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Development of Optical Chemical Sensor Based on Pararosaniline in Sol-Gel Matrix for Detection of Formaldehyde in Food Samples

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ABSTRACT

Optical chemical sensor based on immobilesed pararosaniline into sol-gel matrix tetraethyl orthosilicate (TEOS) is a simple tool that can be used to detect the presence of formalin (formaldehide) in food. Pararosaline in sol-gel matrix was developed when contacted with food sample that contains formalin. The optical signal was produced by changing color from purple to yellow, that can be used to detect quantitative formaldehide in sample. The results, chemo sensor optic, have characteristic, maximum wave length 576.42 nm, with linier range 0 - 100 ppm, linearity coefficient R^2 = 0.999, limit detection (LOD) 0.504 ppm, limit of quantification (LOQ) 1.680 ppm, sensitivity 0.087, disturbed matrix selectivity 1.716 %. The optimum is operational at pH 4, and response time at 150 seconds of 2 ppm. This sensor can be used to detect formalin in food sample in a simple mode and reusable for 4 times application. In addition, the sensor can be regenerated using an acid 0.1 M HCl.

Keywords: Optical Chemical Sensor; Formaldehide; Pararosalin; Sol-Gel; Food Sample

1. Introduction

Some of food in public marketed discovered contains formaldehyde or usually familiar formaldehyde [1]. Formaldehyde is a very dangerous chemical in human health; It gives negative effect to respiration channel, liver and kidney function, and reproducing system [2,3]. Based on the moment conditions, detecting process of formaldehyde in food, conducting by laboratory process, used GC, HPLC and spectrometry instrument. The weakness methods of the mentioned impracticably cannot be prepared out of laboratory and need skilled persons who have backgrounds in chemistry specialty. In addition, such methods are not suitable to be employed in the fields [4]. Therefore, there is an acute need to develop new and inexpensive methods of assessing the formaldehyde contain in food, particularly those that can be employed in the field. The alternative methods to detecting formaldehyde in food have simple process, low cost, and easy to operate by general society [5,6].

In this respect, the chemical sensor represents tools used for simple, quick and low-cost to detect of formaldehyde in food [7-11]. Developing simple specific optical sensor of formaldehyde is very urgent to give solutions to problems in general public to detect formaldehyde contained in food. The detection of formal-dehyde in food has been proposed using spectrometric [7,11]. Pararosaniline is one of the specific reagents to detect formaldehyde, and the reaction between pararosaniline and formaldehyde is presented in **Figure 1**, next page [5,12].

The optical chemical sensor developing is based on reagent immobilizing to sol-gel system. Optical transducers in particular have raised much interest currently [12-15]. Since, various novel materials can be used in optical sensors such as zeolite, conducting polymers, sol-gel etc. [7-9].

Sol-gel for instance, there are many advantages, such as its optical clarity, the ability to entrap specific reagent, thermal and chemical stability, simplicity of preparation and flexibility in controlling its pore size and geometry [11,13].

This research uses Tetra Ethyl Ortho Silicate (TEOS) as sol-gel material and shaping as sol-gel granule. The mechanism process, formaldehyde in solution system of

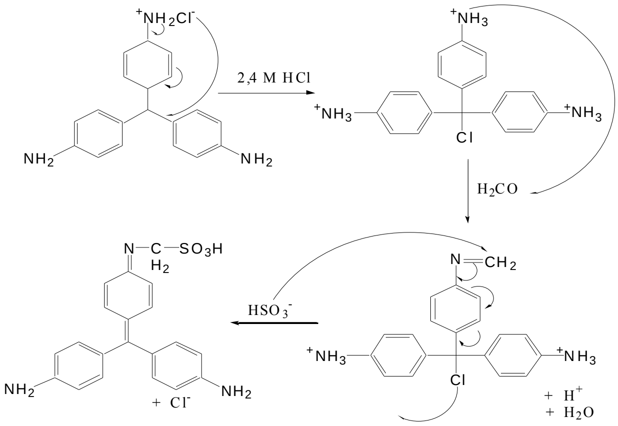

Figure 1. Formaldehyde-pararosaniline reaction.

diluting food, diffuses sol-gel and reacts with pararosaniline reagent producing change color of sol-gel [12]. The specific colors changed sol-gel from yellow to violet indicating that food solution contains formaldehyde, so the food has been solute contains formaldehyde. The sol-gel optical sensor can be used to detect formaldehyde contains in food as qualitative and quantitative manner.

