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Growth of anthraquinone crystals by gel aided solution technique and their characterization

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Abstract. Anthraquinone, an oxidation product of anthracene, has been grown by gel aided solution technique employing sodium metasilicate. Needle shaped crystals were obtained in 0·5% (w/v) solution of anthraquinone for pH 5·5. The grown crystals were characterized by optical microscopy, SEM, IR, UV and XRD.

Keywords. Gel; solution; anthraquinone; crystal growth; oxidation; photoreaction.

1. Introduction

Derivatives of anthracene are convertible to other compounds by direct oxidation. Anthraquinone comes under this class of compounds. Considerable work has been reported on the synthesis of anthraquinone by catalytic oxidation of anthraquinone (Ivan and William 1949; Owens 1958; Noboru *et al* 1969; Grozev *et al* 1976; Chung 1978; Das and Nikhilendu 1982; Malik and Dohnal 1990; Pielichiouski *et al* 1992). The mesopositions in anthracene acquire the numbers 9 and 10, respectively. The successful outcome of the reaction is due to the special reactivity of the mesopositions and the greater stability of anthraquinone. The double bonds in the central ring are rendered inert by incorporation of oxygen in the terminal benzene rings (Louis and Mary 1960). Anthraquinone exhibits optical and photosemiconducting properties in addition to third harmonic generation (Yao 1962; Grozev *et al* 1976; Mizoguchi and Venishi 1991). Anthraquinone crystallizes in the monoclinic system with space group $P2_1/a$ ($a = 1{\cdot}581$, $b = 0{\cdot}3942$ and $c = 0{\cdot}7865$ nm) with two molecules per unit cell. Here, we report the growth of anthraquinone observed during the growth of anthracene by the gel aided solution technique (Rajendra Babu *et al* 1998). The grown crystals are characterized by optical microscopy, SEM, IR, UV and XRD.

2. Experimental

The chemicals used in this study were of BDH/AR grade. Sodium metasilicate of gel density $1{\cdot}05\ \mathrm{g\,cm^{-3}}$ was prepared, treated with glacial acetic acid in the pH range 5–7·5 and mixed with acetone for different gel acetone ratios (2 : 1, 3 : 1, 4 : 1). The mixture was allowed to set. The mixtures with higher pH (> 6·5) were set within 48 h, whereas those with lower pH (5) took nearly one week. Over the set gels, 0·5% (w/v) solution of anthracene in acetone was incorporated as top solution. The samples were kept open to diffuse sunlight. Few samples were kept in a dark room.

3. Results and discussion

It was observed that the level of top solution decreased slightly during the first week due to slow evaporation and diffusion into the gel. Tiny transparent crystals were observed floating on the surface of the top solution. Within two weeks, yellow needles were found growing from the tiny transparent crystals. Formation of yellow needles of anthraquinone is found to depend on several factors. An important parameter which determined the yield of anthraquinone was the concentration of anthracene solution kept over the gel. Higher concentration (1%) of anthracene solution produces a large number of anthracene crystals on the gel surface and tiny needles of anthraquinone were formed after a long period (~ two months). A better yield of anthraquinone resulted in a solution of concentration 0·5% (w/v) within two weeks.

A typical sample of gel, adjusted for pH 5, over which a few yellow needles of anthraquinone were formed is shown in figure 1A. In this case, tiny crystals formed on the surface of the top solution moved down to gel surface and yellow needles of anthraquinone were grown from them. In certain other gel samples when the illumination was high, large number of yellow needles were obtained.

Organic crystals can be grown from a wide variety of solvents, but since these solvents are non-aqueous, pH cannot be used as crystallization variable (Margaret

