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"***Removal of methylene blue dye using activated carbon"***

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قال تعالى :

" وَعَلَّمَكَ مَا لَمْ تَكُنْ تَعْلَمُ " ،«سورة النساء: الآية 113».

اود ان لا استثني احداً في اهدائي لا استثني عائلتي التي ربتني فأحسنت تربيتي ولايمكنني ان اتغاضى عما قدمته مؤسساتي التربوية التي ترعرعت وسط صفوفها ونهلت من انهار معينها واصبحت شيئاً مذكورا واستميح عذراً كل من اعانني وقدم لي الرفد المعنوي والمادي والتربوي

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لكل من سلك طريق النور الى كل من عرف العلم بحقيقة علمه ونال درجات العلى جعلنا الله نقتفي اثار المثابرين منهم

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والله ولي التوفيق

"ثقة الوالدين بإبنتهم هي أول خطوات نجاحها شكراً لكم"

Abstract

Walnut shell (WS), as an economical and environmentally friendly adsorbent, was used to remove methylene blue (MB) from aqueous solutions. Eco-friendly adsorbents with high selectivity and adsorption efficiency meet a real need in wastewater treatment. Walnut shells, which belong to the gametozoa, were subjected to pyrolysis and chemical activation of H3PO4 and ZNCL2. Activated carbon was successfully prepared from walnut shells and used to absorb methylene blue dye after immersing it in zinc chloride and phosphoric acid. It was burned at temperatures of 200, 350 and 600 °C, and the most suitable temperature was chosen. At 600, we noticed that the material volatilized. In this study, details of different starting concentrations, pH, and temperatures were covered. and time change However, the pH value was one of the most important parameters to be examined at these values (pH3, pH7 and pH 11). When the pH is 11, the adsorption of methyl bromide retains an absorption efficiency of 0.55, at a pH of 7, 0.36, and at a pH of 3, 0.27, when the dye concentration was 200ppm. The adsorption kinetics of methylene blue was studied. To determine how well Methylene Blue is removed

Key words: walnut shells , methylene blue , adsorption, activated carbon

Introduction

The wide use of dyes in textile industries has lead to a variety of environmental problems, especially water pollution. Methylene blue (MB) is the most commonly used substance for coloring among all other dyes of its category and is generally used for dying cotton and silk [1]. Due to the harmful impacts of such dye on water, it is environmentally important to remove them from waste streams before discharge to public water sources.Sorption is generally regarded as an effective technique for the treatment of dye-containing wastewater. Activated carbons, because of their large surface area and relatively high sorption capacity for a wide variety of dyes, have become the most promising and effective adsorbent [2], . Nevertheless, their applications are restricted, because the most widely used carbonaceous materials for the production of commercially activated carbon are derived from natural materials such as wood or coal, which are expensive and are often imported [4]. Therefore, in the recent years, there is growing interest in the production of activated carbons from agricultural wastes because of their abundant resources and cheap prices. Several suitable agricultural wastes including coffee husks rice husks pistachio-nut shells cotton stalks [3], coconut husks [4], cherry stones corn cobs, and plum kernels [4] walnut shal. have been investigated in the last years as activated carbon precursors and are receiving renewed attention. Furthermore, converting the agricultural wastes into value-added activated carbons provides a new way for agricultural waste treatment. Typically, the preparation of activated carbon can be divided into physical activation and chemical activation. Physical activation consists of the pyrolysis of the precursor

