Optimization using response surface methodology for the sorptive removal of crude oil spills using a low-cost chitosan-poly(butyl acrylate) grafted copolymer

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ABSTRACT

In this study, the sorption of oil from seawater using chitosan grafted poly(butyl acrylate) copolymer was optimized using response surface methodology (RSM). The effect of various parameters such as time, initial oil concentration, temperature, sorbent dose, and agitation rate on the oil sorption capacity was investigated. Plackett–Burman design was utilized for screening the various sorption parameters. RSM was adopted to acquire the best sorption conditions of two chitosan derivatives namely; CS-g-poly(ButA10) and CS-g-poly(ButA20). In this respect, the Box–Behnken design was applied. A second-order-polynomial model indicated that the sorption was very useful and able to achieve highest sorption capacity ranged from 79.56 to 92.29 g/g using grafted chitosan derivatives compared to 35.2 g/g for native chitosan in 180 min, 41.23–50 g/L of oil concentration, 38°C–41°C at 155–160 rpm. These findings nominate the fabricated CS-g-poly(ButA10) sorbent as an effectual and promising oil sorbent for environmental control of crude heavy oil spills.

Keywords: Chitosan; Sorption; Optimization; Response surface methodology; Box–Behnken design

1. Introduction

The metallurgical and mechanical industries produce significant amounts of oily wastewater, which is usually expelled into nature due to the non-adaptation of the treatment processes [1]. Cleaning contaminated water resources is a great challenge to environmental scientists [2] as it possesses significant environmental threats to the aquatic system and may affect human life and devastates the economy [3]. Generally, spiled oil can appear in three different manners; immiscible mixture, unstable emulsion and secondary oil in water emulsion. The separation of oil in the first example is easy and requires physicochemical or mechanical processes [4,5].

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Among these existing methods, utilizing oil sorbent materials [6,7] becomes one of the best useful ways since they are efficient, economical, and provide easy oil recovery. Ideal oil sorptive material should have essential requirements such as low cost, high oil affinity, minimum water uptake, efficiency, recyclability and long-term biodegradability. So far, numerous sorbents such as straws [8], fibers [9], activated carbon [10], sponges [11] and organoclays [12] have been utilized for oil spills removal from the water surface. Besides, oil sorbents based-natural waste materials have considered natural resources for marine oil spill clean-up with low-cost production and high efficiency. However, the hydrophobic character and the little oil absorbency are the main drawbacks [13] with these natural sorbents.

Chitosan (CS) is a naturally cationic polysaccharide provided by the incomplete deacetylation of chitin elicited from the crustacean's shells. Chemically, it consists of regurgitated built-in units of ß-(1→4)-2-acetamido-2-deoxy-d-glucopyranose and ß-(1→4)-2-amino-2-deoxy-glucopyranose [14]. Chitosan has potential in many applications, including water treatment [15,16], medical and pharmaceutical [17]. Its unique features include a high concentration of hydroxyl and amino groups non-toxicity, bio-compatibility, bio-degradability, eco-friendly and easy modification. Nonetheless, CS has a lower interior surface area and can agglomerate in its natural form as gels. Also, the recycling complexity during the sorption process caused by their solubility in an acidic medium is a major disadvantage [18]. These obstacles lessen the rate of sorption and the maximum sorption capacity. However, it can be lessened by chemical and physical modification such as carboxymethylation [19], sulfonation [20], graft copolymerization [21] and Schiff base formation [22] to allow the creation of new functionalized derivatives having outstanding hydrophilic and hydrophobic characters [23,24].

Much attention has been given for developing oil sorbents-based chitosan in different forms including chitosan flakes, microspheres, powder, solution and chitosan grafted copolymer [3,25,26]. In addition, grafting of various monomers such as acrylamide, methyl methacrylate, N-isopropylacrylamide and acrylic acid onto the OH⁻ and amine groups on the CS structure via grafting copolymerization is an effective method [26] for enhancing the sorption properties. Grafting of CS can be achieved by numerous techniques like ring-opening, γ-radiation, free-radical and cationic polymerization. Recently, new derivatives based on chitosan structure, namely; chitosan-poly(butyl acrylate) grafted copolymer has been fabricated for oil spill removal [27,28].

The experimental design technique is a practical approach to designating several variables' interactions and relativistic significance [29]. The use of statistical designs such as Plackett–Burman and Box–Behnken for optimizing complicated processes can provide marvelous results [29,30]. Response surface methodology (RSM), which involves factorial design and regression investigation, intended to define the importance of singular factors and their interactive controls [1]. Central composite and Box–Behnken Designs are the most prevalent response surface methodologies. RSM can also decrease the number of laboratory trials required to estimate multiple

variables and their interactions [31]. For this research, RSM is a powerful technique as it exhibits statistical patterns employed to comprehend the correlation among the optimized variables [32,33].

This study aims to optimize the sorption process of crude oil spills on the fabricated chitosan grafted poly(butyl acrylate) copolymer. Factors influencing the sorption process such as time, initial crude oil concentration, sorbent dosage, agitation rate, and temperature will be optimized using a RSM to verify the optimum running oil spill sorption conditions with the least experimental trials.

