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Research Article

Application of Taguchi Method in the Optimization of Parameters in the Synthesis of Graphene/Cotton Nanocomposite: An Antibacterial Agent

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Abstract

The purpose of this paper is to optimize the coating process nano graphene particles on cotton using the Taguchi method. Optimization of experimental parameters, including graphene oxide (GO) concentration, the dosage of sodium borohydride ($NaBH_4$), dosage of calcium chloride ($CaCl_2$), and time was performed by applying the Taguchi method of experimental design (L9 orthogonal array). Analysis of variance (ANOVA) was also investigated to find the significance and percentage contribution of each factor. Reaction at room temperature performed. The synthesized nanocomposite was characterized using a scanning electron microscope (SEM), Fourier transforms infrared spectroscopy (FTIR) and X-Ray diffraction (XRD). The Taguchi method was preferred over the factorial method, another design option for optimizing phenomena. Minimal chemical consumption, cost reduction, increase of product efficiency and stability by optimizing the reaction parameters are the advantages of using Taguchi method in this article. The synthesized nanocomposite has antibacterial properties and has a high potential for a wide range of medical and pharmaceutical applications.

Keywords: Graphene Oxide; Cotton; Factorial Method; Optimization; Taguchi Method; Antibacterial

Introduction

Graphene cotton is a nanocomposite of graphene and cotton. Graphene is the only allotropy of carbon in which each carbon is joined to adjacent carbon atoms. Graphene has various forms such as nanosheets, nanoplates, graphene nanoribbons, and 3D graphene [1,2]. Owing to high specific surface area, high porosity, excellent elasticity, and high chemical stability, it is considered an attractive nanomaterial [3]. Graphene find a variety of applications when coatings on different materials, such as fibers [4], metal meshes [5], textiles [6], membranes [7], foams [8], and gauze [9].

Cotton is the purest form of cellulose. Its fibers are non-toxic, lightweight, and eco-friendly [10]. It is a suitable selection for changing graphene to a 3D framework [11]. Pretreatment of fibers with some solutions such as NaOH helps with the easy penetration of the nanoparticles into the surface [12 -20]. Naturally, there are several kinds of reducing agents such as HI, hydrazine derivate, Al, vitamin C, $NaBH_4$ in coating process. To increase the reducing ability, a catalyst is used. $AlCl_3$ and $CaCl_2$ was used as a catalyst [21,22].

The synthesis of a product should be accompanied by the optimization process to increase performance. Taguchi design is one of the experimental design techniques. It is useful for the simultaneous optimization of multiple variables (independent factors) to achieve the best response (dependent factor) within the minimum number of observations [23]. It was successfully applied to improve different fields of industry [24]. Taguchi design analyzes the results using a signal-to-noise (SN) ratio [25,26]. The signal and noise represent the desirable and undesirable values for the output characteristic, respectively. In other words, a signal is an easy to control variable and noise is difficult to control variable. The variability can be expressed by signal-to-noise (SN) ratio [27]. In this research, graphene was used to coat cotton. Operating parameters, including GO concentration, amount of reagent reduction, catalyst dosage, and contact time were optimized using the Taguchi experimental design. For the analysis of the experimental data, analysis of variance (ANOVA) was effectively used.

Instead of having to test all possible combinations like the factorial method, the Taguchi method tests pairs of combinations [28]. The product of this study a carbon-based nanocomposite that acts as a hydrophobic adsorbent with minimum cost and high efficiency [29].

In 2010 reported Graphene oxide (GO) possessed excellent antibacterial. GO can act as a terminal electron acceptor for bacteria [30].

Experimental Study

Material

Cotton was obtained locally. Powder-like graphite with purity 99.9% was purchased from Sinopharm chemical Reagent Co., China. H_2SO_4 (98%), $KMnO_4$ (99.9%), H_2O_2 (30%), NH_4OH (25%), NaOH (analytical grade), CH_3COOH (99.5%), $NaBH_4$ (99.9%), and $CaCl_2$ (99.99%) were provided by Merck Co., Ltd.

Apparatus and software

Fourier transform infrared (FTIR) spectrometer (Thermo Scientific Nicolet 8700) was used to compare functional groups of cotton and graphene coated cotton. FTIR analysis was performed in the range of 400 - 4000. Scanning electron microscope (SEM) (KYKY-EM 3200, SN.01, 25 KV, 1.00KX.10μm, gold coating) was applied to observe the morphology of the surface. To indicate the pattern of nanoparticles synthesized on cotton, X-ray diffraction (XRD) patterns were obtained using a D/Max-2400 X-ray diffractometer. The MINITAB-16 was employed to implement the Taguchi method.