material and activation of the resulting char in steam or carbon dioxide. Chemical activation is a single step process and is held in presence of some chemical reagents, such as KOH, NaOH, K2CO3, ZnCl2, FeCl3, H3PO4, and H2SO4. Chemical activation normally takes place at a lower temperature than that used in physical activation. In addition, the carbon yield in chemical activation is usually higher than in physical activation because the chemical agents possess dehydrogenation properties which can inhibit the formation of tar and reduce the production of other volatile substances. Among the chemical activation agents, ZnCl2 is the most widely used since it resulted in high surface areas and high yields [5], [6], [7].There are many studies in the literature relating to the preparation of activated carbons from agricultural wastes via chemical activation. However, most of the studies at present are carried out under atmospheric conditions. Lua and Yang have reported that activated carbons obtained under vacuum have better properties (e.g., higher specific surface area) than that prepared under atmospheric conditions [7]. Our previous studies also show that the morphology, pore size distribution, Brunauer–Emmett–Teller (BET) surface area, and adsorption properties of activated carbons are closely related to the system pressure [8]. In order to distinguish the traditional chemical activation (i.e., under atmospheric condition) from the chemical activation under vacuum condition, we call the latter vacuum chemical activation. Though the vacuum chemical activation has obvious advantages over traditional chemical activation, as far as we know, there are still very few reports on the preparation of activated carbons by vacuum chemical activation, let alone the applications of activated carbons prepared by this method.
Walnut shell, a good precursor for activated carbon production, is a major agricultural waste in China. According to statistics, there is more than 100,000 tonnes of walnut shells are produced in China annually. To make better use of the cheap and abundant agricultural waste, it is proposed to use it for activated carbon production. Therefore, the objective of this study was to prepare relatively well developed porosity activated carbons from walnut shells on a laboratory scale via vacuum chemical activation utilizing ZnCl2 as the activation agent. To optimize the preparation method, the effects of the main process parameters (system pressure, impregnation ratio, activation temperature) on the characteristics of the prepared activated carbons were studied. The low-cost walnut shell-based activated carbons were fully characterized and subsequently used as an adsorbent for methylene blue removal. Isotherms for the adsorption of methylene blue on the obtained activated carbons were measured and fit to five different isotherm equations to determine the best isotherm model to represent the experimental adsorption data.

Methylene blue

The methylene blue (MB) dye, the most commonly used one, is a heterocyclic compound with the chemical formula C16H18N3SCl. It was first synthesized in 1876 by Heinrich Caro of Badische Anilin and Soda Fabrik as an aniline-based synthetic dye for staining cotton to be used in the textile industry. Soon after this research, it’s utility to stain and inactivate microbial species were realized . Further, it was observed to be an antidote to carbon monoxide and cyanide poisoning in 1932 ، At room temperature, it appears as a dark green powder that produces a blue color in water. It shows

maximum absorption of light at around 665 nm. MB is one of the most thoroughly studied dyes due to its both positive and negative aspects. It has extensive and broad applications as coloring and staining agent in the textile and pharmaceutical sectors, respectively. However, MB has attracted serious attention due to its hostile nature, which poses inharmonious effects on the environment and human health. High blood pressure, irritation of the skin with redness and itching, irritation of throat, mouth, esophagus, and stomach, gastrointestinal pain, nausea, vomiting, diarrhea, dizziness, headache, and fever are some general problems associated with this dye Hence, the control of water pollution caused by the dyes has prevailed to be the most thrust area and strenuous task. Limited accessibility of high-quality clean water supplies and for the concern of human health, is forcing the enactment of in-process water-saving techniques and advanced treatment methods for the recycling of water and scavenging of the industrial wastes. In recent years, various chemical, physical, and biological processes have been established and utilized for the treatment of polluted water and wastewater. Some of these methods are discussed in brief in the subsequent paragraphs.

