RESEARCH NOTE

NOVEL METHOD FOR THE PREPARATION OF COPPER PHTHALOCYANIN BLUE NANOPARTICLES IN AN ELECTROCHEMICAL CELL IRRADIATED BY MICROWAVE

M. Edrissi, B. Nasernejad* and B. Sayedi

Department of Chemical Engineering, Amirkabir University of Technology
P.O. Box 15875-4413, Tehran, Iran
banana@aut.ac.ir - nasernejad@yahoo.com

*Corresponding Author

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Abstract Combined electrochemical and hydrothermal assisted by microwave was used for the preparation of copper phthalocyanin blue (Cu Pc) nanoparticles with sizes ranging from 5 to 35 nm. Phthalic anhydride, urea and ammonium molybdate catalyst were dissolved in aqueous solution of 1 M NH_4Cl containing a small amount of lauric acid as capping agent to suppress the flocculation of pigment. Electrodes were a copper plate as anode and a graphite rod as cathode. The cell was irritated with microwave the solution was stirred and a potential about-0.34 V was applied to the electrolysis cell. The copper (II) ion generated by anodic dissolution of copper electrode reacts with other initial materials dissolved in NH_4Cl solution to produce CuPc. The yield and purity of CuPc is increased and the reaction time and energy consumption are considerably decreased. The product was characterized by ^{13}C NMR, UV-Vis, reflectance spectra, particle size measurement and elemental micro analysis. The procedure of CuPc preparation was optimized using a Taguchi experimental design.

Keywords Nanoparticles, Electrochemical, Microwave, Copper Anode, Copper (II) Phthalocyanine Blue, Taguchi Design

چکیده در این تحقیق یک روش ترکیبی ریز موج برای تهیه فتالوسیانین آبی نانوذره‌ای با فاصله ذرات حدود ۵–۳۵nm معرفی شده است. در محلول مولار HCl شامل انیدرید فتالیک، اوره و کاتالیزور آمونیوم مولیبدات و مقدار کمی مولار یک اسید بعنوان ماده ضد مجتمع شدن ذرات، یک آند مسی و یک کاتد گرافیتی قرار داده شد و در حین تابش ریز موج پتانسیل حدود ۰/۳٤– ولت به محلول الکترولیز اعمال گردید. یون مس تولید شده از انحلال آند مسی با سایر مواد اولیه واکنش داده ابتدا ذرات سبز رنگ و سپس یک دیسپرسیون آبی شامل رنگدانه فتالوسیانین آبی نانوذره‌ای تشکیل می‌گردد. محصول توسط آنالیز عنصری و طیف سنجی‌های UV-Vis, NMR انعکاسی و تست های اندازه گیری اندازه ذرات (LLS, PSA) شناسایی و شرایط بهینه برای تهیه این رنگدانه با کاربر آرایه L_4 تاگوچی مورد بررسی قرار گرفت.

1. INTRODUCTION

CuPc, CI pigment blue 15:0:C.I 74160 is a macrocyclic molecule, having an alternating nitrogen -carbon ring structure. CuPc consists of four isoindole class $[(C_6H_4)C_2N]$ units linked by four nitrogen atoms to form a conjugate structure, with copper (II) ion in its center. CuPc is one of the most important industrial pigments with widespread applications. The pigment demonstrate good overall stability to organic solvents and due to its excellent technical properties, it is used for the production of blue shade in most blue pigment consuming industries. Besides, it has been widely used in other fields such as, chemical sensor, catalysis, optical disk, xerography, non-linear optics, electro-

chromic display devices and photovoltaic cells [1-3]. The versatile features of phthalocyanine blue have stimulated attempts on its synthesis by new methods. Problems in the current classical methods which comprises heating phthalic anhydride urea and copper salt in presence of a catalyst are; production of high amount of acidic wastewater, large thermal energy consumption, low yield and difficulties, in temperature control and purification [1-3]. In this work the CuPc was prepared in an electrochemical cell containing appropriate amounts of phthalic anhydride,and urea ammonium molybdate catalyst, dissolved in one molar NH_4Cl containing small amounts of lauric acid to suppress pigment flocculation. The electrolyte was stirred by a small electric stirrer and a constant potential of about-0.34 V was applied to the electrolysis cell for four minutes: In comparison with several reported methods for the preparation of CuPc which use copper chloride or copper sulphate as one of the initial materials the proposed method uses electrochemically generated copper ion which produces lower particle size product. despite the abundance of reported works on the preparation of copper phthalocyanine blue, there is no information in the available literature on the use of combined electrochemical and microwave processing to obtain the CuPc pigment. [8,9,11] The yield is higher and the time needed for the preparation of product is minimized.