Preparation of graphene oxide

GO was synthesized from graphite powder by a modified Hummers method [31]. Briefly, concentrated H_2SO_4 was poured into a 250 mL volumetric flask, which filled with graphite. Then, $NaNO_3$ was added into the solution. Afterward, solid $KMnO_4$ was gradually added with stirring while the temperature of the mixture was kept below 20ºC. The temperature was increased to 30ºC and excess distilled water was added to the mixture. The temperature was then increased to 80ºC. Finally, 30% H_2O_2 was added to change the color of the mixture to brilliant yellow. The mixture was filtered and washed several times with 5% of HCl and repeatedly with deionized water until a pH of 5 - 6 was achieved [32,33].

Nanocomposite synthesize

Cotton pretreatment

The used cotton fibers were immersed in five different concentrations of NaOH solution (1% to 5%) and kept for 1 to 4 h. Then, the swollen cotton was washed with 10% acetic acid solution and distilled water until the pH level neutralized.

Preparation of coated cotton with graphene

A piece of cotton was first soaked in 4% NaOH solution for 1 h. Then, the swollen cotton was washed with 10% acetic acid solution and distilled water until the pH level neutralized. The obtained cotton was put in a 50 mL of GO dispersed solution (0.05 g/L). Then, 0.5 g $NaBH_4$ as a reduction agent and 0.02 g $CaCl_2$ as a catalyst was added. The mixture was stirred at room temperature for 1 h to obtain RGO. This work is carried out in different concentrations of GO, reducer, and catalyst, as well as time from 15 to 90 min. Finally, the obtained graphene coated cotton was washed several times with distilled water and dried in a drying oven at 60 ºC.

Experiment design

Four factors including GO concentration, reagent reduction, catalyst and time are considered at three levels. With these four factors, in the factorial experimental design 81 experimental units i.e. 3 * 3 * 3 * 3= 81, comprehensive interactions are checked. While the experimental unit of the same study using the Taguchi design method has been reduced to one-ninth. Therefore, The Taguchi method not only helps considerably in saving of time and cost, but also leads to a fully developed process and provides systematic, simple and efficient approach for the optimization of the near optimum design parameters [28].

In Taguchi method, the SN ratio is estimated to change the output response of the analysis. In this study, the optimization of the stability percentage of graphene loaded on cotton is measured from the SN ratio value. There are three categories of the output characteristics in the analysis of the SN ratio, i.e. the lower-the-better (LB), the higher-the-better (HB) and the nominal-the-better (NB) [34]. Here, SN ratio was chosen "larger-the-better". Namely, the aim of the work was to maximize the response. Moreover, ANOVA was performed to analyze the significance of the process variables than the output characteristic. By analyzing the SN and ANOVA, the optimal experimental condition was evaluated.

Results and Discussion

Characterization

SEM analysis

The morphology of graphene nanoparticles deposited on the cotton fiber surface is illustrated in figure 1a and 1b. The figure 1a refers to raw cotton, which is porous and possesses 3D networks. The surfaces of the cotton are relatively smooth. After coating raw cotton with graphene, the skeletons of the network exhibit rough texture associated with the presence of graphene sheets (Figure 1b). This indicates graphene sheets were assembled around the raw cotton skeletons during the reduction process. The image shows that this composite consists of homogeneous cotton fibers interlayer sandwiched between r-GO lamellas, where good compatibility is achieved in this typical "sea- island" (r-GO as the sea and cotton as island) morphology [36,38-40]. The primary particle size is estimated to be less than 81 nm.

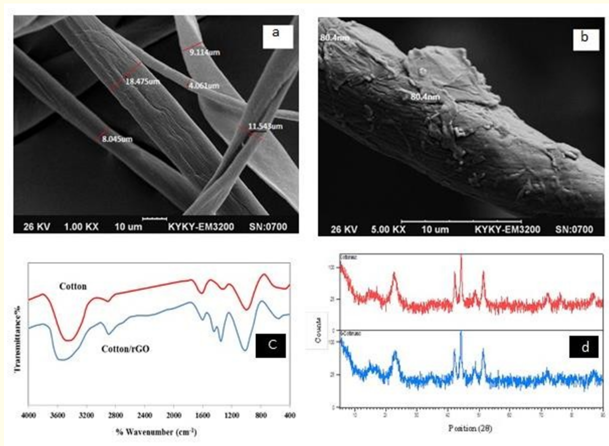

Figure 1: Comparison of Characterization of cotton and graphene coated cotton: (a), (b) SEM, (c) FTIR spectra and (d)X-ray diffraction patterns.