2. Experimental

2.1. Materials

Shrimp shells were accumulated from marine restaurants in Alexandria (Egypt). N-butyl acrylate (ButA; 98%) and potassium persulphate (KPS; 99%) were provided by Sigma-Aldrich (Germany). Hydrochloric acid (HCl; 37%), sodium hydroxide (NaOH; 99%), acetic acid (CH₃COOH; 98%) and ethanol (C₂H₅OH; 99%) were obtained from El-Nasr Company (Egypt). Heavy land Egyptian crude oil was delivered from Belayim Petroleum Company (Egypt).

2.2. Methods

2.2.1. Preparation of chitosan-poly(butyl acrylate) graft copolymer

Firstly, chitosan was synthesized according to the previously published method [18]. In brief, chitin was initially extracted from the shrimp shells. After that, CS was obtained via deacetylation of chitin using NaOH. The concluding product was gathered and washed to exclude the extra NaOH. CS-g-poly(ButA) copolymer was fabricated according to our previous work [18,27,28], by dissolving CS in 2% acetic acid at 25°C followed by drop-wise addition of ethanol under vigorous stirring. KPS solution was added to the dissolved CS by elevating the temperature up to 60°C. Accurately, 10 and 20 mL of ButA were simultaneously injected slowly after 20 min with a supplementary portion of 0.05 g KPS dissolved in 5 mL distilled water. The produced precipitate was recovered upon centrifugation. The grafted copolymer was then washed with acetone and methanol using and dried at 50°C to exclude the ButA homopolymer. The native and grafted CS powders were then grounded and sieved to acquire a particle size <63 μm.

2.3. Batch oil sorption experiments

All the sorption experiments of heavy crude oil from the oil/water system were carried using 0.1 g adsorbent per 300 mL of artificial seawater (distilled water contains 3.5% NaCl) which was agitated in a shaker incubator at a speed of 100 rpm for an anticipated period at room temperature (25°C). Factors affecting the sorption such as the initial heavy crude oil concentration (8.33–50 g/L), contact time (10–240 min), sorbent dose (0.1–1 g), agitation rate (50–200 rpm) and temperature (25°C–40°C) were examined. The sorption capacity was calculated as stated by the standard method (ASTM F726-99) as follows [34]:

$$\text{Oil sorption capacity}\left(g \,/\, g\right) = \left(\frac{W_s - W_w - W_0}{W_0}\right) \qquad (1)$$

where W_s, W_w and W_0 are the weight of the saturated sorbent (water + oil + sorbent), the absorbed water's weight and the initial dry weight of the sorbent in-unit g, respectively. The quantity of absorbed water was concluded through the extraction separation using *n*-hexane as the solvent.

2.4. Plackett–Burman design

For screening purpose, various variables affecting crude heavy oil sorption capacity using CS, CS-g-poly (ButA10), and CS-g-poly(ButA20) have been evaluated. According to the Plackett–Burman factorial design, each factor was examined at two levels: –1 and +1 for a low and high level [35]. This design is employed, mostly when the researcher is handled with many variables and is unclear which settings are anticipated to be nearer to best responses [36]. Table 1 represents the factors under study in addition to levels of each factor used in the experimental design. Plackett–Burman experimental design is based on the first-order model:

$$Y = \beta_0 + \sum \beta_i x_i \qquad (2)$$

where Y is the response (crude heavy oil sorption capacity), β_0 is the model intercepts, β_i is the linear coefficient, and x_i is the level of the independent variable. This model does not specify the interaction amongst factors, but it is accepted to screen and assess the essential factors that control the response. The maximum number of variables that can be evaluated in one design is identical to the number of individual experiments minus one. In the present study, five parameters were screened in twelve experiments. All trials were analyzed in triplicate, and the mean of crude heavy oil sorption capacity was considered a response. The design matrix of this work is exhibited in Table 2. The consequences of the Plackett–Burman trial were analyzed by multiple regression analysis using the Microsoft Excel program.

2.5. Response surface methodology (Box–Behnken design)

A Box–Behnken design [37] was implemented to describe the nature of the RSM in the experimental region and displayed in Table 3, variables that had a positive effect and highest confidence levels were prescribed into three levels, coded –1, 0 and +1 for low, middle and high values, respectively. Table 4 describes the design matrix of a 27 trials experiment. A second-order-polynomial function was fitted to correlate the relationship among independent variables and response (crude heavy oil adsorption capacity) for prophesying optimal point. For the four factors, this equation is:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i X_i + \sum \sum_{i<j} \beta_{ij} X_i X_j \qquad (3)$$

where Y is the response, β_0, β_i, β_{ii}, and β_{ij} are the coefficient constants of the intercept, linear, quadratic and interaction terms respectively, x_i and x_j are coded independent

Table 1
Variables affecting oil sorption capacity process and tested levels for Plackett–Burman experiment