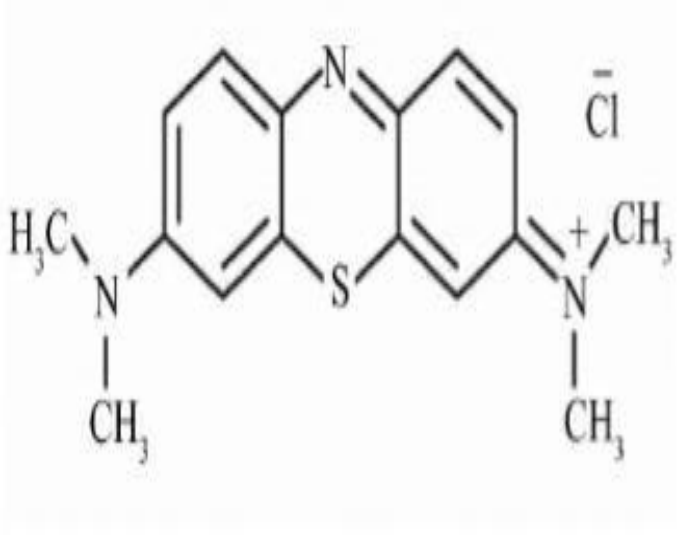


Figure1 : Methylene blue dye structure

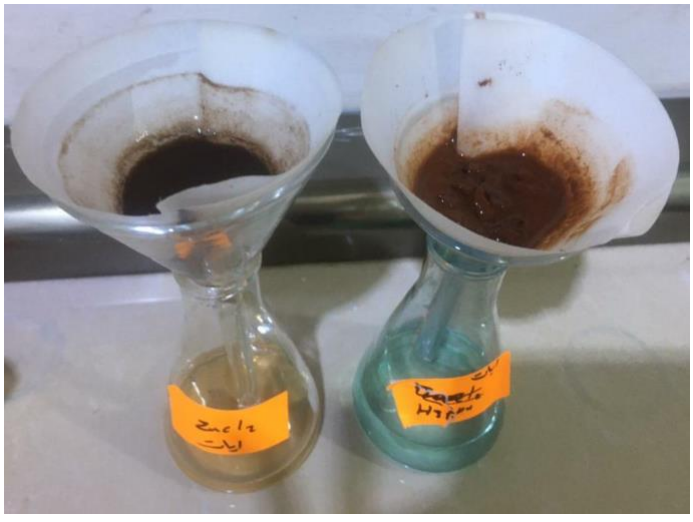
EXPERIMENTAL SECTION

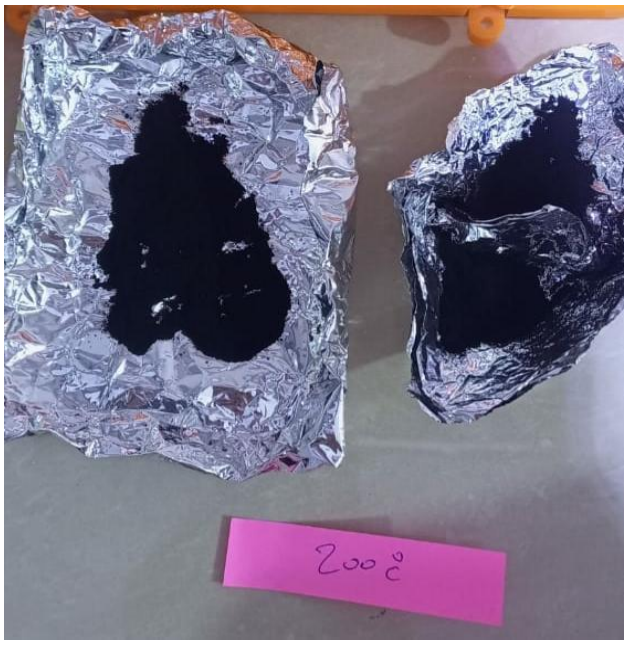
Materials

The walnut shells used in the current project came from Iraqi waste in Babylon, Iraq. After being cleaned with distilled water, the nut shells were left to air dry. The finely sized crushed particles of dried walnut shells were sieved through a 75-mesh screen in the later stages. Merck provided ZNCL2 and H3PO4 as activating agents. Methylene blue, which is a basic (cationic) dye, is an adsorbent model used in adsorption studies; Purchased from Dyes and Chemicals Corporation (China). Exclusively analytical grade chemicals were used; No further action was required.

Preparation of activated carbon

Walnut shells were collected as crunchy (dry), washed vigorously with water to remove dust and other solids and then dried. Then, the walnut shells were crushed using an electric mill and sieved with a 75-μm diameter mesh. 10 ml of deionized water was added in a beaker containing 3 g of walnut shell powder. Then, 5 g of concentrated ZNCL2 was added and stirred continuously until the powder was well immersed. Leave for 2 hours and then wash with water 3-5 times to remove all acid. Then the sample was dried under normal conditions for 1-2 nights. Then the dried powder was carbonized in an oven at 350 °C for 2 hours. A complete experimental methodology is presented in Figure 2. Also, we dissolved 2.5 ml of phosphoric acid and supplemented it with 10 ml of distilled water and added it to 3 grams of walnut shells. The same steps were repeated, as the burning was done at temperatures of 200, 350 and 600 °C.





