

Elimination of Methylene Blue from Solution using Modified Scrap Tire

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Abstract

The disposal of the waste tires has become a serious problem faced by many countries today; recycling offers a powerful solution to this problem, for example using it as an adsorbent. In this research, we studied the modification of scrap tire by radiation with gamma ray in trichloroacetic acid solution and elucidated the possibility of using it as an adsorbent to remove Methylene Blue dye (MB) from aqueous solution. The effect of various variables, such as time passing, primary concentration of MB, the quantity of adsorbent and PH of the medium was studied in order to obtain the maximum dye removal. Equilibrium time was at 45 min, maximum adsorption was at PH=9. The results showed the scrap tires' ability to be modified and the possibility of using it as an available and inexpensive adsorbent, as well as providing a safe disposal of solid waste.



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Introduction

With the development of country's economy and population, the amount of scrap tires is increasing and represent a major ecological issue since it occupies a large area and non-biodegradable¹. In many countries, scrap tires are recycled to obtain valuable products such as fuel derived from tires, and used in asphalt, in paving roads and floors, with all these uses, large quantities of old tires are remain discarded annually^{2,3}. Therefore, it is necessary to explore other applications like utilize as an adsorbent. Scrap tires include (30% W/W) carbon black, which

has properties similar to activated carbon but less surface area.^{4,5}

Many factories use methylene blue dye (MB) to color their products. It is used in textile, wool, cotton, plastics and pharmaceutical industries. This dye is visible even in low concentrations and may absorb or reflect sunlight in the water, which affects the growth of bacteria and when human take these dyes, it causes different diseases, including eye irritation and diseases related to the digestive system, so it was necessary to remove these dyes from the water.^{7,8}

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There are many ways to remove dyes from the water and between these methods; adsorption technique is the perfect way for being an economical and easy and does not produce wastes are difficult to get rid of them.⁹

We found a lot of researchers using old tires in the process of adsorption to remove organic and inorganic contaminants and dyes from their solutions. Hamadi *et al.*¹⁰ studied the removal of Cr (VI) from aqua. solution by adsorbent derived from the used tires, Amenaghawon study the Adsorption of Toluene from aqua. Solution in Scrap Tires¹¹ F.A. Aisien *et al* studied Ethylbenzene adsorption from aqua. solution by Scrap tires¹, F. Calisir *et al*, studied elimination of Copper(II) from its solutions using scrap tire rubber¹², Knocke and Hemphill studied adsorption of Mercury (II) on scrap tire rubber.¹³

Many studies have shown that the irradiation process of recycled rubber improves its mechanical and morphological properties. Yassin *et al.*¹⁴ investigated the effect of irradiation on the physicochemical properties of waste tire rubber and noted that ionizing radiation provides a solution to the problem of tire recycling due to its ability of crosslinking or the cleavage of a wide range of materials. Borriello *et al* studied the effect of irradiation on the thermoplastic polymers¹⁵. Telnov *et al.* explained that an electron beam with ranging energy from (6 - 10) MeV could provide an alternative method of recycling waste rubber and to reactivate based on butyl rubber¹⁶. Shanmugaraj *et al.*¹⁷ studied the effect of ultraviolet radiation in the presence of allylamine on crumb rubber and the results of the study showed improvement in tensile strength and elongation, which had ascribed to the energized crumb rubber surface. Adnan *et al.*¹⁸ studied the "Mechanical and Curing Properties of Crumb Rubber Irradiated in Polar Media Filled the Tire Tread Blend". High polar media such as Acetic acid and Trichloroacetic acid (TCA) show better tensile and elongation properties.

This study focused on the possibility of using rubber granules after exposure to radiation in trichloroacetic acid (TCA) and to investigate the possibility of improving their adsorption capacity.

Materials and Protocols

The crumb rubber (CR) utilized for this investigation had brought from General Motors Company in Najaf City, Iraq. There was no steel content. The CR size 0.04 to 0.6 mm was utilized in this work. At that point, washing the CR with refined distilled water to expel any foreign materials, then it was dried at 50-60°C for 4 h and stored in containers for following apply. 18

Adsorbate (MB) Preparation

Methylene Blue ($C_{16}H_{18}N_3SCl$) was utilized to prepare the stock solution (1000 ppm) by dissolving 0.5 g in 500 ml distilled water. A series of diluted dye solutions were prepared (1-30) ppm. The PH of the solution was adjusted using diluted solutions of (0.1 M NaOH) and (0.1 M HCl).