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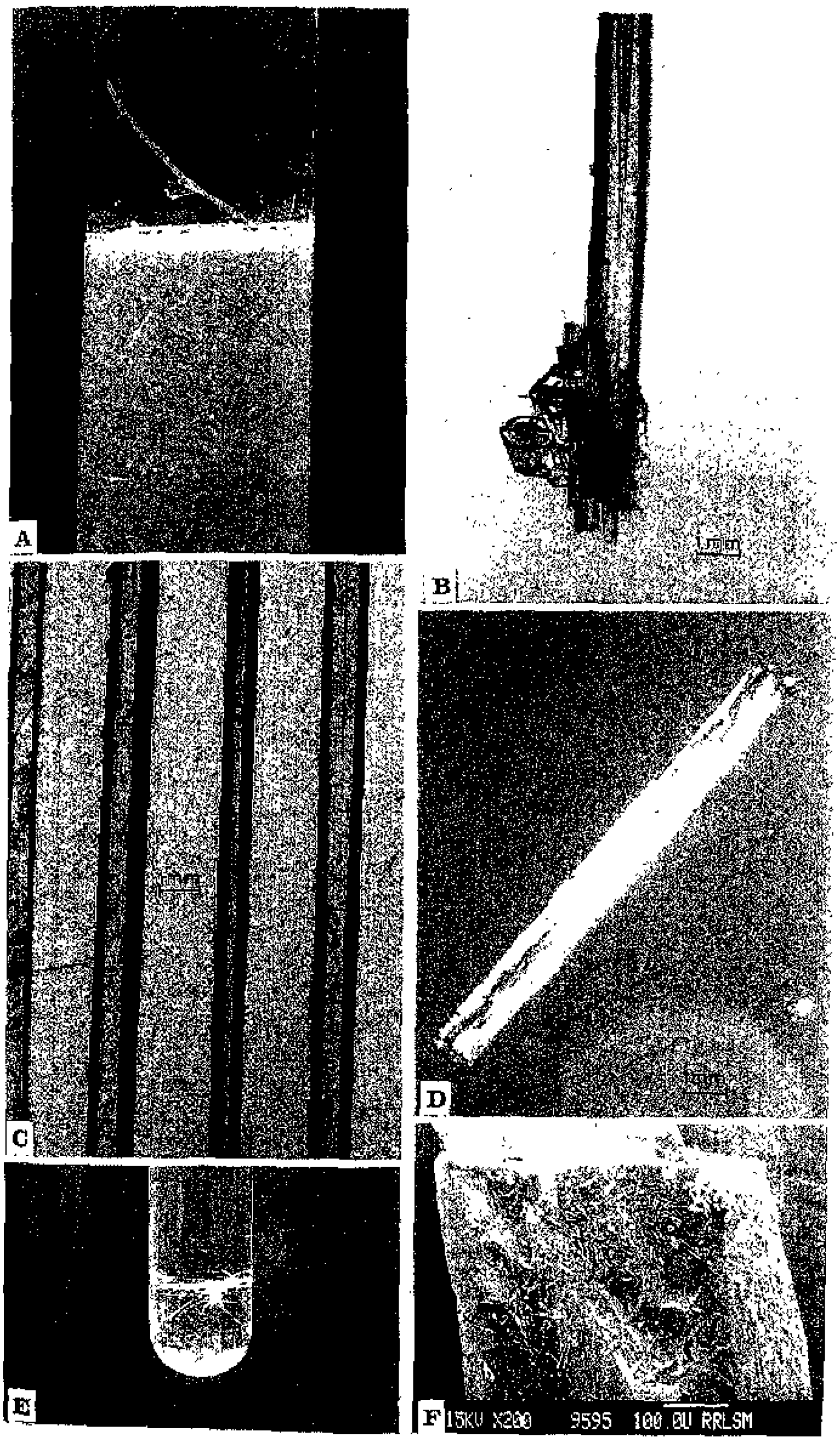

Figure 1. (**A**) Needles of anthraquinone seen growing in the supernatant solution kept over the gel, (**B**) a needle of anthraquinone grown from a cluster of anthracene crystals, (**C**) micrograph of needles obtained under crossed nicol prism, (**D**) a single crystal of anthraquinone photographed in straight extinction position with nicol in 45°, (**E**) micrograph showing the growth of a large number of yellow needles of anthraquinone in acetone–water solution of anthracene and (**F**) SEM photograph of a needle of anthraquinone.

et al 1986). However, in the present study, crystals were formed only in the top solution of particular pH (~6), irrespective of the gel pH. Hence, pH of top solution and in turn pH of the gel should have some effect on the nucleation of anthraquinone. Crystals of anthraquinone were found to grow in all pH values tried (5, 5·5, 6, 6·5, 7 and 7·5). But, better yield was obtained in 5–6 range. Most favourable pH was 5·5 in which yellow needles were found to grow into the gel medium in addition to that in the top solution. The rate of growth of these needles were studied. A uniform increase in the growth rate of needles into the gel medium was observed up to six days. After one week, the crystals attained maximum size, with a lower growth rate. This was followed by dissolution of crystals and the size of crystals fluctuates as shown in figure 2.

