shows that the proposed model is statistically significant.

P-values less than 0.05 indicate that the conditions of the model are significant. The coefficient of determination value for this design, (R^2) 0.9823, indicates a strong relationship between independent variables and response values. Experimental results have been presented, showing that reducing pH and increasing two other parameters improve harvesting efficiency. The better harvesting of microalgae at acidic pH can be attributed to the fact that in acidic conditions, the surface charge of microalgae cells becomes more positive.

4- Conclusions

In this study, we investigate the impact of three independent variables nanoparticles concentration, harvesting time, and pH on the microalgae Chlorella sorokiniana.pa91 was investigated using various Fe3O4/PACl-based nanoparticles as adsorbents. The findings of our study showed that the magnetic flocculent method is very effective for harvesting and isolating microalgae from the culture medium, making it a valuable approach for industrial applications. This experiment the individual effects of each variable, their interactions, and their combined effects. The results showed that the separation efficiency increased significantly with increasing time and concentration of nanoparticles, and decreasing pH. The main aim was to determine the optimal conditions for nanomaterials concentration, harvesting time, and pH using Design Expert software. According to the results, achieving an efficiency of 90% requires a consistent concentration of 0.075 cationic flocculant, a pH of 4, a duration of 40 minutes, and a concentration of 3.5 g/L for Fe3O4/PACl nanoparticles. While the lowest efficiency, at 22%, was observed at pH 6.5 with a nanoparticle concentration of 0.5 g/L.

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