Removal of Methylene Blue Dye from Water using Ecofriendly Waste Product (Eggshell) as an Adsorbent and Using the Optimum Adsorption Conditions with Real Water Sample from Tigris River

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Abstract

Environmental pollution is a worldwide issue that affects the human being health, water pollution is one of the causes of this phenomenon. Dyes represent the raw materials in many industries such as textile, paper, plastic and leather industries as well as they considered as toxic water pollutants. The adsorption method is one of the most effective methods for removing dyes from polluted water. In this search, ecofriendly food waste (eggshell) was used as an adsorbent for removing methylene blue dye (MB) from waste water. In this research, eggshell morphology was studied using Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX). The stability of the eggshell adsorbent was tested by Thermal Gravimetric Analysis (TGA). Whereas checking with various MB dye concentration for eggshell the maximum adsorption was noticed at (8ppm) and this concentration was used for further optimization. MB solutions was prepared at pH 7.2 and at 21℃ same conditions as in Tigris River water which was used to compare the activity of the eggshells adsorbent using analytical standard MB solutions and on the other hand using real sample solutions. The results show that using eggshells adsorbent with standards solution and real sample solutions of MB provide the same general trends with respect to MB removal. Consequently, using eggshell as an ecofriendly adsorbent was successfully tested to be used with both MB analytical standard solutions and real river MB solutions.

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1- Introduction

The term dyes refer to organic chemicals that used broadly in different industries such as cosmetic cloth painting and printing [1]. However, these industries produce huge amounts of waste which need expensive treatment to lower down the dyes concentration before clearing it into natural water streams [2]. Recently, as mention by Yagub et. al., there more the seven billion tons of dyes west per year [3] and since most of these dyes is water soluble therefor, it bring a great danger in terms of environmental pollution [4]. As a result, researchers used wide range of Separation strategies as methods to treat wastewater for example, ion-exchange, precipitation, adsorption, extraction, etc. [5]. However, each one of these techniques has its advantage and some problems. Adsorption method may be viewed as a chance to be a successful procedure compared with different separation systems for wastewater. With respect to cost, simple design, and suitable for wide range of chemicals [6,7]. Finding an environmental friendly adsorbent is one of the most important duties for the researches and one of these adsorbent might be the eggshell waste. Calcium Carbonate is the main composed of eggshell which represent about (94. 03%) and it additionally holds calcite and calcareous [8]. The cellulosic structure of eggshell also contain amino acids; thus, it may be anticipated a chance to be a great bio sorbent [9]. Furthermore it might have been accounted that a huge quantity of waste eggshells have been produced in some area worldwide and find their way to landfills each year [10]. Many attempts have been done to use eggshells as an adsorbent such as: Ziad Tark Abd Ali et al., used egg shell powder to remove Cu (II) and Cd (II) from aqueous solutions [11]. Arami M. investigate the capability of eggshell to adsorb dyes textile [12]. Mohammad A. Al-Ghouti and Mariam Khan have used the eggshell as a biosorbent for Boron remediation from desalinated water[13]. Moreover, Dhuha, D. Salman,et al., have determined the optimum conditions of methylene blue adsorption by the hen eggshell [14]. Afrah A. Hassan et al., studied the behavior of eggshell as an adsorbent in removing of dye from aqueous solution [15]. On the other hand, Gupta, V. K.,et al., considered eggshell a low cost adsorbents in wastewater treatment [16]. M. Pettinato et al., have been worked on eggshell as a green adsorbent to be used for heavy metal removal process [17] B.A. Dar et al., also considered eggshell as an excellent and low cost sorbent for the removal of Ni (II) ions from wastewater [18].

In this research the author used eggshells to remove a Methylene Blue dye (MB) from aqueous solution; however, a real sample had been collected from Tigers River and contaminated with MB to compare the result obtained under lab conditions.

2- Materials and Methodology

2.1 Eggshell adsorbent preparation

Eggshells with its membrane have been collected from kitchen waste. The eggshells were washed with deionized water several times and left to dry. the membranes were manually separated from eggshell then left to dry in oven under 105ºC for 30 minutes. The dry product was grounded and sieved to obtain 200 – 250 µm particles size. Lastly, it kept in sealed container for further use.

