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Department of Chemistry

Removal of malachite green dye using activated carbon

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﴿ فَتَعَالَى اللَّهُ الْمَلِكُ الْحَقُّ ۗ وَلَا تَعْجَلْ بِالْقُرْآنِ مِنْ قَبْلِ أَنْ يُقْضَىٰ إِلَيْكَ وَحْيُهُ ۖ وَقُلْ رَبِّ زِدْنِي عِلْمًا)

الاهداء

الى النور الذي ينير لي درب النجاح

أبي

ويامن علمتني الصمود مهما تبدلت الظروف ومن علمتني وعانت الصعاب لأصل الى ما انا فيه

أمي

اهدي لكم هذا النجاح

Abstract

Walnut shell (WS), as an economical and environmentally friendly adsorbent, was used to remove malachite green (MG) 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 malachite green 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 (pH4, pH7 and pH 11). When the pH is 11, the adsorption of methyl bromide retains an absorption efficiency of 0.55, at a pH of8 0.36, and at a pH of 3, 0.27, when the dye concentration was 200ppm. The adsorption kinetics of malachite green was studied. To determine how well malachite green Is removed

Keyword.. malachite green, PH, walnut shell

INTRODUCTION

Malachite green (MG) dye is an N-methylated diaminotriphenylmethane dye and exists in the form of a green crystal powder with a metallic luster. It is commonly used in the textile and aquaculture industries. However, MG dye is very toxic, carcinogenic, irritating to the skin, and has negative effects to the kidney, gonads, liver gill, intestines and gonads of aquatic organisms. Therefore, it must be removed before it is discharged into receiving streams The most efficient and low cost method that has been used in the removal of some pollutants (dyes, heavy metals, and etc) from the environment is adsorption. A variety of adsorbent materials have been used, such as orange peel, jackfruit peel, guava peel carbon and groundnut and gram husks. All of these adsorbent materials were successfully utilized for the removal of dyes from aqueous solutions.

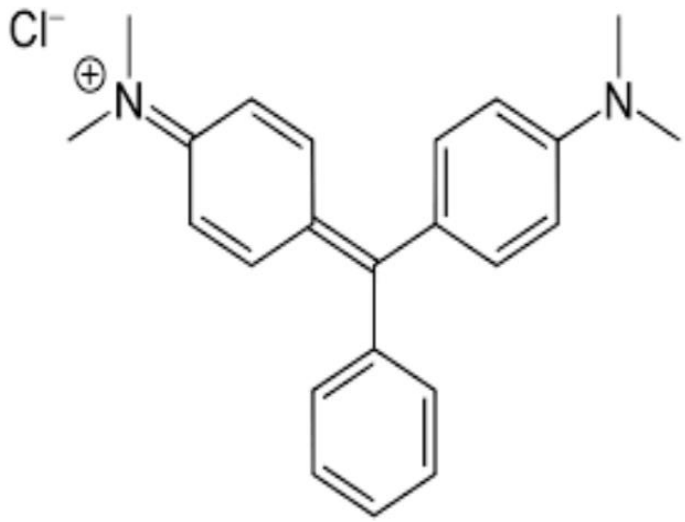


Figure .1: Malachite green structure

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, NaOH, ZnCl2, 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 mostWidely 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 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 (PH , 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 malachite green removal. Isotherms for the adsorption of methylene blue on the obtained.