2. Experimental

2.1. Reagent

All reagents were used as purchased without further purification. Pararosaniline hydrochloride (SIGMA P3750) was supplied from Sigma (UK). Tetra ethyl orthosilicate (TEOS), hydrochloric acid (HCl 37% pa), Ethanol 96%, Triton X-100, and sodium sulfite (Na_2SO_3) as precursor of sol-gel, were obtained from BDH-Merck (UK). For immobilization a phosphate buffer solution (PBS) with pH 6,5 was prepared by adjusting amounts of NaCl, KCl, Na_2HPO_4 and KH_2PO_4 buffer systems; in all cases, the mixture were 0.1 M in each constituent. The standard formaldehyde solutions of (2; 6; 10; 20; 100; 200; 300; 400; 500) ppm (grade of analytical, Merck) were prepared by appropriate dilution with an appropriate buffer solution in order to produce solutions of lower concentration at a desired pH. Salt and sugar use as interference material. All reagents and inorganic salts were of analytical grade and made using double distillate water.

2.2. Reagent Immobilizations

Pararosaniline reagent prepared by making solution, take of 0.03 g pararosaniline hydrochloride, diluting by water to total volume 10 mL used volumetric flask, this solution concentration is 3000 ppm. The solution on Na_2SO_3, made of 0.1 g Na_2SO_3 diluting by water to total volume 10 mL used volumetric flask. Pararosaniline sol-gel made by composing of 1.5 mL pararosaniline reagent, 0.5 mL HCl 37%, 250 µL Na_2SO_3 solution, 2 mL ethanol, 1.75 mL water, and 4.5 mL TEOS composing in beaker glass, stirring a long 3 - 5 hours. After that adding 5 drops of triton X-100 and stirring again 30 minutes, after that molding sol-gel as sol-gel.

2.3. Optical Fiber Biosensors Construction

The construction of the optical fiber sol-gel chemo sensor has been carried out by carefully placed a single sol-gel of pararosaniline into the specially designed flow-cell (**Figure 2**). This flow-cell (15 × 10 mm and 15 mm depth) has been designed as back pressure free flow cell, so that the effect of pulse from the pump and air bubbles could be removed. Since these problems often faced in flow system, which in turn increasing noise in signal response. This optical chemical sensor design also allows reducing the effect of other incident light levels on the flow-cell and optical system.

2.4. Results and Discussion

2.4.1. Sol-Gel Sensor Product.

The sol-gel sensor product fabrication and it color change before to after interaction with formaldehyde presenting as **Figure 3**.

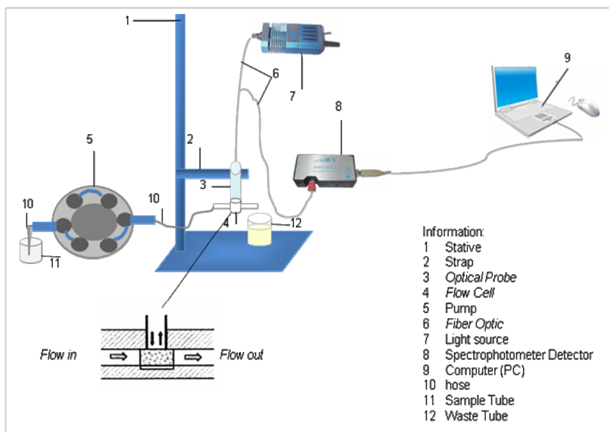

Figure 2. Flow-cell for optical fiber chemical sensor.

(a) (b)

Figure 3. Shape and color change of chemical sensor.(a): Chemical sensor before interaction with formalin; (b): Chemical sensor after interaction with formalin.

2.4.2. Optimization of Experimental Parameters

1) Optimum Wave Length Operational and Linearity Range Concentration

The first step in parameter optimization is to finding the optimal wave length, base on the scanning the spectra of blank solution and some standard formaldehyde solution, 2 ppm, 10 ppm, 20 ppm, 100 ppm, 200 ppm, 800 ppm and 1000 ppm. Result of scanning as presenting by **Figure 4**, from this spectra, have been result the optimum wave length base on the correlation between standard formaldehyde concentrations with intensity of reflectance produced by sol-gel sensor after reacted with formaldehyde in solution.