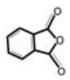
2. EXPERIMENTAL

Materials and Methods An electrolytic analyzer Eberbach was used for electrolysis. The electrochemical cell used was a four necked round-bottom flask equipped with a reflux condenser, thermometer and stirrer. A copper plate was used as anode and a graphite rod as cathode. The UV-Visible spectrum was taken by Shimatsu 2100 spectrophotometer.

A Samsung microwave generator (300 GHZ, 900 W) was used for heating the electrochemical cell.

The elemental analysis was carried out by a flash EA112 automatic elemental analyzer. ^{13}C NMR spectrum was recorded by Bruker 1VM-400 using CCl_4 as solvent. Particle size were measured by Fritch Particle Sizer Analysett 22 (P.A.S) and Laser light scattering (LLS), SEMATECH (230V, 50 HZ). Reflectance spectrums were recorded with color eye-700A (Gratog-Macbeth) with reflectance attachment. All chemicals were reagent grade supplied by Fluka.

2.1. Synthesis of CuPc The electrolyte is composed of 4.2g phthalic anhydride, 4.5g. Urea and 0.1g ammonium molybdate dissolved in 100 ml 1 molar NH_4Cl containing 0.1 g lauric acid as capping agent. A small plastic stirrer (rpm 60) was used for mixing the solution. A potential of about-0.34 applied to the electrodes, the cell was heated by microwave to a temperature ranging from 100-105°C and maintained at this range for 4 minutes, A greenish suspension is produced which turns blue at the end of reaction time. The product was precipitated by addition of saturated NaCl and ethanol, then washed with hot distilled water and acetone and dried at 100°C in an air oven. The gross reaction equation for the synthesis of CuPc may be written as follows:

4  $+ 4\ (NH_2)_2CO + Cu^{++} + 2e^- \rightarrow CuPc + 8H_2O + 4CO_2$

3. RESULT AND DISCUSSION

Copper (II) ion is generated inside the electrochemical cell via homogeneous anodic dissolution of copper electrode.

Results for the elemental microanalysis of prepared pigments are given in Table 1 which are in agreement with theatrical data. The results of particle size analysis are shown in Figure 1 (a,b and c). The sizes of particles are between 5-35 nm. The mean diameter of particles (7.4 nm) were obtained from LLS size distribution carve using RTG correlates software. The reflectance spectrum of blue pigment (360-720 nm) λ_{max} 440 nm is given in Figure 2. The UV-Visible spectrum of pigment suspension has a λ_{max} at 710 nm in agreement with the reported value [3,9], no shift in the position of λ_{max} was observed by 1 and 2 times dilution with distilled water. The chemical structure and the ^{13}C NMR spectrum of CuPc in CCl_4 with the

TABLE 1. Elemental Analysis of Copper Phthaocyanine Blue (CuPc).

Elements	C %	H %	N %
Calculated for $CuC_{32}H_{16}N_8$	66.72	2.79	19.42
Found $CuC_{32}H_{16}N_8$	66.70	2.83	19.67

assignments are given in Figure 3. The taguchi L_4 array, [14] was used to study the effect of three factors at two levels (high and low) on the yield of reaction Table 2. The notation L is for latin square and the subscript 4 refers to the number of rows in the table which indicates the number of combinations. The y_1, y_2, … are responses at different experimental conditions. The Taguchi experimental design utilizes a modified and standardized design of experiments for practice in research and industry. It helps us to study the effect of several factors simultaneously on the result of experiments, and seek out the best design among the many alternatives. [16] The three main factors studied in this work are A (time of irradiation, min.), B (agitation rate, rpm) and C (amount of catalyst, g). The levels assigned and the results obtained for yield are given in Table 3.