Adsorption experiments

25ml of different concentrations of methylene blue dye solution (20–200 mg/L) was mixed with 0.04 g of absorbent and subjected to stoning for 60 min at room temperature. Samples were centrifuged at 3,000 rpm after adsorption, and the filtration was checked. Using UV-Vis spectrophotometers and calibration curves, dye concentrations in water were initially measured and held at the highest absorbance wavelengths (665 nm). The following equations were used to calculate the removal ratio and adsorption capacity of MB dye**:**

$$R\% = \frac{C_0 - C_t}{C_f} \times 100$$

$$Q = \frac{(C_0 - C_t)}{m} \times V$$

Where the starting dye concentration (Co) (measured in mg/L for MB), the residual concentration (C) of MB dye in mg/L was measured and the final dye concentration (C) (measured in mg/L for MB) was given. R% is the percentage of MB dye solution removed after adsorption; Q is the adsorption capacity (mg/g) at different times; and m is the amount of FLAC (g). In order to create the necessary dye solutions, a methyl bromide stock solution (1000 mg/L) was dissolved in deionized water. The adsorbent was added in 25 mL of a broad spectrum of concentrations (20, 40, 80, 120, 200 mg/L) solution with 0.04 g to test the effects of contact time and initial dye concentration on desorption and adsorption capacity. At pH (3, 7, 11), at a concentration of 80 mg/L of MB dye, the effect of pH was shown. Using solutions of 1 M HCl and 1 M NaOH, the pH of the solution was changed. 0.04 g of absorbent was added to 25 mL of an 80 mg/L solution of MB dye at 60 min. Samples were centrifuged after absorption and then examined. The concentration of MB dye was 80 mg/L and the supernatant was 0.04 g. Also, the absorbance of the activated carbon prepared by phosphoric acid was measured with different concentrations of methylene blue dye 40ppm and 100ppm.

Results and discussion

●Effect of Initial PH

It was found that the pH of the aqueous solution significantly affects the adsorption capacities of the dyes on the adsorbents [9]. Accordingly, the adsorption capacities of methyl bromide on WS were investigated under different aqueous solution pH. Figure 2 shows that under acidic conditions (pH=7), the MB dye removal percentage (71.8 _ 98.6%) on WB increased significantly with increasing pH, while under basic conditions (pH=10.5), the removal percentage was MB dye (59.7 _ 86.5%), while at (pH = 4) the percentage of MB dye removal was (60.3 _ 84.2%) MB solutions were used without pH adjustment to study the effect of the dose of adsorbents in addition to kinetic and thermodynamic studies .Therefore , there was less electrostatic attractive force between the dye cations and the adsorbent surface, which can result in lower adsorption capacity at lower pH.