2.2 SEM EDX and TGA analysis test.

The eggshells powder surface was analyzed using SEM morphology technique by using FEI SEM manufactured in Netherland in Al Nahrain University College of Science. The sample was coated using gold coating technique by Quorum from England. The EDX analysis was conducted using Burker X-flash 6110 from Germany followed spot procedure to study the eggshell elements. STA PT-1000 from Linseis Germany was used for TGA test.

2.3 Eggshell acidity solvation test

Ten solutions of different pH values (2, 3,4,5,6,7,8,9, and 10) were prepared by adding 10 ml of deionized water to 25 ml beaker. 0.1 M HCl and 0.1 M NaOH solutions were added to these solutions drop by drop to adjust acidity using Hana pH meter from USA under room temperature. 0.1 gram of eggshell adsorbent was added to each beaker to test the solvation for each solution. The solutions were kept in shaker for 10 minutes, filtered and lift to dry under 105℃ for 30 minutes. Finally, the products were weighed to calculate the recovery percentages.

2.4 Preparation of dye polluted standard solutions:

Five standards solutions of methylene blue (MB) which was purchased from BDH, England have been prepared as 2, 4, 6, 8, and 10 ppm. The stock solutions were prepared by dissolving a proper amount of MB in 100 ml deionized water. The 2 ppm standard solution was selected to determine the maximum wave length of MB using UV-Vis spectrophotometer (Shimadzu, Japan). The calculated wave length was 664 nm. All the solutions were kept in dark place for later experiments.

2.5 Connection time test.

A 0.1 gram of eggshell adsorbent in 10 ml of MB standard solution was added to conical flask and kept in shaker under room temperature for 5,10,15,20,25,30,and 35 minutes to examine the contact time effect on adsorption process between MB and eggshell.

2.6 Preparation of dye polluted real sample solutions

Water sample has been collected from the mid–stream of Tigris River in Baghdad to prepare polluted solution of MB. The river water was firstly, filtered, centrifuged for 5 minutes and 3000 RPM and finally the sample filtered again to remove any solid particles. All the solutions were kept in dark place for later experiments.

2.7 Batch Experiments

This section has two parts: firstly using standard polluted solution and secondly using real sample polluted solutions. Five conical flasks have been used in each part and 0.1 gram of eggshells have been added to each flask. In the first part 10 ml portion of standard solution was added to each flask while in the second part 10 ml portion of Tigers River water was added to each flask. The ten conical flasks of each experiment were placed in water bath shaker from Jeio tech Korea under 21°C (Tigers River temperature at the time of sample collection) for 25 minutes. Finally, each solution was filtered and centrifuged for 5 minutes and 3000 RPM and transfer for UV-VIS spectrophotometer to measure solution absorbance at 664 nm.

3- Results and Discussions

In this section, the results obtained will be discussed and ending up with a conclusion statement. The discussion will start with morphology analysis for the eggshell by using scanning electron microscope and EDX analysis for the eggshell surface. The other sections will discuss the results obtained from this project to determine the optimum adsorption conditions using eggshell waste as adsorbent.

3.1 Characterization of egg shell

3.1.1 SEM morphology analysis

Eggshell morphology has been examined to study the surface of the eggshell adsorbent as in Fig.(1). The SEM image as in Fig.(1a) shows that the eggshell particles have relatively regular micro sizes which might increase the adsorption process on the eggshell surface. The surface area is directly proportional to the active surface area which allows to the polluted solution to penetrate to the adsorbent surface which leads to minimize waste water pollution. Fig.(1b) shows the EDX analysis of eggshell which show that the Calcium is the dominate element in the eggshell contain which is representing the Calcium carbonate in the eggshell. The element showing on the EDX analysis might be referring to the coating process conducted before testing the eggshell sample using SEM technique.

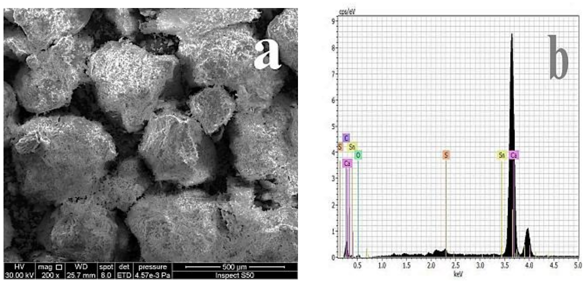

Fig.(1): SEM image and b EDX of egg shell adsorbent.