Modification of Crumb Rubber

Samples were taken from a crumb rubber with different sizes (0.04-0.6 mm) and subjected to gamma rays with TCA solution (20%W/V) to increase its surface activity during the adsorption process. The samples were placed in plastic bags and exposed to radiation from 60-Co source at dose 0.5 kGy/h. After that the samples were cleaned with water and dried at 50 °C for 6 hours and then place in containers inside the desiccator for later use.

Batch Experiments

Experiments were conducted in batch mode. 0.5 g of modified CR was taken with 50 ml solution from different concentrations of MB dye placed in the Erlenmeyer flasks in a water bath with a shaker (120 rpm). Several variables were studied, such as time period, PH of the medium, concentration of dye, quantity of CR and granule size. Each time one of the variables was studied and the other variables were kept constant, thus obtaining the optimum conditions for the adsorption process. The solution was agitated until both the solid and the liquid medium reached equilibrium at which point the dye concentration on both mediums was constant. The solutions were filtered at the end of each experiment using Whatman No.1 filter paper, and the remaining concentration of dye was measured spectrophotometrically at λ_{max} 665 nm.

The adsorption capacity of CR for MB q_e was expressed the amount of MB retained by CR. This is expressed as:

$$q_e = (c_0 - c_e)V/W \quad \dots(1)$$

Where: C_0 is the initial dye concentration (mg/L), C_e is the equilibrium con.(mg/L), V is the solution volume (L) and W is the amount of CR (g).

Percentage removal (%R) of MB was calculated utilizing this equation:

$$\%R = c_0 - c_e / c_0 \times 100 \quad \dots(2)$$

Results and Discussion

Impact of Contact Time

Different contact time at initial concentration of MB (20 ppm) was done in a batch sorption test. The Erlenmeyer flasks were taken out the water path-shaker at periodic intervals and the samples were filtered, the filtered solution was used to determine the MB concentration. The concentration of MB in solution was analyzed using a UV-VIS spectrophotometer by measuring the absorbance at λ_{max} 665 nm. Adsorption of MB on CR is shown in fig. (1).

Initially, the number of active sites is very large which allows adsorption to take place very easily. But as the time passes, the active sites get saturated thus slowing down the removal of dye. The figure shows that the highest removal is at the equilibrium time of 45 minute, and after this time we notice that the concentration of the dye remains constant.

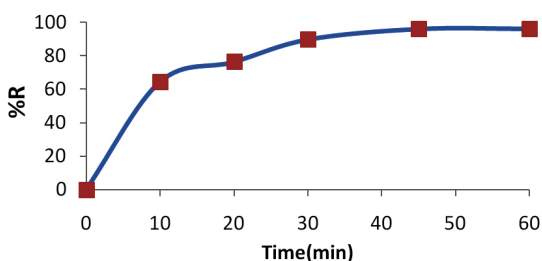


Fig. 1: Variation of MB percentage removal vs. time by modified crumb rubber (Condition: 20 ppm primary dye conc., PH=9, 0.5 g adsorbent, agitation speed 120 rpm)

Runping et al, reported that the equilibrium time of MB adsorption by other adsorbent (tree's leaves) was 30 min.¹⁹

Impact of PH

One of the most important factors affecting the process of adsorption is the PH, as it affects the protonation and deprotonation of adsorbent surface in addition to the formation of new species of solute. The effect of the PH on the adsorption process was studied in a range from 3 to 9. Acidic and basic solution was adjusted using 0.1M HCl and 0.1M NaOH, other conditions were kept constant. Fig. (2) shows the influence of PH on the removal of MB.