The samples kept in darkness did not yield yellow crystals of anthraquinone, but only platy crystals of anthracene. This confirms that the yellow needles of anthraquinone were produced by the photoreaction of anthracene as reported earlier (Corey and Taylor 1964). By the irradiation of anthracene in acetone, anthraquinone is obtained as a final product as represented by the following conversion (figure 3).

Investigation on the solvent (acetone) incorporated over the gel in this experiment revealed that there was a gradual increase in the density, surface tension and conductance of the solvent. Hence, it can be presumed that such changes might have modified the anthracene solution favourably for being converted into anthraquinone by photoreaction. Density measurement of solvent and solution (table 1) showed that the supernatant solution of anthracene undergoes a change similar to the behaviour of acetone–water mixture. Thus the supernatant solution might have been tuned for the growth of yellow needles. The differences in growth of anthraquinone in pure gel and acetone mixed gel is also noted. When the solution was kept over pure gel, the changes in supernatant solution was fast and resulted in the nucleation and growth of large number of anthracene crystals. Solution over the acetone-mixed gel was found to undergo a slow change in parameters and few anthracene crystals were

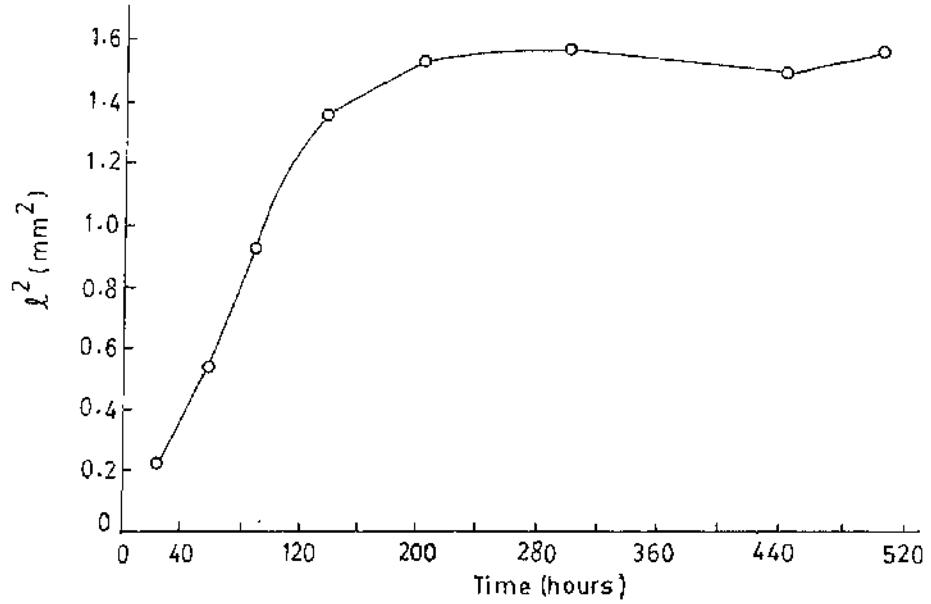

Figure 2. Growth kinetics of anthraquinone crystal.

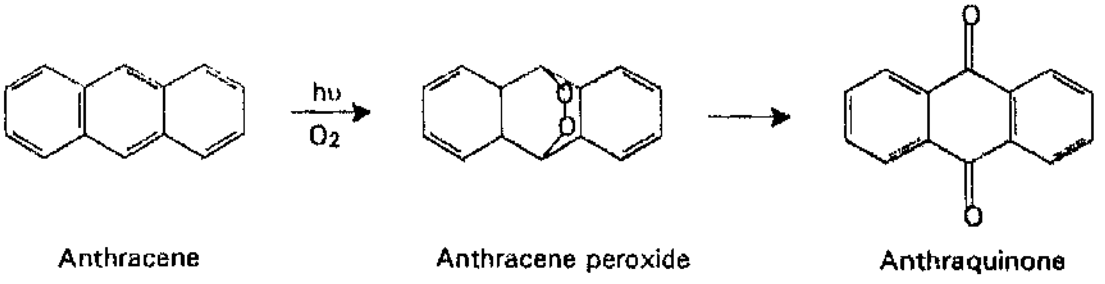

Figure 3. Photoreaction of anthracene.

formed. Within this time the solution is tuned for easy photoreaction and growth of anthraquinone.