Variable	Variable code	Low level (–1)	High level (+1)
Time (min)	X_1	10	180
Initial oil concentration (g/L)	X_2	8.33	50
Temperature (°C)	X_3	25	45
Sorbent dose (g)	X_4	0.1	1
Agitation rate (rpm)	X_5	50	250

Table 2
Randomised Plackett–Burman experimental design for evaluating factors affecting oil sorption capacity using chitosan (CS), CS-g-poly(ButA10) and CS-g-poly(ButA20)

Trial	Time	Oil concentration	Temperature	Sorbent dose	Agitation rate	Sorption capacity (g/g)		
						CS	CS-g-poly(ButA10)	CS-g-poly(ButA20)
1	–1	–1	–1	+1	–1	0.19	0.37	0.65
2	–1	–1	+1	–1	–1	2.82	3.79	7.51
3	–1	+1	+1	+1	–1	3.95	5.85	10.53
4	–1	+1	–1	+1	+1	2.09	3.31	5.08
5	+1	+1	+1	+1	+1	10.99	15.5	21
6	–1	–1	+1	–1	+1	5.75	7.49	11
7	+1	–1	+1	+1	+1	7.53	10.06	18.18
8	+1	–1	–1	–1	+1	4.5	7.53	9.93
9	+1	+1	–1	–1	–1	6.99	9.64	17.68
10	+1	–1	–1	+1	–1	2.11	3.05	7.03
11	–1	+1	–1	–1	+1	4.29	5.75	6.95
12	+1	+1	+1	–1	–1	9.97	13.62	23.49

Table 3
Levels of variables chosen for the Box–Behnken optimization experiments

Variable	Variable code	−1	0	+1
Time (min)	X_1	10	60	180
Initial oil concentration (g/L)	X_2	8.33	33.33	50
Temperature (°C)	X_3	25	35	45
Agitation rate (rpm)	X_4	50	150	250

variable [38]. Experiments were achieved in triplicates, and the mean of crude heavy oil sorption capacity was regarded as a response. JMP program was adopted for analyzing the regression analysis of the experimental data obtained. The determination coefficient R^2 proved the fitting quality of the polynomial model equation. The optimal value of oil sorption capacity using chitosan (CS), CS-g-poly(ButA10), and CS-g-poly(ButA20) was calculated using the JMP program. The four most meaningful independent factors'

simultaneous effects on each response were visualized using a three-dimensional graph generated by Statistica 7.0 software [30].

3. Results and discussion

3.1. Preliminary experiments

The oil sorption rate is an essential key feature for the choice of oil sorbents. The correlation between the sorption time and oil sorption capacity is depicted in Fig. 1a. As inferred from the accomplished results, the oil sorption capacities of CS and the advanced hydrophobic-oleophilic grafted copolymers increased exponentially with rising the contact time up to 180 min, then start to diminish with further increase up to 300 min. It was clarified that the initial oil sorption rates are very fast so that the floating oil spills will be absorbed quickly by the prepared sorbents in several minutes upon the supplement to the artificial seawater. This behavior is because of van der Waals forces' interactions and the hydrophobic interaction, facilitating the diffusion of extra oil to the interior free sites

Table 4
Box–Behnken factorial experimental design, representing the response of crude heavy oil sorption capacity (g/g) as influenced by time, initial oil concentration, temperature and agitation rate for CS, CS-g-poly(ButA10), and CS-g-poly(ButA20), respectively

Trial	X_1	X_2	X_3	X_4	CS		CS-g-poly(ButA10)		CS-g-poly(ButA20)	
					Measured	Predicted	Measured	Predicted	Measured	Predicted
1	+1	0	0	−1	28.92	29.82	66.18	67.36	73.54	74.41
2	0	0	+1	−1	13.93	15.31	33	32.76	38.64	38.22
3	0	+1	+1	0	18.17	18.55	39.41	42.02	46	48.23
4	0	+1	−1	0	15.23	15.13	20.97	25.76	28.57	31.92
5	−1	−1	0	0	1.76	2.47	14.03	16.16	23.47	22.99
6	−1	0	+1	0	5.03	4.36	13.65	14.40	16.07	17.40
7	+1	0	+1	0	32	30.78	72.62	71.91	81.31	80.49
8	−1	+1	0	0	6.41	6.25	19.68	13.99	21.02	16.40
9	+1	+1	0	0	31.36	32.27	78.14	74.74	89.16	88.08
10	0	0	0	0	26.12	26.02	46	46.14	52	52.13
11	0	0	0	0	26.06	26.02	46.11	46.14	52.41	52.13
12	0	+1	0	+1	20.17	18.77	39	38.27	43.76	43.62
13	0	−1	−1	0	10.5	9.73	24.54	23.26	26	25.88
14	+1	0	−1	0	25.9	25.34	55.02	54.21	62.01	60.14
15	+1	−1	0	0	22	23.78	48	52.41	55	58.06
16	0	0	−1	+1	15	15.25	28.91	27.87	31.53	30.39
17	0	0	+1	+1	16	16.43	35.03	36.08	40	38.94
18	0	−1	0	+1	14.45	12.85	29.17	26.70	32	31.20
19	−1	0	0	−1	4.83	3.54	14.91	15.06	17	18.23
20	−1	0	−1	0	4.45	4.43	14.07	14.72	16.21	16.49
21	0	0	−1	−1	9.93	11.13	25.92	23.60	26	25.50
22	+1	0	0	−1	29.57	27.75	62.91	62.24	69.99	69.83
23	0	+1	0	−1	16	16.37	30.58	32.99	39.86	40.12
24	−1	0	0	1	5.28	6.71	15.53	17.53	16.99	19.26
25	0	−1	+1	0	11.97	11.68	27.83	24.37	32.07	30.82
26	0	−1	0	−1	9.84	10.01	23.72	24.39	29.5	29.10
27	0	0	0	0	25.89	26.02	46.32	46.14	51.99	52.13