Fig. (2) clearly shows that the highest dye removal is at pH=9 and that the least removal is in the acidic medium and this is due to a number of reasons that may relate to the dye and the PH of the medium. The surface may contain active sites in large numbers and the adsorption of the dye is related to these sites. It also relates to the surface chemistry of the solute at the low PH. The surface of the CR is surrounded by hydrogen ions that may compete with the dye ions on the active sites on the surface. The surface may get a negative charge, which may lead to electrostatic attraction between the surface and dye molecules. Other adsorbent material such as oak saw dust gave the same results for the effect

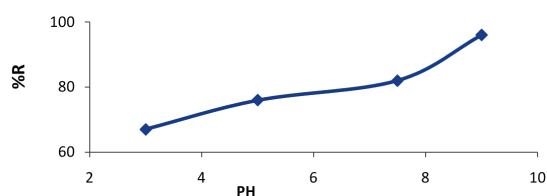


Fig. 2: Variation of MB percentage removal vs. PH of medium by modified crumb rubber (Condition: 20 ppm primary dye conc., contact time 45 min, 0.5 g adsorbent)

of the PH on adsorption of MB²⁰, Satish Patil et al, found the maximum removal of methylene blue by teak tree was at PH=11.21.

Influence of Primary Dye Concentration

Fig. (3) illustrates the adsorption capacity of MB dye for different concentrations, which is clearly increased with the primary concentration of dye.

This is explained by the fact that when the dye concentration is increased in the solution, the driving force of the mass transfer increases, so the dye molecules transfer from the bulk solution to the surface of CR. Ould Brahim reported similar

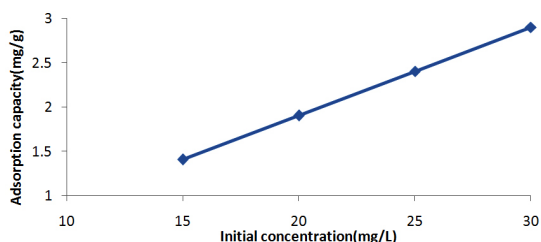


Fig. (3) Variation of MB adsorption capacity vs. primary dye concentration by modified crumb rubber (Condition: PH=9., contact time 45 min, 0.5g adsorbent)

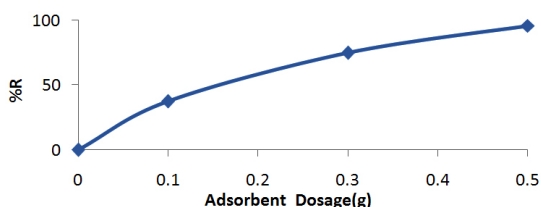


Fig. 4: Variation of MB percentage removal vs. adsorbent dosage by modified crumb rubber (Condition: PH=9. contact time 45 min, 20 ppm primary dye conc.)

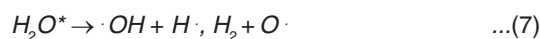
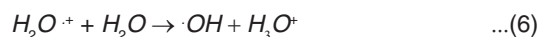
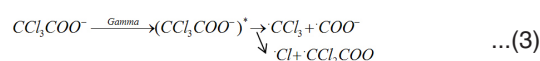
observation when he was studied the removal of Azo Dye by adsorption on AC Prepared from used tires²²

Determination of the Optimum Quantity of Adsorbent

The study of the amount of adsorbent gives an idea about the effect of it on the dye adsorption process with a minimum dosage. The results of this study are represented on the fig. (4) And it is shown that the percentage of dye removal increases with increasing the quantity of the adsorbent and this is due to the increase in the number of effective sites

with increasing the quantity of the adsorbent. Similar observations were reported in other studies^{23,24}

The radiolysis of TCA by gamma rays created a series of reaction that led to the formation of many types of radicals such as: Cl , OH , CCl_2COO , COO and CCl_3 as seen in Eqs. (3)– (8), in addition to the radiolysis products of water ($OH\cdot$, $H\cdot$, $H_2O\cdot$ and e_{aq}^-). The existence of one or more of these radicals may be modified chemical and physical nature of the crumb rubber surface toward adsorption of the dye under study.



Conclusions

This study showed the possibility of using modified rubber granules (irradiated in TCA solution) as an adsorbent to remove MB dye from solution. The irradiation process has improved the surface properties of the adsorption process. The adsorption process affected by many factors, these factors can be optimized In order to obtain the best removal of MB dye. Modified rubber granules can be used to remove other dyes and can also be used in the removal of heavy metals from the aquatic environment. The use of crumb rubber provided cheap and available adsorbent, in addition to the safe disposal of solid waste.

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