In order to have better understanding of the role played by water–acetone system, water was mixed with acetone in different proportions. This mixture was used to prepare anthracene solution so as to grow crystals by slow evaporation without the aid of gel. A notable observation was that yellow needles of anthraquinone were formed in acetone–water system only if a seed was added. Good yield (figure 1E) was obtained when the mixture containing 5–30% of water was kept in an illuminated room. The crystals were separated, washed, dried and characterized with X-ray powder diffraction, IR, UV-visible spectroscopy, optical and scanning electron microscopy.

Table 1. Density of solvent/solution at 30°C.

Solvent/solution	Density (g cm^{-3})
Pure acetone	0·753
Acetone kept over the gel for one week	0·895
Saturated solution of anthracene in acetone	0·764
Top solution in which anthraquinone is formed	0·847

Table 2. IR spectral data of anthraquinone.

Yellow needles grown in acetone solution kept over the acetone mixed gel (cm^{-1})	Yellow needles grown in acetone-water mixture by solution growth (cm^{-1})	Assignments
937	935	CH out of plane bending
810	810	
621		Skeletal deform
694	690	Ring breathing
1170	1160	CH in plane bending
1284	1280	
1304	1330	Ring stretching
1332	1470	
1473	1560	
1522	1620	
1635		
1591	1580	Aromatic vibrations of quinones
1653	1678	C=O stretch of quinones
1676		

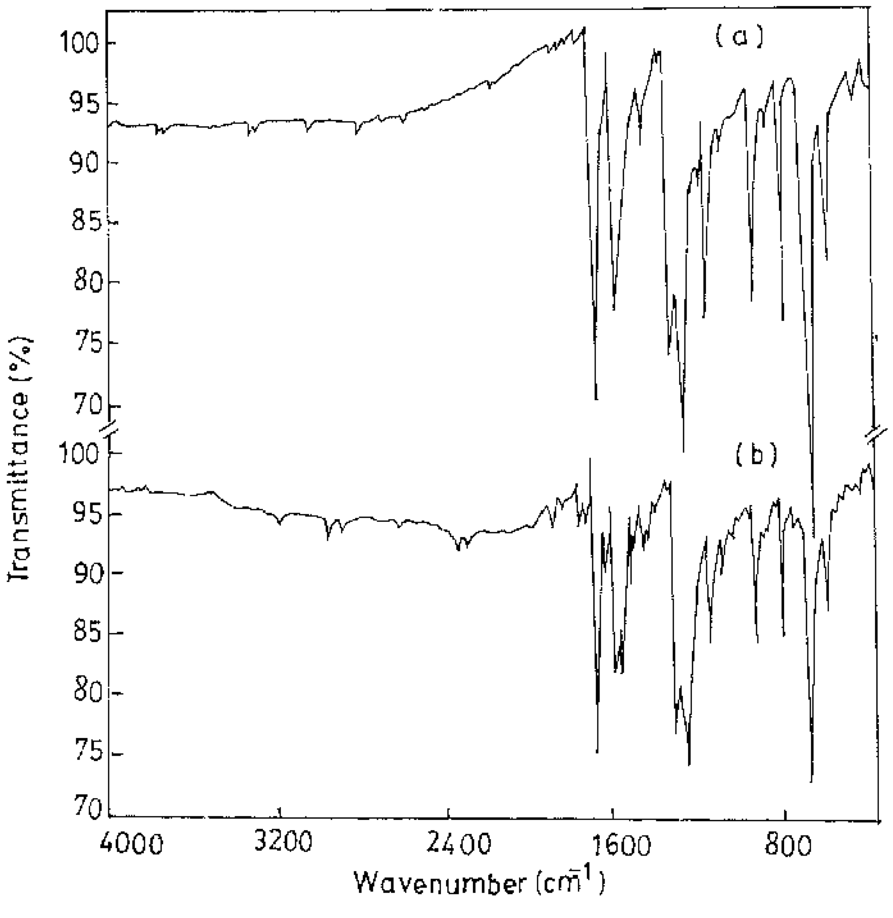

Figure 4. Infrared spectrum of anthraquinone needles grown (**a**) in acetone solution incorporated over acetone mixed gel and (**b**) in acetone–water solution.