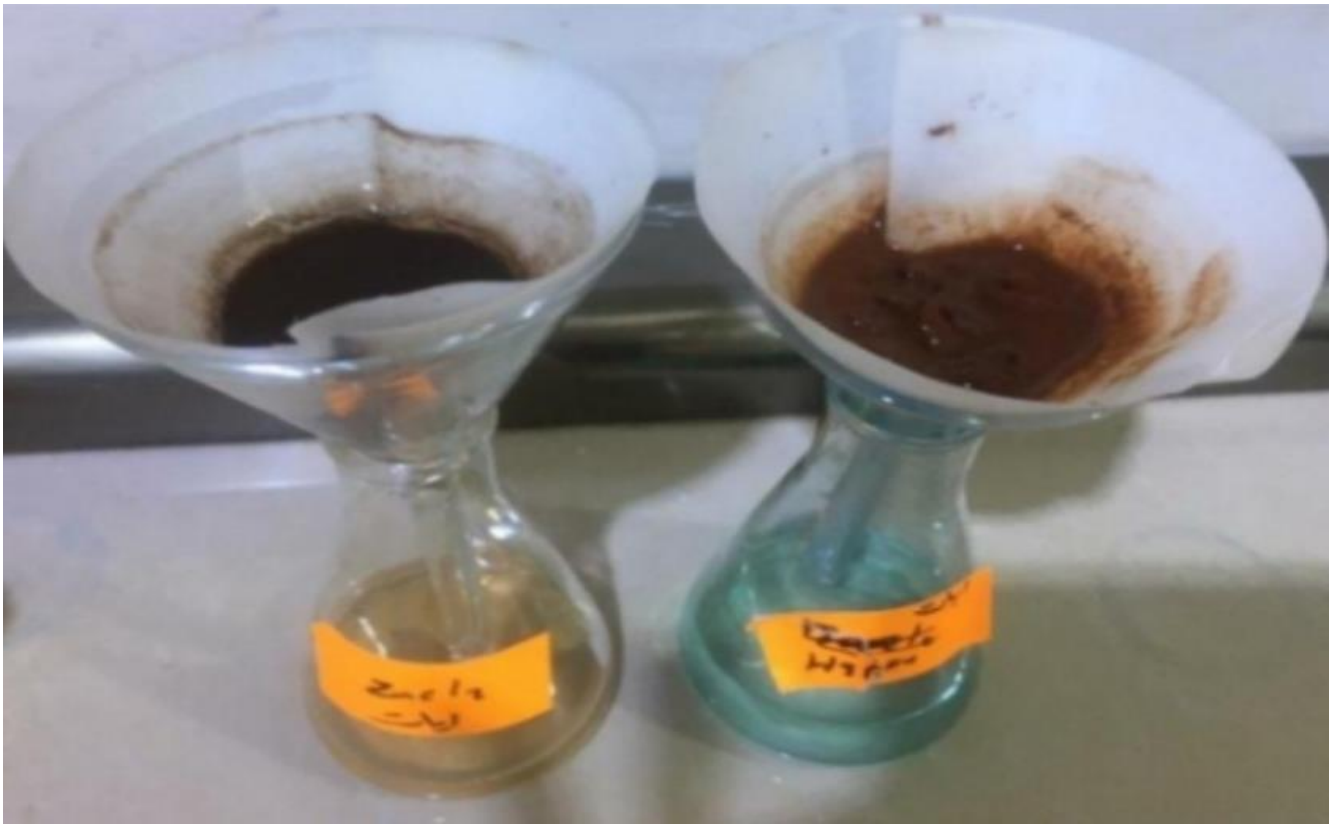
EXPERIMENTAL SECTION

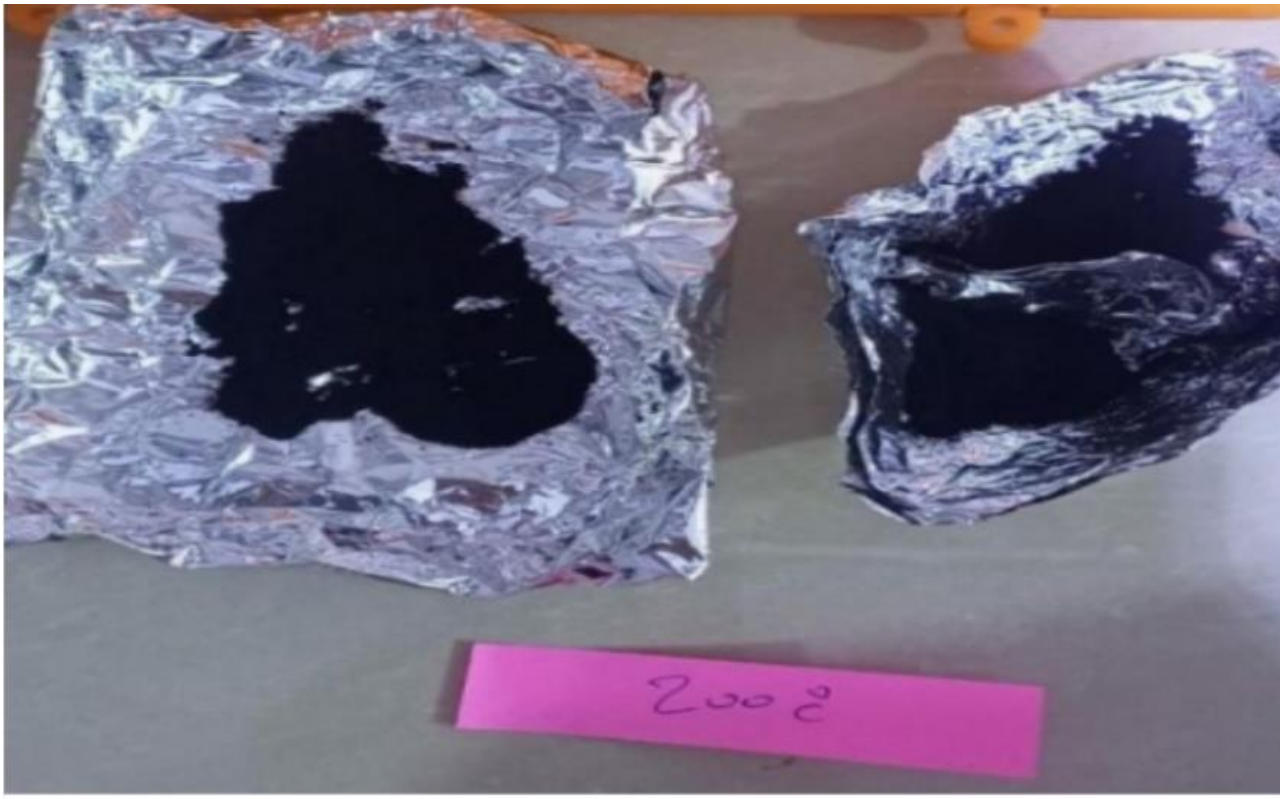
Materials

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. Malachite green, which is a basic (cationic) dye, is an adsorbent model used in adsorption studies; Purchased from Dyes and Chemicals Corporation . 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 stirredcontinuously 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.




200 g

Absorption experiments

25ml of different concentrations of malachite green dye solution (20-40/80 mg/L) was mixed with 0.04 g of absorbent and subjected to stoning for 80 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 (624 nm). The following equations were used to calculate the removal ratio and adsorption:capacity of malachite green dye

Where the starting dye concentration (Co) (measured in mg/L for MG), the residual

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

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

concentration © of MG dye in mg/L was measured and the final dye concentration © (measured in mg/L for MG) was given.R% Is the percentage of MG dye solution removed after adsorption; Q is the adsorption capacity (mg/g) at different times; and m is the amount of walnut shells (g). In order to create the necessary dye solutions, 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, 100mg/L) solution with 0.08 g to test the effects of contact time and initial dye concentration on desorption and adsorption capacity, according At pH (4, 7,10.5), at a concentration of 80 mg/L of MG dye, the effect of pH was shown. Using solutions of 1 M HCl and 1 M NaOH, the pH of the solution was changed. 0.08 g of absorbentWas added to 25 mL of an 80 mg/L solution of MG dye at 60 min. Samples were centrifuged after absorption and then examined. The concentration of malachite green dye was 80 mg/L and the supernatant was 0. 12 g.

Also, the absorbance of the activated carbon prepared by phosphoric acid was measured with different concentrations of malachite green dye 40ppm and 100ppm.