FTIR analysis

Figure 1c exhibits two FTIR spectra of raw cotton and graphene coated cotton. The spectral analysis was performed to reveal the reactive site during in situ synthesis and examine the interaction between graphene oxide (GO) nanoparticles and cotton fabric. In cotton spectrum, the weak band at 2898.64 cm^{-1} is assigned to C–H stretching vibration of cellulose. The peak at 3299.96 cm^{-1} is corresponding to stretching vibrations of hydroxyl groups of cellulose [38]. In the cotton/rGO spectrum, the bond of hydroxyl groups of cellulose transferred to higher wavenumber (3307.80cm^{-1}).

XRD analysis

The XRD pattern of the cotton and graphene coated cotton nanocomposite are illustrated in figure 1d. In the XRD pattern of cotton, well- defined peak near $2\theta=15.19^\circ$, 16.85°, 20.57°, 22.71°, 37.30° related to the (101), $(10\bar{1})$, (021), (002) and (040) planes, respectively. In the XRD spectrum of graphene coated cotton sample is significantly reduced in intensity when compared to cotton. On the other hand, the intensity ratio of cotton band to the graphene coated cotton was 1.26, which demonstrated that the average size of the crystalline cotton decrease after coating. Also, band of graphene oxide shifted from 11.55° to 23.03°, indicating a considerable reduction of graphene oxide (r-GO) was achieved on the cotton [39].

Bactericidal activity

Figure 3 shows SEM images of E.coli growth on cotton and Cotton-GO, 4h incubation at 37°C. It also shows E. coli cells before and after incubation with GO for 2h.

Results of Taguchi method

Statistical analysis

The 4% NaOH for 1 hour showed the best pretreatment for cotton. NaOH treatment leads to the formation of new Na-cellulose-I lattice, a lattice with large intervals between the cellulose molecules. These spaces are filled with water molecules. In this structure, the OH-groups of the cellulose are converted into ONa-groups, expanding the dimensions of molecules. Subsequent rinsing with water will remove the linked Na-ions and convert the cellulose to a new crystalline structure. Cellulose-II, which is thermodynamically more stable than cellulose-I [14]. The data obtained indicate that alkaline treatment increases the surface area. Moreover, it destroys the intermolecular hydrogen bonds and helps nanoparticles for penetrating the surface. Adhesive bond quality was improved remarkably by this treatment [33].

The four independent process factors (GO concentration, reagent reduction, catalyst, time) and their corresponding levels for the present study are given in table 1. Table 2 presents the experimental design matrix along with the mean coating values and the calculated SN ratio. It can be concluded that the GO concentration with 34.657% of contribution and time with 32.859% of contribution, have the greatest effect among the factors. Conversely, the effect of reagent reduction can be ignored. Table 3 presents the ranking of the parameters based on the delta values (the difference of the SN ratio values between the highest and the lowest levels of process factors).

Process parameter	GO concentration (g)	Reagent reduction (g)	catalyst (g)	Time (min)
Level 1 (L1)	0.025	0.500	0.01	30
Level 2 (L2)	0.050	0.570	0.02	60
Level 3 (L3)	0.075	0.687	0.03	90

Table 1: Levels for the various parameters studied to produce graphene coated cotton.

Table 4 expresses that the GO concentration with 34.657% of contribution and time with 32.859% of contribution have the greatest effect among the factors.

Contour plot

Figure 2 displays the contour graphs of the interaction of two factors simultaneously. According to the previous results, the concentration of GO had the greatest effect, so in this figure, three graphs, including the interaction of GO and time, GO and reducing agent, as well as GO and catalyst are presented. The normal distribution in figure (a) is greater than the other ones. Therefore, the time has the most effect on the coating efficiency after GO concentration.

Run no.	Sample	Parameters					
		GO (g/L)	Reagent reduction (g)	Catalyst (g)	Time (min)	Coating (%)	SN ratio
1	S1	0.025	0.500	0.01	30	94.20	39.48
2	S2	0.050	0.570	0.01	60	59.50	35.49
3	S3	0.075	0.687	0.01	90	97.50	39.78
4	S4	0.025	0.570	0.02	90	77.60	37.79
5	S5	0.050	0.687	0.02	30	82.50	38.33
6	S6	0.075	0.500	0.02	60	89.20	39.00
7	S7	0.025	0.687	0.03	60	80.10	38.07
S	S8	0.050	0.500	0.03	90	91.90	39.26
9	S9	0.075	0.570	0.03	30	98.10	39.83

Table 2: L9 orthogonal array design matrix along with the mean conversion values and the SN ratios.