[26]. Moreover, during the initial stage, a large number of vacant surface localities were available.

In contrast, after a lapse of time, the remaining vacant surface sites were difficulty packed attributable to the repellence forces amongst the oil molecules on the solid and bulk phases. With increasing contact time beyond 180 min, the diffusion becomes more difficult as the vacant volume within the adsorbent decreases. Thus, the affinity of sorbent towards oil molecules decreased. Besides, the desorption process could occur, which cause a reduction in sorption

capability. This investigation is consistent with the findings of other authors [15,39].

Indeed, the impact of the primary sorbent dosage is an essential feature in extensive scale application. The consequence of the sorbent amount on the sorption capacity was studied (0.1–1 g), with an initial oil concentration of 16.67 g/L at 25°C (Fig. 1b). The figure revealed a sharp drop in the sorption capacity befalls with the increase in the sorbent mass. This decline is fundamentally attributable to the residual unsaturated active sites during the
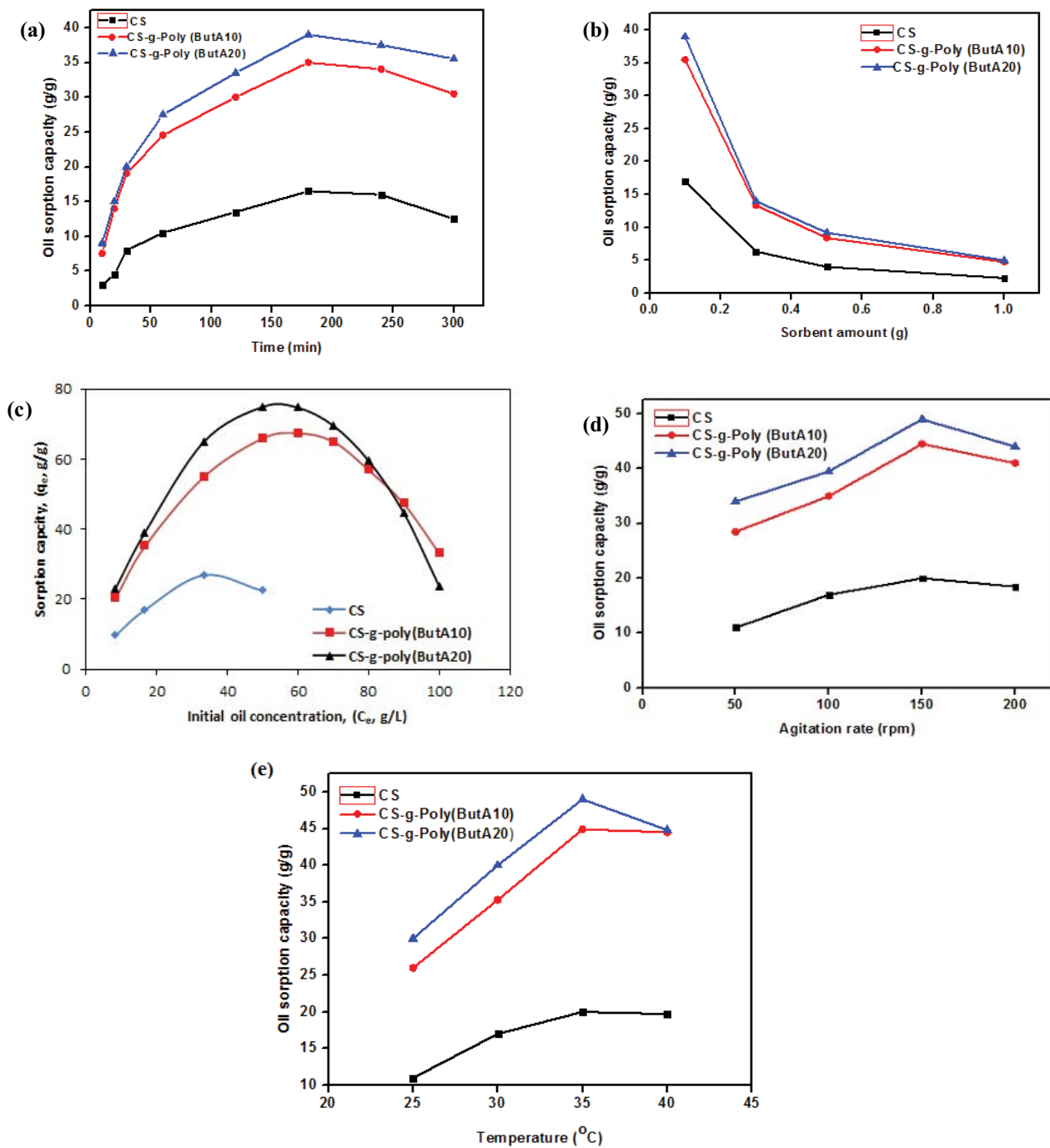

Fig. 1. Effect of various parameters on the crude oil sorption capacity.

process. This observation agreed with other relative publications [40,41].