3.2 Adsorbent thermal stability test

Thermal gravimetric analysis (TGA) technique was used to examine the thermal stability of eggshells adsorbent as shown in Fig.(2). The TGA plot shows an excellent stability during the experiment. The eggshells adsorbent resists temperature up to 600°C. Which was an evidence of high stability structure of the eggshell and it could be used under severe conditions, unlike the other low cost adsorbents such as coconut fiber, banana fiber [19] which might not resist high temperatures.

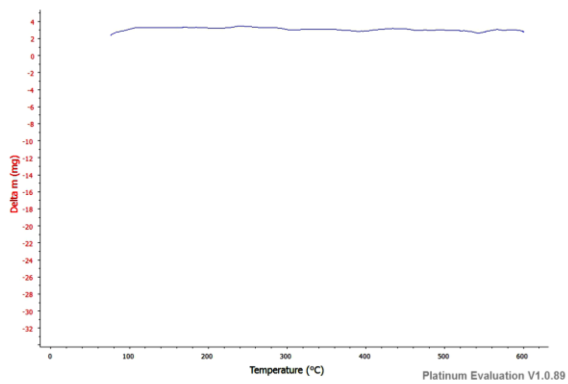

Fig.(2): thermal analysis test for eggshell adsorbent.

3.3 Eggshell acidity solvation test

Solvation analysis with respect to the medium acidity is one of the most important tests to study the adsorbent optimum conditions; this is because the acidity has an essential impact on the solvation of the eggshell adsorbent. The results were determined by calculation the weight difference of eggshells, as in Table (1) the recovery percentages show there is no solvation on the range of pH values solutions between pH 5 to 10. However, the eggshells partially dissolved at pH 4 and end up totally dissolved at pH 2 and 3. The important point in this step is to examine eggshell solvation at pH range from 7 to 8 which is mainly the pH of real sample acidity as it was measured for real sample solution.

Table (1)
0.1 gm. eggshell solvation test with respect to pH value.

Solution Acidity/pH	Solvation	Recovery %
10	No	99.5
9	No	99.6
8	No	99.4
7	No	99.7
6	No	99.5
5	No	99.6
4	Partially	46.8
3	Yes	0.0
2	Yes	0.0

3.4 Effect of contact time on MB. Absorbance

Fixed amount of eggshell adsorbent of 0.1 gram have been tested with 8 ppm of MB dye with respect to different contact time under 200 shaking frequent per minute. As shown in Fig.(3), the optimum contact time was 25 minute and after that time the absorbance percentage of the MB dye was steady which means there is seem to be longer than 25 minute time has not significant effect on the absorbance progress. This might be due to the adsorbent capacity which indicate that under this conditions (0.5 gram and 8 ppm MB. concentration) 25 minute contact time reach the maximum decoloring. However, increasing the eggshell weight might increase the adsorbent capacity using the same dye concentration.

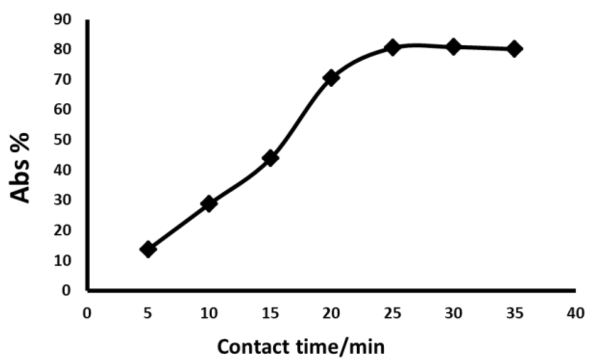

Fig.(3): Effect of contact on MB percentage absorbance.

3.5 Calibration curve analysis

A calibration curve has been presented in this study to examine the general tendency of MB adsorbent variance values i.e., (MB. absorbance before and after adsorption with eggshell) with a range of concentration between 2-10 ppm. As shown in Fig.(4) the main trend of the MB absorbance goes steady with direct proportional to MB concentration which refers to the eggshell adsorbent stability with 25 minute contact time and at room temperature. However, the absorbance value at 6 ppm concentration showed a little deviation which slightly affects the correlation coefficient value R^2.