Level	Reagent reduction amount (g)	GO (g/L) concentration	Catalyst amount (g)	Contact time (min)
1	38.25	38.45	39.25	39.21
2	38.37	37.69	37.70	37.52
3	39.05	39.54	38.72	38.94
Delta	0.80	1.85	1.55	1.69
Rank	4	1	3	2

Table 3: Response table for SN ratio.

Factor	DOF (f)	Sum of Sqrs. (S)	Variance (V)	F-ratio (F)	Pure Sum (S^2)	Contribution C (%)
Reagent reduction (g)	2	1.124	0.562	1.74	1.124	7.473
GO (g/L)	2	5.214	2.607	0.88	5.214	34.657
Catalyst (g)	2	3.763	1.881	0.24	3.763	25.009
Contact time	2	4.944	2.472	1.50	4.944	32.859

Table 4: Analysis of variance (ANOVA) results of Taguchi design for coating yield.

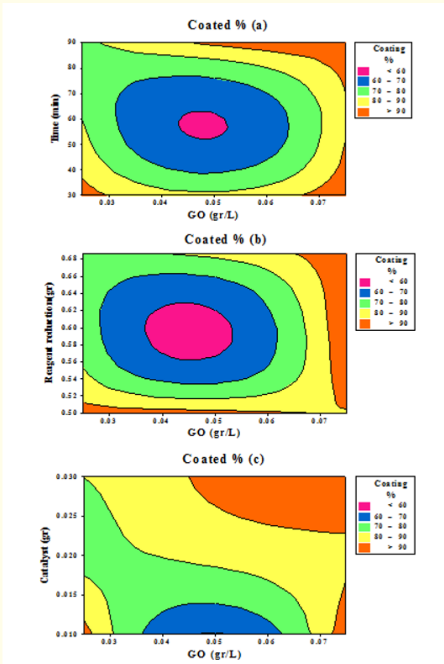

Figure 2: Contour graphs related to the effect of (a) GO and reaction time, (b) GO and reducing agent, (c) GO and catalyst on the percentage of covering.

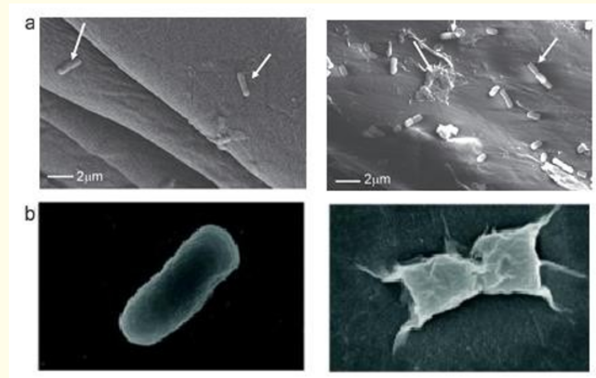

Figure 3: SEM images of a- E. coli growth on cotton(Left) and graphene cotton(Right) 4h incubation at 37ºC b- *E. coli* in the absence(Left) and after incubation with GO dispersions (40 μg mL−1) for 2 h (Right).

Bactericidal activity

The antibacterial effect of graphene and substrates containing graphene nanoparticles has been proven by scientific evidence and articles. Figure 3 shows that the bacteria are flattened, have lost their cell integrity by GO.

Therefore Graphene oxide (GO) is an excellent bacteria-killing nanomaterial. Antibacterial tests show that cotton containing GO has strong antibacterial properties and even after repeated washing can inactivate almost one hundred percent of bacteria [33].

Conclusion and Recommendations

In this study, graphene coated cotton was successfully synthesized. The characterization of this nanocomposite was investigated using FTIR, XRD, and SEM methods. Experimental design (Taguchi) was used to obtain the optimum conditions for coating rate. These parameters include GO concentration, amount of reagent reduction, the dosage of catalyst, and time. Taguchi results were analyzed based on choosing the best run by examining the SN and delta. Results of ANOVA demonstrated the GO concentration and time were the essential effects among the other factors.

These results were possible in the design of factorial experiments with 81 experimental units. While this study, through Taguchi, similar results were obtained with only 9. Taguchi wills effects of many factors to study the influence of individual factors to determine which factors has more influence. So in terms of cost and time, this result is a significant advantage for researchers. The Taguchi has good potential in examining the effective parameters in the manufacture of medical and pharmaceutical products because it is simple, fast, cheap [43,44].

Antimicrobial substrates used in medical products, including filters and masks, have gained a lot of fans in recent years. Graphene cotton is an example of this and has significant performance in both the medical, pharmacology and non-medical fields [44].

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