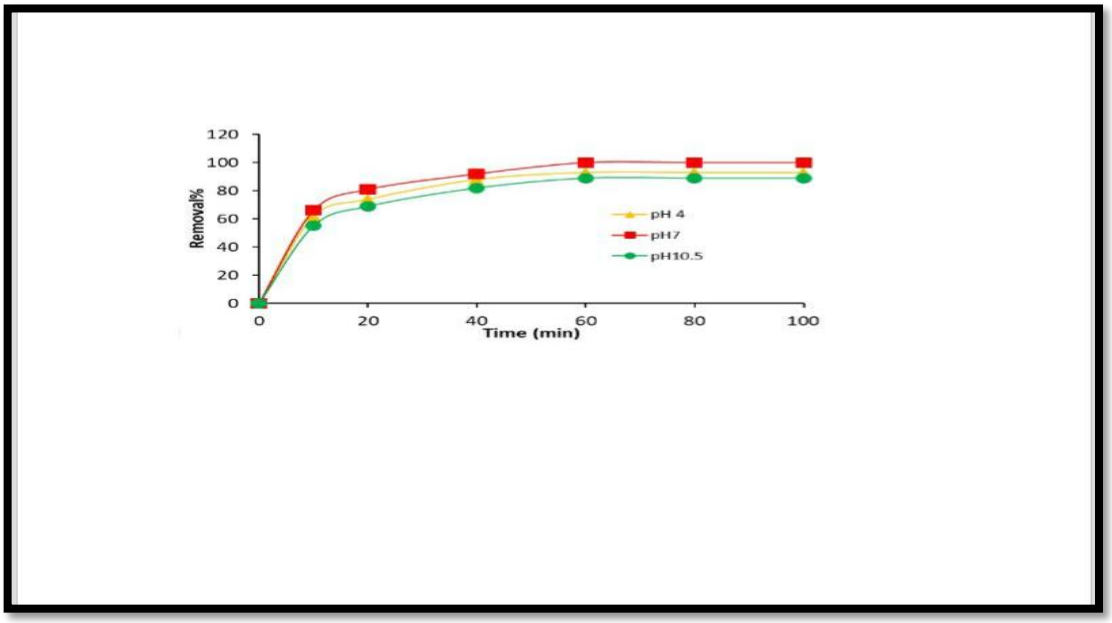


Fig.2 :effect of initial PH

●Choose an activated factorAnd the appropriate burning degree

In this study, we compared the burning degrees that were 200,350,600 °C, and 200 °C was chosen because it gave a better absorption rate (0.27), while at 350 °C it gave an absorption result (1.41).

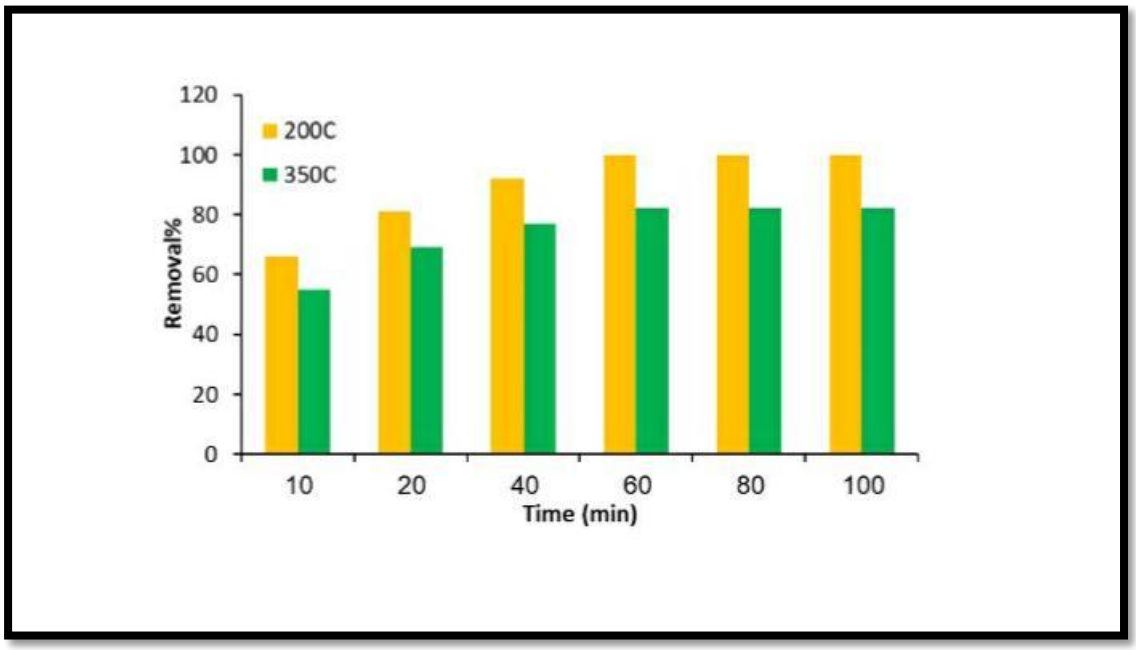


Fig.3 : Burn degrees

Then we have experimented with the selection of the appropriate material for the adsorption where ZnCl2 was because they gave better results than H3PO4