Besides, Fig. 1c reveals the relation between the initial oil concentration and the sorbed amount by the CS and its grafted forms. The plots explain that oil's sorption improves with increasing the initial oil concentration up to a certain level and attains equilibrium. Further, increase in the oil concentration above 60 g/L leads to a decrease in the sorption capacity. The oil sorptive capacity increases dramatically after the modification with ButA owing to the presence of hydrophobic groups from ButA [26]. Furthermore, grafted poly(ButA) is oleophilic, and its incorporation onto CS makes lipophilic copolymer. Indeed, at higher concentration, the gradient between the bulk solution and the center of sorbent particle improves oil residue distribution through the film surrounding the particle and in the interior network of the prepared sorbents, as well, high sorption rate and proper consumption of available vacant sites [39].

Furthermore, Fig. 1d investigates the significance of altering the shaking speed from 50 to 200 rpm on the sorption capacity. The obtained results demonstrate that increasing the shaking rate up to 150 rpm has a positive result on the sorption capacity of CS and the grafted copolymers; where, it increased from 11 to 18.5, from 28.4 to 41, and from 34 to 44 g/g for CS, CS-g-poly(ButA10) and CS-g-poly(ButA20), respectively. These results could be ascribed to the enhancement in oil dispersion and increase the exposed sorbent surface area to the spiled oil. Additionally, raising the agitation rate improves the diffusion of oil towards the sorbent surface [42]. In contrast, a further rise in the agitation velocity up to 200 rpm creates a decline in the sorption affinity. This decline could be due to a further speedup in the agitation rate beyond 150 rpm, which could increase the process of the oil–water emulsion and, consequently, diminish the attraction forces between the sorbent and oil surface and promote the occurrence of the oil desorption process. This investigation is matched with other published results [43].

Moreover, the oil adsorption process's performance for all adsorbent samples was evaluated under different adsorption medium temperatures ranged from 25°C to 40°C, as explained in Fig. 1e. It was understandable from the results that the adsorption capacity was enhanced by increasing temperature from 25°C to 35°C, decreasing with a further acceleration of temperature to 40°C. These consequences could be described by promoting the segmental movement for all analyzed adsorbents. The distribution rate of oil spill molecules into the adsorbent surface enhanced with raising the temperature to 35°C. The increase of temperature exceeding 35°C (up to 40°C) could accelerate the adsorption medium's Brownian motion rate. More energy is required to hold the oil molecules onto the adsorbent surface [44]. Hence, high temperature induces less oil attachment on the adsorbent surface, and the oil desorption process could occur. Furthermore, the oil viscosity drop at raised temperatures and the oil solubility increased, so, the adsorption capacity values decrease consequently [44,45].

3.2. Plackett–Burman design

Plackett–Burman design was practiced using five variables affecting oil sorption capacity (Fig. 2). Values of sorption capacity using CS, CS-g-poly(ButA10), and CS-g-poly(ButA20) ranged through trials from 0.19 to 10.99 g/g, 0.37 to 15.5 g/g and 0.65 to 23.49, respectively as exhibited in Table 2. The main consequence of the five studied variables on sorption capacity was estimated and presented graphically (Fig. 1). Analysis of the regression coefficients showed that time, oil concentration, temperature and agitation rate positively impacted the oil sorption capacity; however, sorbent dose had a negative influence. The polynomial model describing the correlation between the five factors and sorption capacity is presented as:

$$Y = 5.098 + 1.917X_1 + 1.282X_2 + 1.737X_3 - 0.622X_4 + 0.76X_5 \quad (4)$$

$$Y = 7.163 + 2.737X_1 + 1.782X_2 + 2.222X_3 - 0.807X_4 + 1.11X_5 \quad (5)$$

$$Y = 11.586 + 4.633X_1 + 2.536X_2 + 3.699X_3 - 1.174X_4 + 0.438X_5 \quad (6)$$

The variance analysis using analysis of variance (ANOVA) test was estimated and summarized in Table 5 which declare that there is a statistically significant
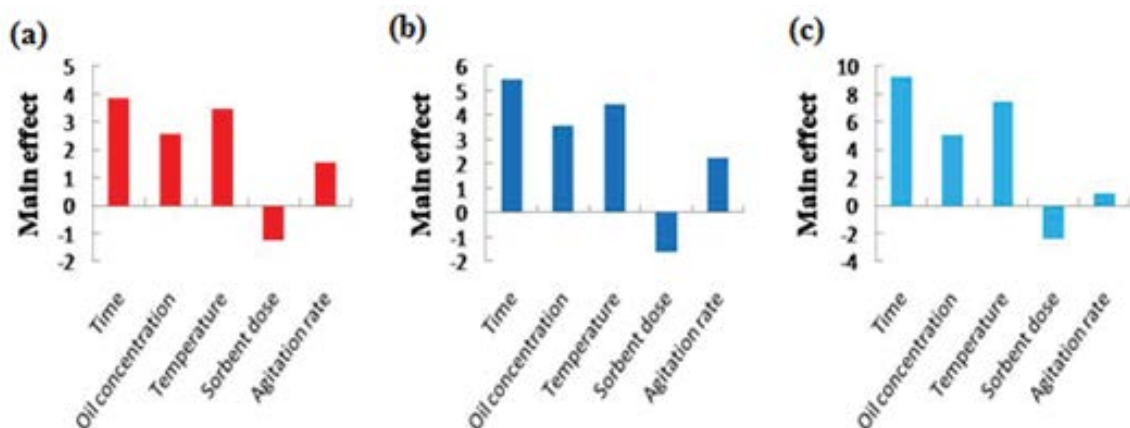
Fig. 2. The main effect of the five studied variables on the sorption capacity by Plackett–Burman design using (a) CS, (b) CS-g-poly(ButA10) and (c) CS-g-poly(ButA20).

Table 5
Analysis of variance (ANOVA) for Plackett–Burman experiments for crude oil sorption by CS, CS-g-poly(ButA10) and CS-g-poly(ButA20)

Source	Degree of freedom	Sum of squares	Mean square	F-ratio	P-value
CS[a]					
Regression	5	111.556	22.311	20.925	0.00098
Residual	6	6.397	1.066		
Total	11	117.953			
CS-g-poly(ButA10)[b]					
Regression	5	209.787	41.957	27.407	0.00046
Residual	6	9.185	1.531		
Total	11	218.973			
CS-g-poly(ButA20)[c]					
Regression	5	517.733	103.546	34.133	0.00025
Residual	6	18.202	3.035		
Total	11	535.934			

[a]R-squared = 0.945; Adjusted R-squared = 0.9;
[b]R-squared = 0.958; Adjusted R-squared = 0.923;
[c]R-squared = 0.97; Adjusted R-squared = 0.94.

relation amongst the variables. The R-squared and adjusted R-squared values also specify that the model is best fitted. According to the results acquired by Plackett–Burman design, the following conditions are anticipated to be adjacent optimum: time, 180 min; oil concentration, 50 g/L; temperature, 45°C; sorbent dose, 0.1 g and agitation rate, 250 rpm. Sorption capacity of oil achieved using CS, CS-g-poly(ButA10), and CS-g-poly(ButA20) at these conditions was 19.41, 42.69 and 58.99 g/g, respectively.

Based on the anticipated coefficients, t-values and P-values; time, oil concentration, temperature and agitation rate were selected for further optimization since these factors had the most notable responses on the sorption capacity. The variable of sorbent dose that had a significant negative effect was not incorporated in the next optimization experiment but instead was used in all trials at its (–1) level.

3.3. Response surface methodology (Box–Behnken design)

According to Plackett–Burman design results, the four most significant variables influencing oil sorption capacity were studied at three levels with 27 trials to complete RSM using Box–Behnken design. Data were investigated using a linear multiple regression analysis methods. Syuhada et al. [46] used Box–Behnken design to reach the optimum conditions for removing oil by banana peel as biosorbent. They considered the effect of time, sorbent dose, and oil concentration on the adsorption capacity. Others optimized adsorption conditions concluded time, sorbent dose, and salinity to eliminate petroleum compounds from the marine environment using modified activated carbon fiber by RSM [47].

At the model level, the correlation measures for evaluating the regression equation are the multiple correlation coefficients R and the determination coefficient R^2.

When R's value is closed to 1.0, this indicates that the correlation among the measured and the prophesied values are the better. In this investigation, the value of R was 0.994, 0.992 and 0.997 for oil sorption capacity using CS, CS-g-poly(ButA10), and CS-g-poly(ButA20), respectively. The value of the determination coefficient $R^2 = 0.989$ for CS, 0.984 for CS-g-poly(ButA10) and 0.994 in case of CS-g-poly(ButA20), being a measure of the model fitness, indicates that about 1.1, 1.6 and 0.6% of the total variations are not explained for oil sorption capacity (g/g) using CS, CS-g-poly(ButA10), and CS-g-poly(ButA20), respectively.

The multiple linear regression models illustrate the relationship between oil sorption capacity and four independent variables. The ANOVA results for oil spill removal using the prepared sorbents is defined in Table 6. The ANOVA of these sorbents revealed that the model is highly significant as established from F-ratio's value and the very low probability P-value (P-value < 0.01) [1,48].