The yield expected at optimum conditions is calculated by the following equation [14].

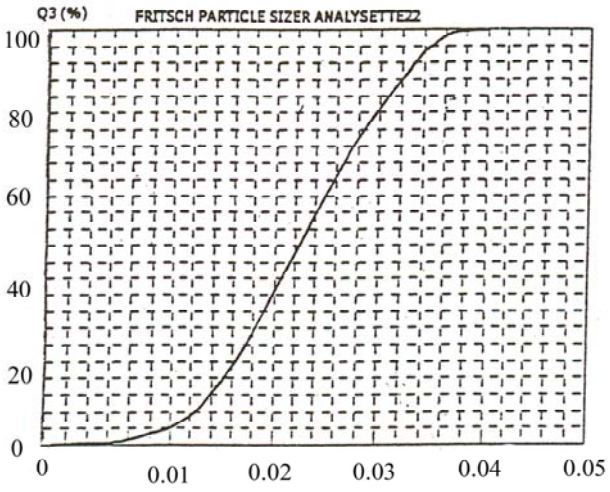
$$y_{opt} = \overline{T} + (\overline{A}_2 - \overline{T}) + (\overline{B}_1 - \overline{T}) + (\overline{C}_2 - \overline{T})$$

T = Grand Average

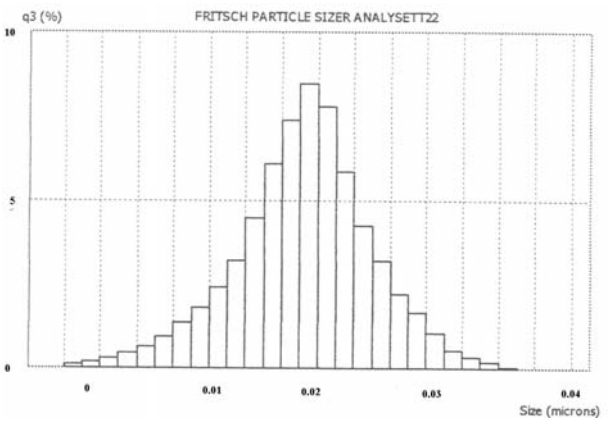
$$T = \frac{94 + 95 + 97 + 92}{4} = 94.5$$

The average effects of, $\overline{A}_2, \overline{B}_1$ and $\overline{C}_2$ are calculated as follows:

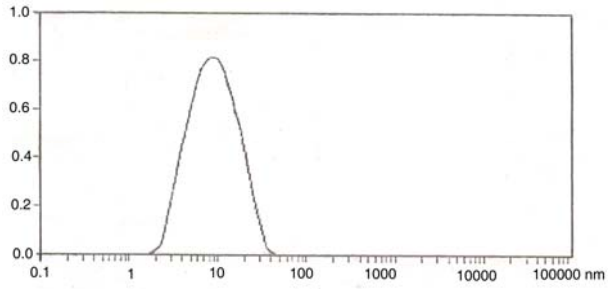
$$\overline{A}_2 = \frac{y_3 + y_4}{2}$$



(a)



(b)



(c)

Figure 1. a, b and c particle size measurements.