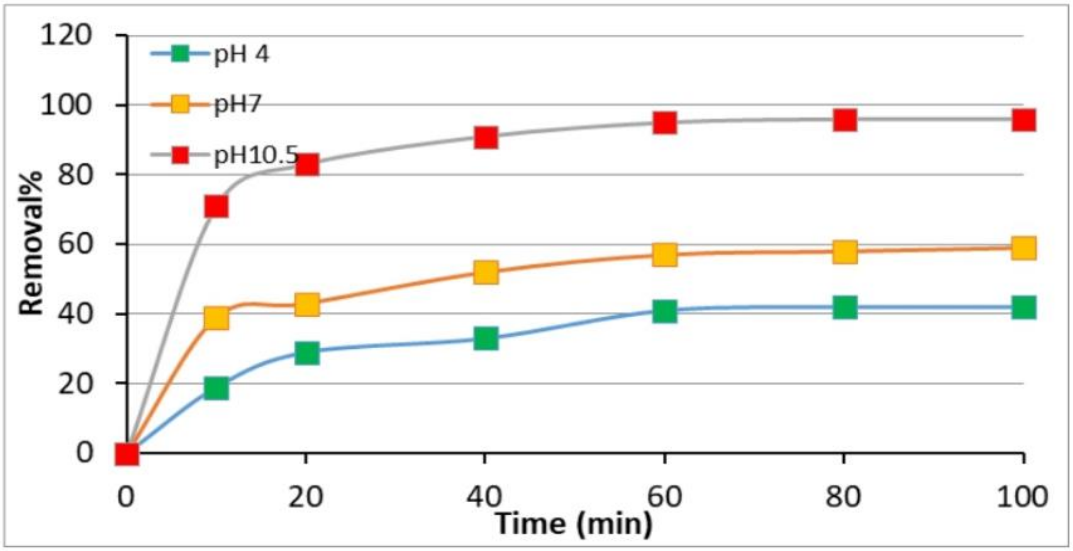
Result and discussion

Effect of Initial PH

The aqueous solution pH was found to significantly affect the adsorption capacities of dyes onto adsorbents [9]. Accordingly, the adsorption capacities of MG on WS were investigated under various aqueous solution pH. Figure 3 shows that, under acidic conditions (pH = 4), MG dye removal percentage (from 67.8 to 98.6%) and (from

10.84 to 15.78 mg/g) on WB increased significantly with pH increasing, while under base conditions (pH =8), MG dye removal percentage (from 98.7 to 99.5%) and (from 15.79 to 15.95 mg/g) on WB were similar.

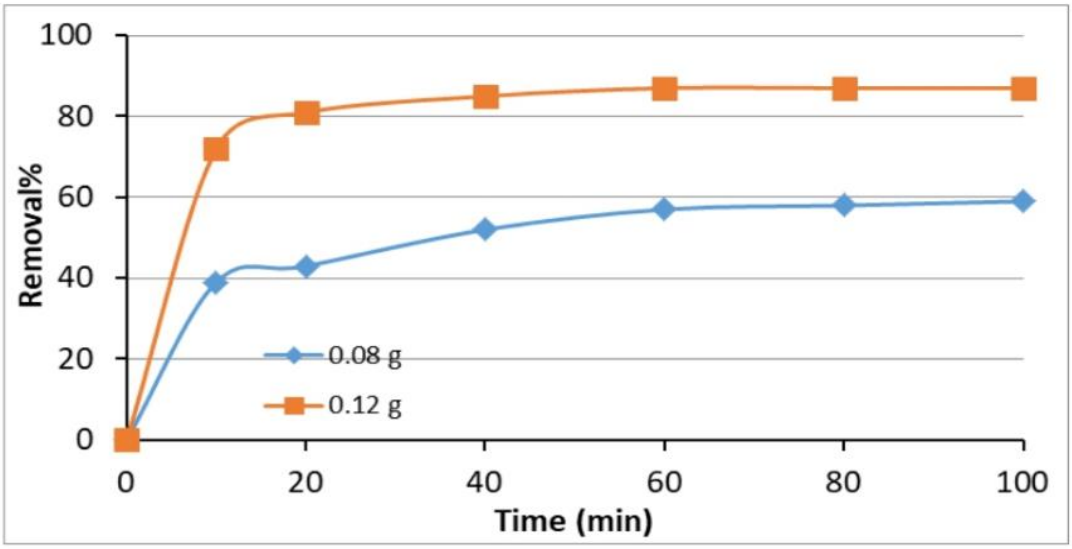
The differences In adsorption behavior under various pH values can be explained well from theElectrostatic forces between the surface charge of WS particles and MG dyes. The zeta potentials (<) of WS under varying pH values are shown in Table 2. Results showed that the WS particles were all negatively charged under our pH conditions (pH =)87/4/10.5. However, the WS surface was significantly less negatively charged at lower pH than at higher pH. 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. Also, under acidic conditions, large amounts of H3O+ ions existed, which can compete with dye cations adsorbing on the active sites of WS, resulting in the significant decreasing in the