Three-dimensional plots (generated by Statistica 7.0 software) were drawn to know the interaction between different variables affecting oil sorption capacity. These show that higher levels of oil sorption capacity using CS, CS-g-poly(ButA10) and CS-g-poly(ButA20) were achieved with increasing of time, oil concentration and temperature where a moderate agitation rate maintains a high level of the sorption capacity (Figs. 3a–c). These effects were related to the results achieved by Alam et al. [49] they reported that maximum adsorption capacity of 2,4-dichlorophenol using activated carbon was obtained at a maximum time and the higher concentration of a 2,4-dichlorophenol solution with a moderate agitation rate. For divining the optimal point, a second-order polynomial function was tailored to the laboratory results (linear optimization algorithm) for oil sorption capacity using CS, CS-g-poly(ButA10), and CS-g-poly(ButA20), respectively.

Table 6
Analysis of variance (ANOVA) for Box–Behnken experiments for crude oil sorption by CS, CS-g-poly(ButA10), and CS-g-poly(ButA20)

CS[a]

Source	Degree of freedom	Sum of squares	Mean square	*F*-ratio	*P*-value
Regression	14	2,186.424	156.173	78.831	1.35×10^{-9}
Residual	12	23.773	1.981		
Total	26	2,210.197			

CS-g-poly(ButA10)[b]					
Regression	14	8,852.84	632.345	54.229	1.21×10^{-8}
Residual	12	139.926	11.661		
Total	26	8,992.767			

CS-g-poly(ButA20)[c]					
Regression	14	10,907.61	779.115	139.398	4.66×10^{-11}
Residual	12	67.069	5.589		
Total	26	10,974.68			

[a]*R*-squared = 0.989; Adjusted *R*-squared = 0.976;
[b]*R*-squared = 0.984; Adjusted *R*-squared = 0.966;
[c]*R*-squared = 0.993; Adjusted *R*-squared = 0.986;

$$Y = 26.023 + 11.833X_1 + 3.068X_2 + 1.341X_3 + 1.310X_4$$
$$+ 1.178X_1X_2 + 1.38X_1X_3 - 0.275X_1X_4 + 0.368X_2X_3$$
$$- 0.110X_2X_4 - 0.750X_3X_4 - 3.685X_1^2 - 6.142X_2^2$$
$$- 6.110X_3^2 - 5.384X_4^2 \qquad (7)$$

$$Y = 46.143 + 24.250X_1 + 5.041X_2 + 4.342X_3 + 1.898X_4$$
$$+ 6.123X_1X_2 + 4.505X_1X_3 + 0.6625X_1X_4 + 3.788X_2X_3$$
$$+ 0.743X_2X_4 - 0.240X_3X_4 + 1.570X_1^2 - 8.389X_2^2$$
$$- 8.901X_3^2 - 7.165X_4^2 \qquad (8)$$

$$Y = 52.133 + 26.688X_1 + 5.861X_2 + 5.314X_3 + 1.403X_4$$
$$+ 9.153X_1X_2 + 4.860X_1X_3 + 0.890X_1X_4 + 2.84X_2X_3$$
$$+ 0.350X_2X_4 - 1.043X_3X_4 + 1.834X_1^2 - 7.586X_2^2$$
$$- 10.336X_3^2 - 8.536X_4^2 \qquad (9)$$

For CS, the optimal levels of the four factors (180 min; 41.23 g/L (oil concentration); 38°C and 155 rpm) were derived from the maximum point polynomial model and computed using the JMP program. The predicted value of sorption capacity using CS equal to 35.2 g/g. In the case of CS-g-poly(ButA10), the four variables' optimal levels were 180 min; 50 g/L (oil concentration); 42°C and 170 rpm with predicted adsorption capacity equivalent to 79.56 g/g. The optimal levels were 180 min; 50 g/L (oil concentration); 41°C and 160 rpm with predicted sorption capacity of 92.29 g/g in case of CS-g-poly(ButA20). Behnood et al. [50] used raw bagasse for the adsorption of crude oil from saline wastewater and optimized the conditions affecting adsorption capacity using RSM. They found that a temperature of 46.53°C was the best temperature for oil removal that was closed to the estimated optimum temperature for oil sorption capacity using CS-g-poly(ButA10) and CS-g-poly(ButA20) in this study. While Nwokoma and Anene [51] reported that the optimum crude oil adsorption temperature for using meshed groundnut husk ranged between 25°C to 45°C.

3.4. Verification of the model

A verification experiment was carried out under predicted optimal condition as determined previously to define the quadratic polynomial accuracy. The % accuracy was calculated from the following formula:

$$\text{Accuracy} = \frac{Y_{\text{Experiment}}}{Y_{\text{Calculated}}} \times 100 \qquad (10)$$

Sorption capacity achieved experimentally using CS, CS-g-poly(ButA10), and CS-g-poly(ButA20) was 37.39, 78.21 and 90.45 g/g, respectively. This implies that the calculated model accuracy was 106.2%, 98.3% and 98.01%, respectively.