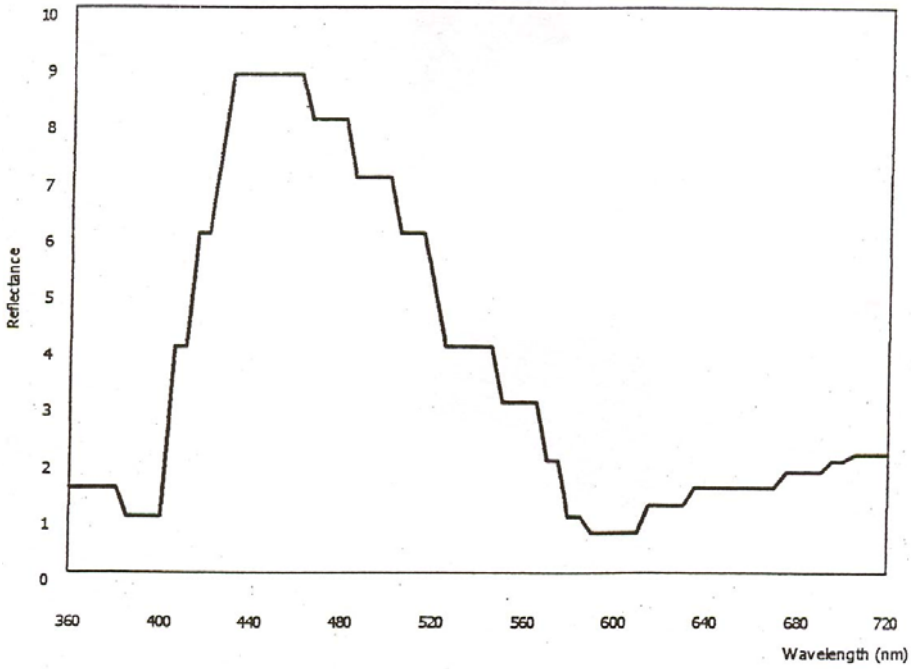


Figure 2. Total reflectance spectrum of CuPc.

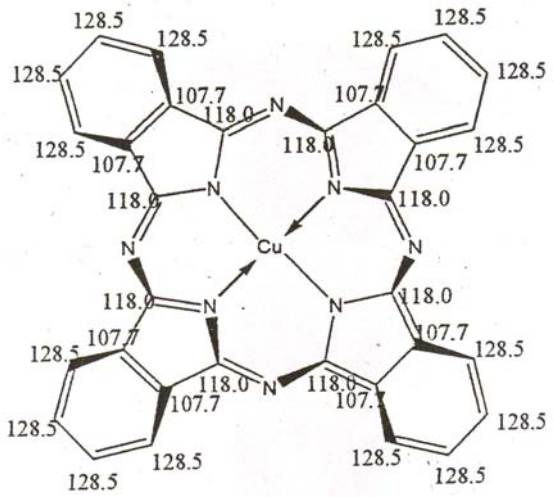


Figure 3. CuPc chemical structure and ^{13}C NMR assignments.

$$\overline{A}_2 = \frac{97+92}{2} = 94.5$$

$$\overline{B}_1 = \frac{94+97}{2} = 95.5$$

$$\overline{B}_1 = \frac{y_1 + y_3}{2}$$

$$\overline{C}_2 = \frac{y_3 + y_4}{2}$$

$$\overline{C}_2 = \frac{95+97}{2} = 96.0$$

The expected result for optimum yield is:

$y_{opt} = 94.5+(94.5-94.5)+(95.5+94.5)+(96-94.5) = 97$

Therefore the optimum conditions for obtaining the highest yield is in row 3 of Table 3.

4. CONCLUSIONS

The present work of electrochemical generation of copper (1) cation combined with the microwave irradiation lead to the preparation of a stable dispersion of nanoparticles of copper pbthalocyanine blue pigment in aqueous solution. For heating purpose the microwave process has proven to be quite effective due to its intense internal heating. The copper phthalocyanine was prepared in lower temperature (~100°C) and shorter time than other microwave preparations [7-20]. The sample synthesized had nanosize particles about (5-35 nm) which helps the pigment to be dispersed easily with high dispersion stability. The evaluations of product show that under the proposed combined conditions a small average particle size pigment (7.4 nm) with high yield (97 %) is obtainable.

5. REFERENCES

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TABLE 2. The L_4 Orthogonal Array for 3 Two Level Factors.

Experiment	Factor			
	A	B	C	Response
1	1	1	1	y_1
2	1	2	2	y_2
3	2	1	2	y_3
4	2	2	1	y_4

TABLE 3. Experimental Design with the Amount Used for the High and Low Level and Calculated Yields.

Experiment	Factor			
	A (min)	B (rpm)	C (g)	Yield (%)
1	3	60	0.1	94
2	3	80	0.2	95
3	4	60	0.2	97
4	4	80	0.1	92

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