Figur. 2Effect of Initial PH

Effect duse

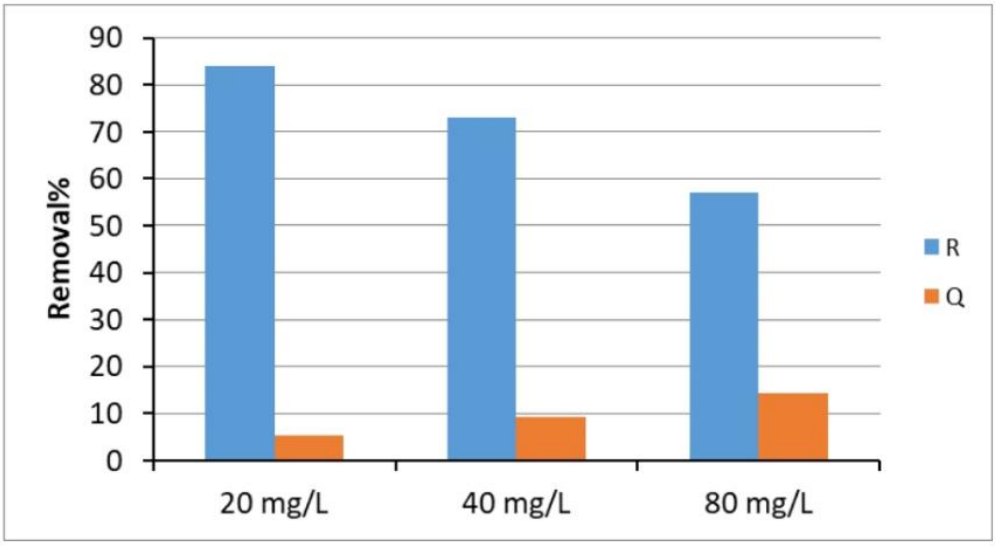
We prepared 2 conclaves and put in each of them 25ml of MG dye with different weights 0.08g of active carbon and 0.12g of active carbon at different times. We put them in the shaker and pulled out the material at a time of 20 minutes, at a time of 60 minutes, and at a time of 80 minutes after that. We put it in a center fuse device, and then we measured the absorbance of the material



Figur. 3 effect duse

Effect of Initial temperature

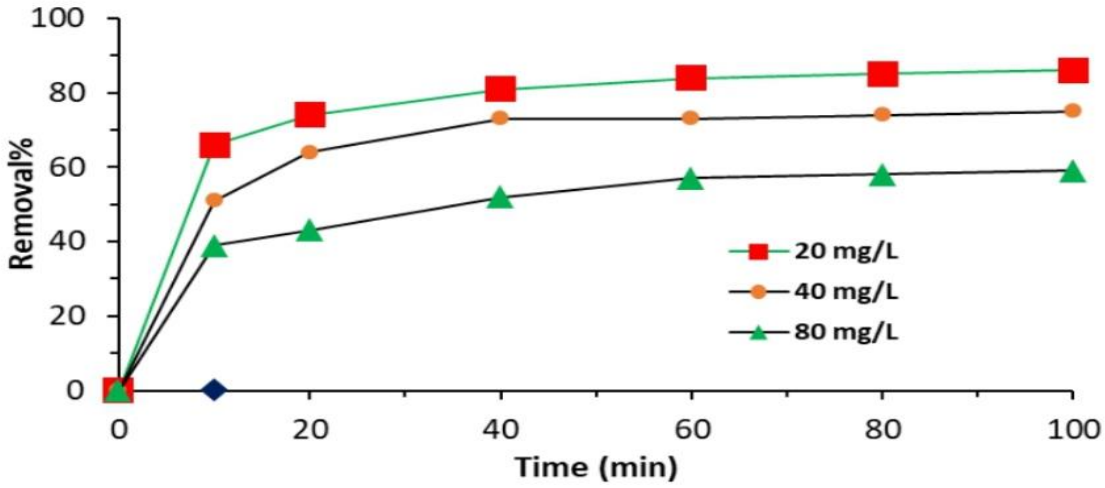
We used different temperatures, it was 200/350, we used 5g of Zncl2 and activated carbon from walnut shells burned at temperatures 200/350, so the best results were burned at a temperature of 200C, as it gave the best absorption and quantities of 20,40.80mg/l