4. Characterization

4.1 *Optical and scanning electron microscopy*

Optical micrographs of the single crystals of anthraquinone were taken using 'LEITZ ORTHLUX II POL BK' petrological microscope. Figure 1B shows a needle of anthraquinone nucleated from anthracene crystal substrate. Hollow cavity of the anthraquinone is also seen in the crystal. Figure 1C gives the micrograph of certain needles of anthraquinone obtained under crossed nicol position. A single crystal of anthraquinone photographed in straight extinction position with nicol in 45° for maximum illu-

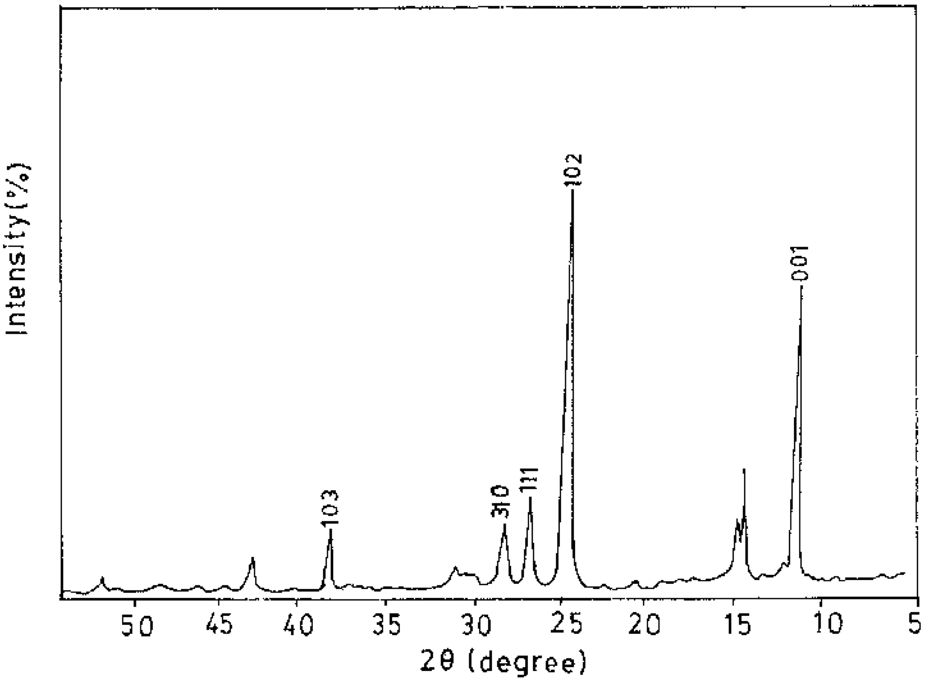

Figure 5. XRD pattern of anthraquinone crystals.