Based on **Figure 4**, it is able to resume the reflectance intensity as **Table 1** follows.

Base on **Table 1**, the optimum wave length operational is 576.42 nm, and the linearity range concentration (0 - 100) ppm, has slope or sensitivity 0.087, intercept 10.310, and linierity coefficient $R^2 = 0.999$ [15,16].

2) Test the Confidence Level Linearity

Linearity test includes a margin of error sensitivity (slope error) and the margin of error intercept (intercept error). The results of calculations with a 95% of confidence level obtained error bounds of sensitivity 0.087 ± 0.0003 and a margin error of intercept 10.31 ± 0.0109 [10,16].

3) Limit of Detection (LOD) and Limit of Quantification (LOQ)

Referring to **Figure 4** and **Table 1** further tested the linearity of the calibration curve in detail for the concentration range of 0 ppm to 100 ppm, with measurements repeated 7 times for each standard solution. The concentration of the standard solution used is a concentration of 0 ppm, 2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm, 12 ppm, 14 ppm, 16 ppm, 18 ppm, 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 ppm. The next linearity test based on the average concentration measurements every standard. The test results give the following data as **Table 2** and **Figure 5**.

Based on data from the linearity of the curve in **Table 2** and **Figure 5**, it obtained the limit of detection (LOD) worth 0.5041 ppm and limit of quantitation (LOQ) of 1.6804 ppm [16].

4) Sensor Reproducibility

The data resumes to detecting Sensor Repro-ductivebility Measurement from 7 repeatbles as presenting **Table 3** followed. **Table 3** data give reality, the variance coefficient measurements base of reflectance signal, minimum 0.025% and optimum 0.557%. The variance coefficient measurements base of formalin contains, minimum 0.8768% and optimum 4.7875%. This condition are lowest of 5%, so the chemical sensor is usable as formalin detector [10,16].

5) Sensor Responses Time

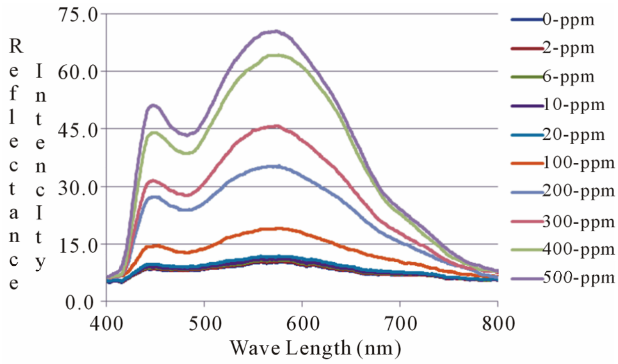

Figure 4. Spectra profile of formaldehyde by pararosaline TEOS optical chemical sensor.

Table 1. The optimum reflectance intensity some standard formadehyde solution.

$[H_2CO]$ (ppm)	Left peaks		Right peaks		λ Tested		
	λ	Int.Reflt	λ	Int.Reflt	447.30	448.26	576.42
0	448.26	8.538	576.42	10.377	8.456	8.538	10.377
2	444.42	8.653	576.42	10.547	8.429	8.511	10.547
6	446.82	8.882	576.42	10.888	8.871	8.830	10.888
10	442.5	9.112	576.42	11.228	8.907	8.995	11.228
20	447.30	9.685	576.42	11.867	9.685	9.627	11.867
100	453.06	14.551	576.42	18.989	14.284	14.443	18.989
200	448.26	27.294	576.42	35.354	27.245	27.294	35.354
300	447.30	31.518	574.98	45.763	31.518	31.438	45.634
400	447.30	44.015	574.94	64.237	44.015	43.976	61.213
500	448.26	51.101	574.02	70.497	50.405	51.101	70.249

Table 2. Reflectance intensity data of linierity curve 0 ppm - 100 ppm on 576.42 nm.