Figur. 4 Effect of Initial temperature

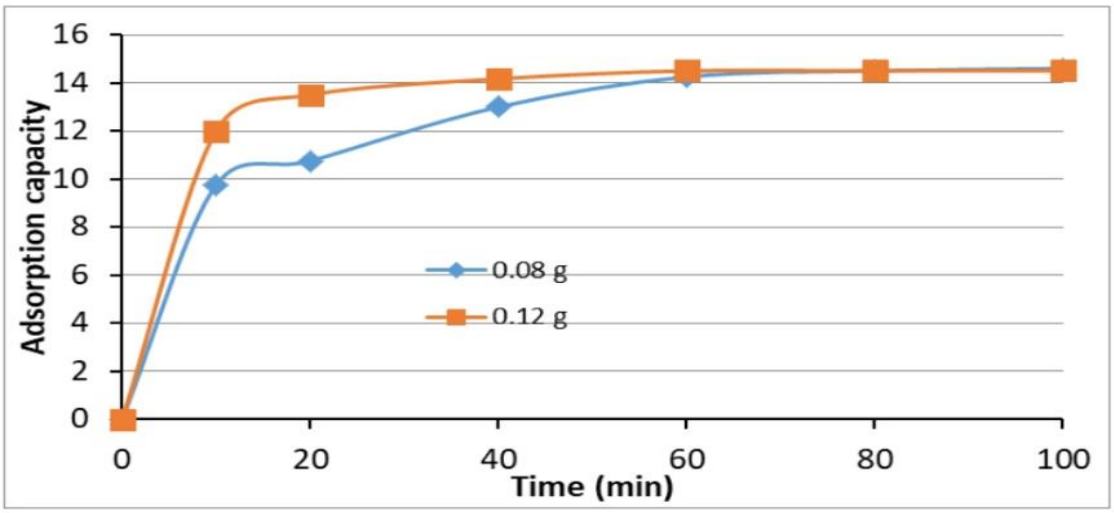
Effect of initial MG concentration

We used different concentrations of green malachite, the concentrations are 20, 40, 80 mg/l, and the active substance is Zncl2, which was burned at a temperature of 200 at a time of 20, 40, 60, 80, 100, so the absorption results were good



Effect of walnut shells amount

The amount of walnut shells that we use has an effect on the amount of absorption, as we worked with different weights, and the weights are 0.08, 0.12g, where in the weight of 0.08, the absorption efficiency of malachite green dye increased, and the reason is due to the high number and locations of the empty space for absorption, but the higher the quantity, the lower the absorption rate



Determine the material that gives the best results

We did some experiments to compare the material prepared by Zncl2 and the substance banned by H3P04, and the results showed that the material prepared in Zncl2 is better than that prepared in H3PO4, because zinc chloride results in high surface areas and high yieldsAnd also with other experiences we choose the most appropriate burning degree and 200 °C, where they gave better results than 350 and 600 where the material and then weight experience the best weight experience where 0.04 g gives the results of absorption and a better absorption of 0.02 grams The results have no clear

CONCLUSION

We used three temperatures, namely 600, 350, and 200, to burn walnut shells and make activated carbon, so we noticed that the material at the temperature of 600 had completely volatilized, and at the temperature of 350 a small part of it volatilized, but at the temperature of 200 it gave the best results for the activated carbon, but we worked at temperatures of 200,350 in measuring absorbance and it was better The results are at a temperature of 200 degrees, and we used several materials, including H3PO4 and ZnCl2, and the best results were for the absorption of ZnCl 2, as it gave good results, and we used several times of 20, 40, 60, and 80 minutes.

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