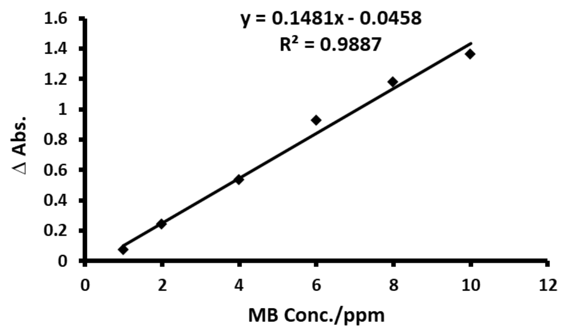

Fig.(4): calibration curve of MB. with different concentration.

Fig.(5) present the trends of MB absorbance percentage against the different dye concentrations as in calibration the absorbance increased as the concentration increased of MB. However, the curve showed a steady behavior using 6, 8 and 10 ppm of MB all the solutions was absorbed with the same eggshell amount and at the same acidity under room temperature.

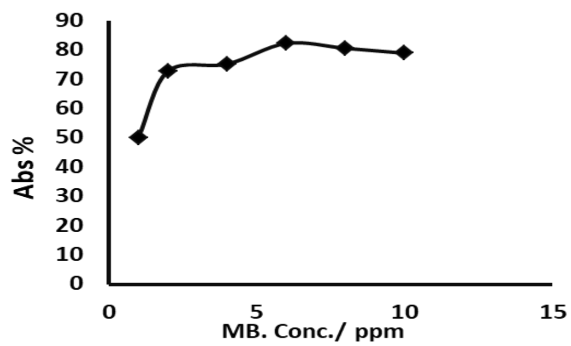

Fig.(5): MB. Absorbance percentage with different concentration.

3.6 Real sample analysis

In this section of the research, water sample have been collected from Tigris River in Baghdad city/Iraq. The sample has been used instead of deionized water to prepare MB solutions. The results will be compared with that obtained under laboratory conditions. As presented in figures 6 and 7 the general trend of MB absorbance percentage or difference whereas the same obtained using deionized water.

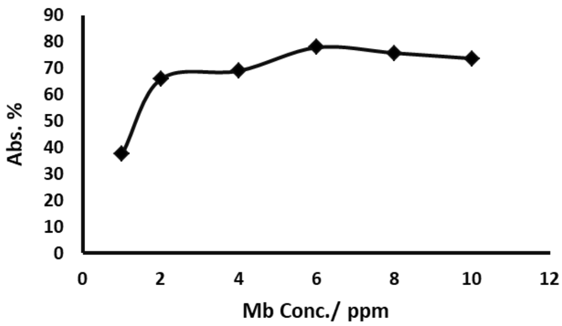

Fig.(6): MB. Absorbance percentage with different concentration in Tigris water.

The calibration curve as in figure 7 showed nearly the same value as in lab conditions of correlation coefficient value R^2 which is indicate the stability of eggshell adsorbent. The pH value of Tigris water was measured which was equal to 7.6 although, in first section the acidity condition was occurred using pH 7 solutions. Finally, the temperature was kept under room temperature for both parts of this project.

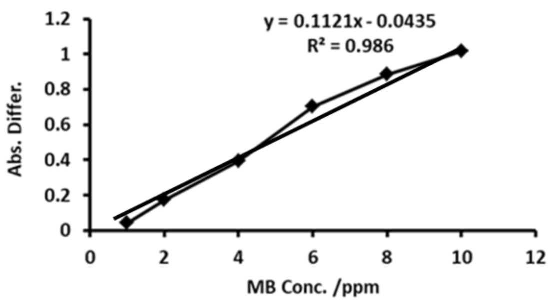

Fig.(7): calibration curve of MB with different concentration in Tigris River water.

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4- Conclusion

In conclusion, using eggshell as an ecofriendly adsorbent was successfully tested to remove MB dye from solutions using deionized and Tigris water solutions. The experiments were conducted under room temperature and pH 7 for part one, and pH 7.6 for part two of this research. The calibration curves for both parts show stable trends with nearly the same correlation coefficient value R2 which indicate the stability of eggshell as adsorbent.

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