[Formalin]	Measuring Intensity (Y)	Kurve Intensity (Ŷ)	$(Y-\hat{Y})^2$
0	10.328	10.310	0.00034
2	10.504	10.484	0.00040
4	10.669	10.658	0.00013
6	10.845	10.832	0.00017
8	11.026	11.006	0.00039
10	11.191	11.180	0.00013
12	11.348	11.354	0.00003
14	11.520	11.528	0.00007
16	11.693	11.702	0.00008
18	11.859	11.876	0.00028
20	12.037	12.050	0.00018
40	13.802	13.790	0.00014
60	15.539	15.530	0.00009
80	17.287	17.270	0.00028
100	19.019	19.010	0.00008
Deviasion Standard		0.01462	

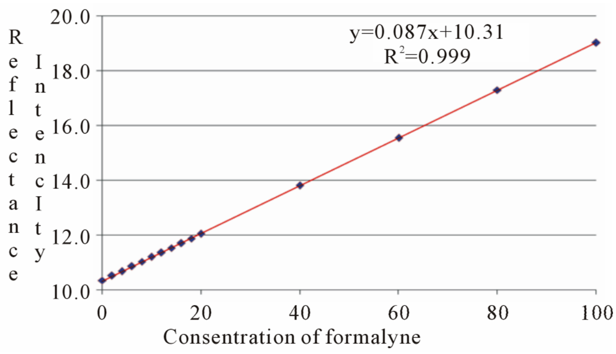

Figure 5. Test product of linearity on concentration range of 0 ppm - 100 ppm, on wave length 576.42 nm, by 7 time repetition for each standard solution.

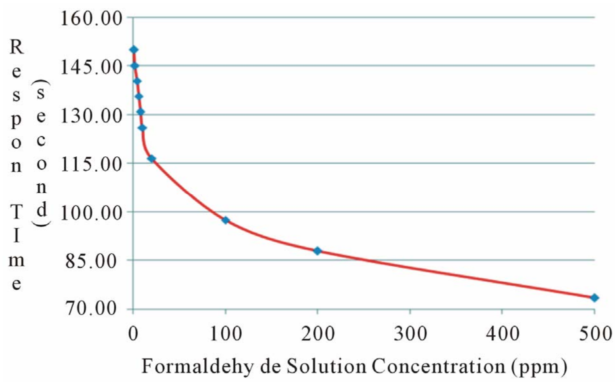

Figure 6. Response time of sensor base formaldehyde concentration.

Table 3. Data of reproducibility measurements.

$[CH_2O]$ ppm	Sensor Reflectance			Measurement Concentration		
	Averg.	STDev	% KV	Averg. (ppm)	STDev	% KV
0	10.328	0.015	0.142	0.948	0.0126	1.3240
2	10.504	0.003	0.025	2.355	0.0297	1.2598
4	10.669	0.017	0,160	4.361	0.1958	4.4902
6	10.845	0.022	0.200	6.784	0.2498	3.6826
8	11.026	0.022	0.197	8.617	0.2494	2.8939
10	11.191	0.039	0.347	10.125	0.4457	4.4017
12	11.348	0.038	0.331	11.358	0.4315	3.7992
14	11.520	0.041	0.355	13.208	0.4677	3.5411
16	11.693	0.062	0.530	14.865	0.7117	4.7875
18	11.859	0.030	0.249	16.832	0.3387	2.0122
20	12.037	0.066	0.551	19.847	0.7619	3.8390
40	13.802	0.077	0.557	41.860	0.8829	2.1092
60	15.539	0.047	0,302	61.426	0.5386	0.8768
80	17.287	0.086	0.495	80.996	0.9828	1.2134
100	19.019	0.045	0.238	100.564	0.5194	0.5164

The responses time of sensor has been affected by concentration of formaldehyde in solution system. Type of formaldehyde concentration affected to sensor response time presenting like **Figure 6**, follow. Base on **Figure 6**, the response time of sensor between 75.88 seconds for 500 ppm to 150 seconds for 2 ppm formaldehyde concentrations.

6) Operational Conditions of pH Sensor

The reaction between pararosaniline with formalin affected by the pH, the influence of pH conditions the sample system to the intensity of reflectance sensor interaction with formalin results provide **Figure 7**, presented above. Based on the **Figure 7**, obtained information that the system for the detection of formaldehyde in the solution pH conditions are optimal system operating at pH 4.