4. Conclusion

The possibility of using chitosan grafted copolymer as a natural sorbent for the removal of crude oil spillage had been investigated in this study. The optimal levels of the most four influential factors identified from Plackett–Burman factorial design were sequentially specified through the RSM employment. The quadratic model applied in this research indicates a high correlation between experimental and predicted results. Additionally, the ANOVA analysis illustrates a high determination coefficient values ($R^2 \sim 1$), verifying an adequate adjustment of the second-order regression model with the experimental data. The obtained optimal levels from the maximum point of the polynomial model were evaluated and determined to be 180 min, 41.23–50 g/L, oil concentration, 38°C–41°C, and 155–160 rpm.
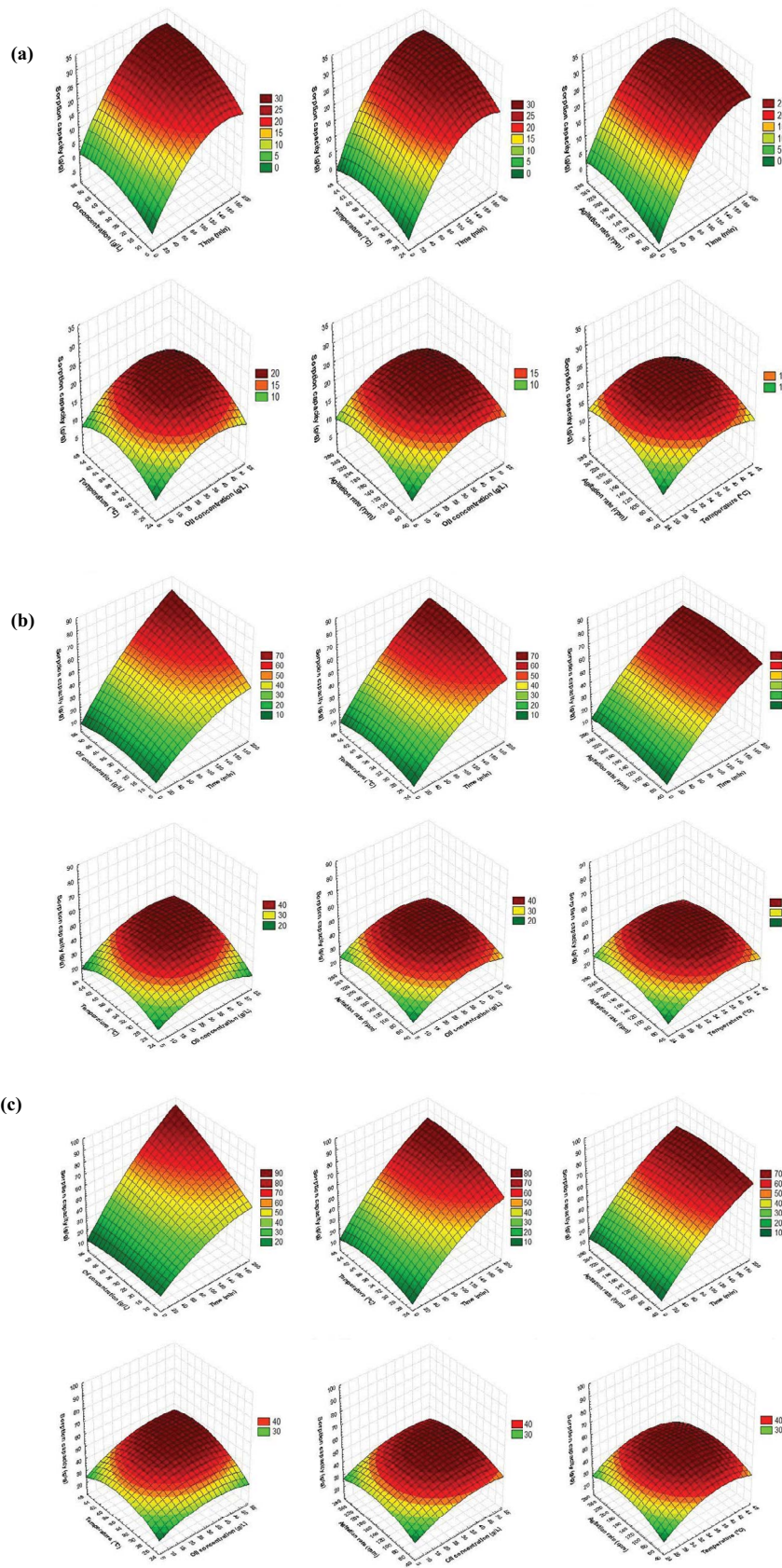
Fig. 3. Three dimensional response surface plots of oil sorption capacity using (a) chitosan (CS), (b) CS-g-poly(ButA10), and (c) CS-g-poly(ButA20).

Further, grafted copolymers showed the highest maximum sorption capacity, that is, 79.56 and 92.29 g/g for CS-g-poly(ButA10) and CS-g-poly(ButA20) copolymer compared to 35.2 g/g for native CS at the optimum levels. These observations demonstrated that the easy and low-cost fabricated superoleophilic chitosan-poly(butyl acrylate) grafted sorbent is a promising substitute for the conventional oil adsorbents. It can also be applied efficiently in a large-scale for removing the spilt crude oil from seawater surface.

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