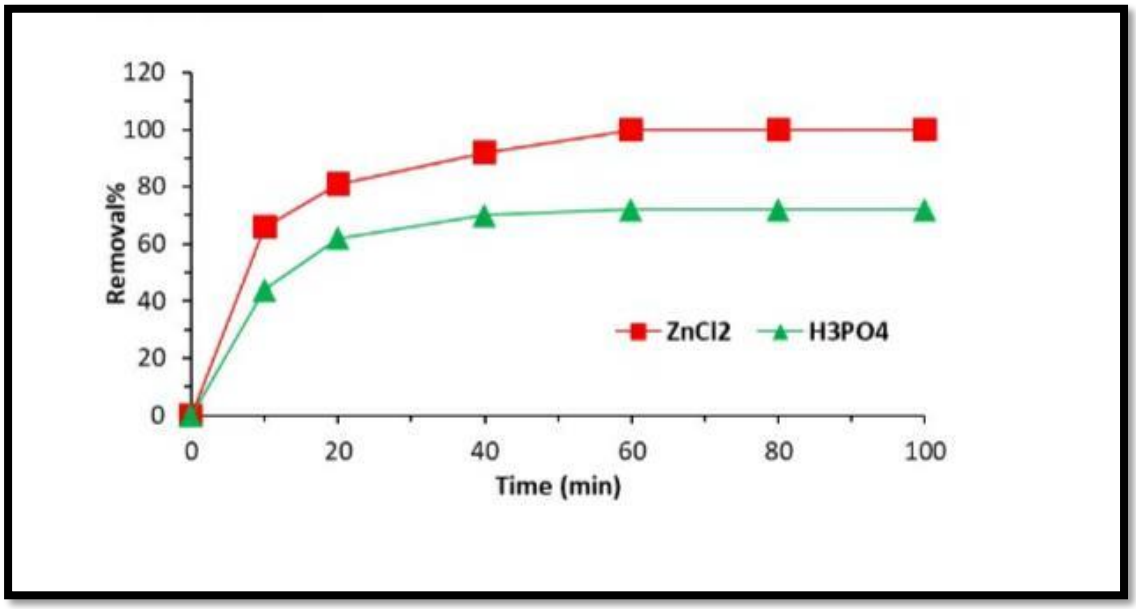


Fig.4 : The best article for adsorption

And Figure 5 illustrates the results of weight difference for maze, where 0.04 g

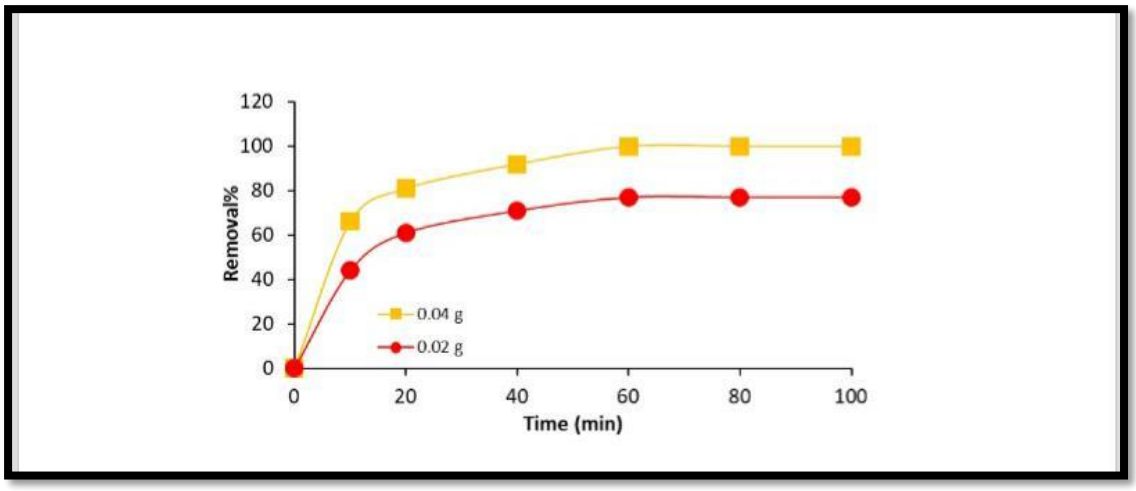


Fig.5 Difference weight

Conclusion.

In this study, a comparison between the carbon recorded in phosphoric acid and carbon recorded zinc, and found that the latter gives better results and absorption is also better as the result was given 0.27 at the appropriate 200 °C after the comparison of temperatures The combustion was 200.350. 600 ° C where 200 ° C was selected because at 600 ° C flying the whole article and 350 ° C do not give good results due to part of the part of them, then we studied the hydrogen effect on the absorption of dye in general, had a clear effect where when PH = 11 Absorbization will be 0.55 and at PH = 7 absorption gives 0.36 and at PH = 4 The absorption is 0.27, and the difference in the dye concentrations also leads to difference in the final results of absorption

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