7) Sensor Selectivity

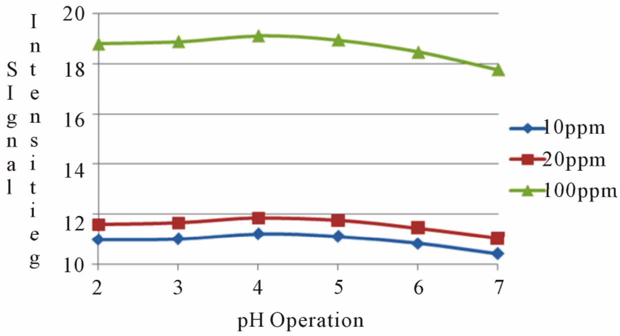

Figure 7. Effect of pH on the intensity of reflectance operational.

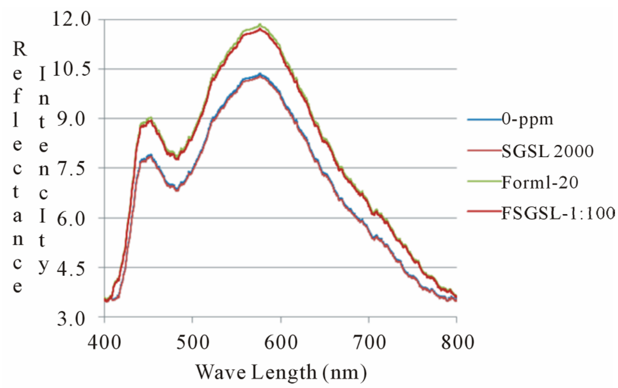

Figure 8. Sensor selectivity curve formalin to interference ratio of sugar-salt at a concentration of 1:100.

The selectivity of the sensor for the identification of formaldehyde in the system through the test solution with sugar and salt. Selectivity trials conducted with formalin concentration ratio, salt and sugar 1:10, 1:100 and 1:1000. Sample spectra pattern measurements sugar disorders and formalin shown as **Figure 8** and the data as **Table 4(a)** the following.

According to the test result tampering sugar and salt at **Table 4(a)**, obtained information that the existence of sugar and salt in aqueous system can provide a distrac-

Table 4. (a): The intensity of reflectance on the condition of Interference Salt, Sugar, and Sugar-Salt Against Formalin; (b): Recovery of optical chemichal sensor on determining formalin in sample solution using standard and standard addision methode.

(a)

Composition of Test Sample	Reflectance Intensity	Interferences	% Interferences
0 ppm (Blank)	10.377		
Formalin (F) 200 ppm	**35.354**		
Salt (Sl) 2000 ppm	10.194	0.081	0.229
F:Sl = 1:10	35.273		
Sugar (Sg) 2000 ppm	10.425	0.062	0.175
F:Sg = 1:10	35.292		
Sugar-Salt 2000 ppm	10.306	0.145	0.410
F:Sg:Sl = 1:10:10	35.209		
Formalin (F) 20 ppm	**11.867**		
Salt (Sl) 2000 ppm	10.194	0.028	0.236
F: Sl = 1:100	11.839		
Sugar (Sg) 2000 ppm	10,425	0.100	0,843
F: Sg = 1:100	11.767		
Sugar-Salt 2000 ppm	10.306	0.126	1.062
F: Sg: Sl = 1:100:100	11.741		
Formalin (F) 2 ppm	**10.547**		
Salt (Sl) 2000 ppm	10.194	0.025	0.237
F:Sl = 1:1000	10.522		
Sugar (Sg) 2000 ppm	10.425	0.159	1.507
F:Sg = 1:1000	10.388		
Sugar-Salt 2000 ppm	10.306	0.181	1.716
F:Sg:Sl = 1:1000:1000	10.366		

(b)