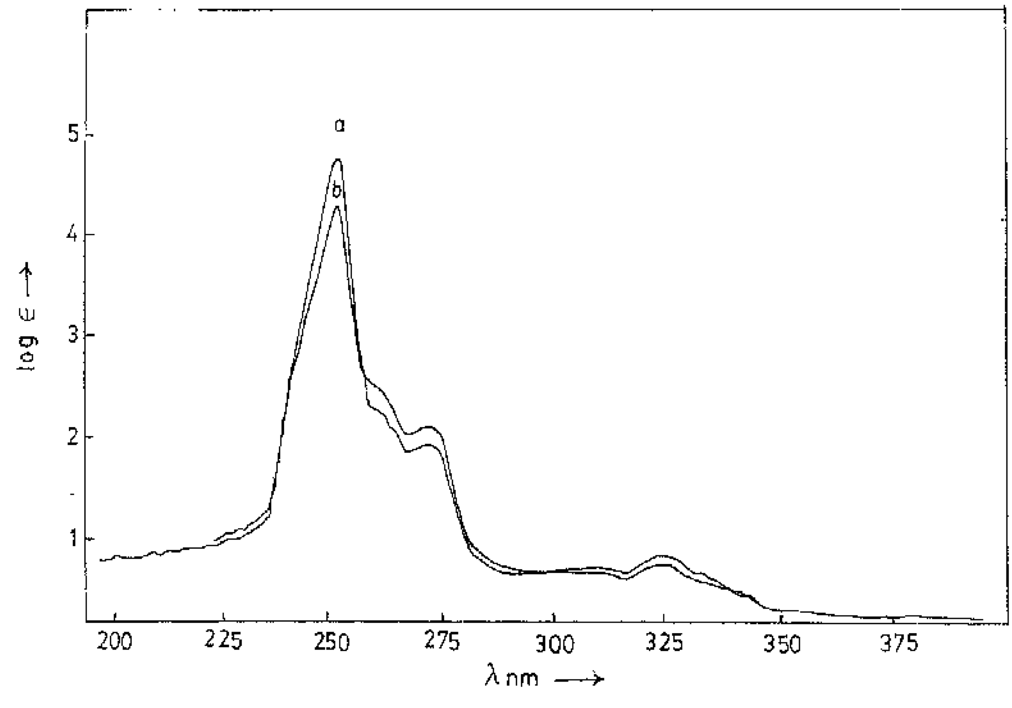

Figure 6. UV visible spectra of anthraquinone crystals (a) grown in acetone–water mixture and (b) grown by solution–gel technique.

mination is given in figure 1D. Yellow needles of anthraquinone crystals grown in the supernatant solution kept over the gel is shown in figure 1A. Figure 1E shows the growth of large number of yellow needles in acetone–water solution of anthracene. The transparent tiny crystals at the bottom of the test tube are anthracene. Figure 1F gives the SEM picture of an anthraquinone needle.

4.2 *Infrared analysis*

The infrared spectra of the crystals were recorded in the range 4000–400 cm^{-1} by KBr pellet method. Preliminary analysis of the transparent crystals formed on the top solution by IR spectroscopy has confirmed that the crystals are anthracene. The IR spectrum of yellow needles grown in acetone solution and those grown in acetone–water mixture are given in figures 4A and B, respectively. The vibrational frequencies and their assignments are given in table 2. The intense bands at 1676 and 1653 cm^{-1} can be assigned to the carbonyl grouping not present in anthracene but seen in the case of anthraquinone (Singh and Singh 1968). The intense band at 694 cm^{-1} is identical to the ring breathing frequency reported for anthraquinone (Singh 1991).

4.3 *X-ray diffraction analysis*

The XRD scan of the crystals with CuK_α radiation in the 2θ range 0–50° is shown in figure 5. The calculated '*d*' values (0·360, 0·762 and 0·314 nm) are found to be in close agreement with the ASTM '*d*' values (0·352, 0·769 and 0·314 nm) of anthraquinone.

4.4 *Ultraviolet and visible spectroscopy*

UV-visible spectra of the anthraquinone crystals grown in this study were recorded using a SHIMADZU UV-2100S, UV-visible recording spectrometer. The UV-spectrum of the anthraquinone crystals dissolved in chloroform is displayed in figure 6. Very strong band at 253 nm and the medium intense band at 273 nm are in agreement with reported values (Morton and Earlam 1941).

5. Conclusion

Formation of anthraquinone crystals was observed during the growth studies of anthracene. For all the pH values (5–7·5) tried, crystals of anthraquinone were obtained with varying nucleation time and quality. Better crystals of anthraquinone were obtained in 0·5% (w/v) solution of anthracene kept over acetone-mixed gels of pH 5, 5·5 and 6. Growth of needles into the gel medium was observed for pH 5·5. At higher concentration (1% w/v), nucleation and growth of anthracene occurred hindering photoreactive conversion to anthraquinone. Acetone mixed gel was found to be a better medium in aiding the growth of anthraquinone rather than the pure gel. Solution studies have revealed that acetone–water mixture can also be used as a solvent for growing anthraquinone crystals by photo reaction.

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