		Standard Method				**Addition Method**			
Sample Obyek	**[Formalin] (ppm)**	**[Formalin] Retrieval**	**Std Dev**	**Recovery (%)**	**t-Test**	**[Formalin] Retrieval**	**Std Dev**	**Recovery (%)**	**t-Test**
Sea Fish Meat	10	9.524	0.299	95.241	2.755	9.847	0.171	98.470	1.552
	20	19.286	0.353	96.432	3.498	19.487	0.303	97.434	2.932
	60	58.153	0.848	96.921	3.772	58.865	0.512	98.108	3.837
	100	98.636	0.778	98.636	3.036	98.379	0.755	98.379	3.716
Noodles Soggy	10	9.879	0,072	98.794	2.911	9.964	0.050	99.640	1.246
	20	19.548	0,265	97.740	2.959	19.826	0.153	99.132	1.969
	60	59.533	0,266	99.221	3.045	59.704	0.157	99.507	3.257
	100	98.969	0,625	98.969	2.857	99.411	0.661	99.411	1.545

tion to the measurement of the levels of formaldehyde in solution. The higher the concentration of sugar and salt, or in solution, the greater the percentage of its disorders. Selectivity of the sensor towards the sugar and salt as the interference was 1.716% [10,16].

8)Sensors Acurration

The accuracy of the sensors are tested through sensor application to a sample simulation known concentrations of formaline content. Testing using two sample object i.e. meat fish and noodles soggy, each with 4 kinds of concentration, that is 10 ppm, 20 ppm, 60 ppm and 100 ppm. Testing is done through standard methods and standard addisi. The test results are shown in **Table 4(b)** up.

Based on the data of **Table 4(b)**, indicating that the retrieval of chemical sensor hoses both in standard methods as well as standard addisi have trust between the area range 95.241% - 99.640%. Test results of t-test accurasion, have been obtained a quantity t-test is smaller than the price of t-test table reference of 4.3. Such conditions mean optical chemical sensors worth applies.

9) Reuse Sensor

Test reuse (regeneration) is done by using a solution of formalin solution and blank with concentration of (10 ppm, 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 ppm). The test results give a picture of a decrease in the performance of the sensor as shown in **Table 5**.

Based on the data in **Table 5**, obtained the fact that optical chemical sensors can be used repeatedly for four times, because its still 92.611% compared to the initial state, means meets the minimum limit analysis method rule capabilities sensor 90 % for reuse.

3. Applications Sensor for Real Samples

Application sensors for real samples performed using standard additions methods tested Sea-Fish meat and noodles soggy use of 5 sample objects. The results of measurements of formaldehyde content in the real sample by using optical chemical sensors and UV-Vis as a comparison method, as shown in the **Table 6** below. Based on the data in **Table 6** brings about reality, that the determination of formaldehyde in food samples between using the chemical sensors and methods UV-Vis provides a different quantity. But quantitatively the difference is relatively low and still meet the criteria analysis.

Table 5. Chemical sensors measure power capacity on the use in the regeneration based on the intensity of reflektan.

[Formalin]	Reflectance intensity and sensor % capacity				
	1st	2nd	3th	4th	5th
10	11.191	11.013	10.962	10.804	10.663
	100%	98.414	97.958	96.542	95.284
20	12.040	11.839	11.658	11.454	11.162
	100%	98.331	96.822	95.126	92.705
40	13.856	13.607	13.266	12.869	12.260
	100%	98.203	95.748	92.883	88.484
60	15.659	15.264	14.867	14.183	13.575
	100%	97.479	94.945	90.578	86.692
80	17.361	16.931	16.474	15.699	14.789
	100%	97.520	94.887	90.427	85.182
100	19.064	18.584	18.063	17.178	16.130
	100%	97.480	94.751	90.108	84.611
Average % capacity		97.905	95.852	92.611	88.826

Table 6. Formaldehyde content determination results in real sample solution by standard addition method.

Real Sample	Sample object	Real sample [Formalin]	
		Chemical sensor	UV-Vis
Sea Fish Meat	S1	413.199	412.875
	S2	417.238	416.439
	S3	410.818	410.783
	S4	419.381	407.992
	S5	412.253	411.753
Average		414.578	411.968
Noodles Soggy	S1	34.877	34.898
	S2	34.753	33.786
	S3	35.923	35.253
	S4	36.943	36.856
	S5	34.689	34.540
Average		35.437	35.066

Furthermore if the review of the results of the analysis of the paired t-tests (Paired t-Test), found no difference between the two methods of determination of the results of the two system analysis [10,16].

4. Conclusion

Based on the test results of the operational characteristics of the optic chemical sensor fabrication yield, it can be concluded that the sensor has the feasibility to use in the process of identifying and determinating the presence of formalin in food. In addition, the sensor can be regenerated using an acid solution.

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