RESEARCH ARTICLE

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Evaluation Low Cost Adsorbent of Walnut Bark Granule for Methylene Blue Dye Removal from Aqueous Environments

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Background & Aims of the Study: Methylene blue (MB) is a risk for human and environment. Adsorption process is one of the removal mechanisms of MB. The purpose of this research was the evaluation of low cost adsorbent of walnut bark granule for MB dye removal from aqueous environments.

Materials & Methods: In this experimental research, the effect of various operating parameters such as dose of dye (100-500 mg/L), contact time (10-50 min), adsorbent dosage (1-5 g/L) and pH (3-8) was investigated. Color concentration was measured by spectrophotometer (Shimadzu Model UV-120-02) at 663 nm wavelength and pH was analyzed through pH meter (Digimed model DM-20, Digicron AnaliticaLtda, Sao Paulo, Brazil).

Results: The findings of this research were showed that the walnut bark granule was able to remove up to 41% of MB dye (100 mg/L) from solutions at initial pH 7. Removal efficiency was increased by adsorbent dosage and contact time. MB concentration has a reverse effect on removal. Also, the equilibrium data were also fitted to the Freundlich equilibrium isotherm model (R^2=0.95).

Conclusions: Present study showed that use of walnut bark granule, as an absorbent, could be utilized in methylene blue removal. Therefore, considering the production wastes of this compound, utilization the essence of this substance as inexpensive absorbent with inexpensive and available raw material is clear.

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Background

Due to increasing industrial activities, the increase of contaminated water sources are considered as environmental problems such as chemical oxygen demand (COD) by the water body, and an increase in toxicity(1). Methylene blue (MB) that belongs to cationic dye classification of thiazine, used in textile, paper, plastics, food industries and medicine (Fig.1) (2). Sewage released by these industries pollutes and colorize the fresh water of streams, rivers and underground water (3). MB has not biodegradability and cause environmental

problems to the water sources. Thus, color may still remain in the effluent (2,4).

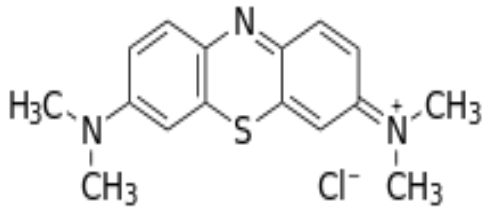

Figure 1) Molecular structure of methylene blue.

Colored effluent caused to damages the aesthetic nature of the water surface and lowering photosynthesis (4). Dyes may cause skin irritation, dysfunction of brain, reproductive effects on kidney; also, have mutagenic and carcinogenic effects, too (5,6). As most of these dyes are hazardous and toxic to living aquatic organisms and human, removal of them has become vital (5). Various physical (6,7), chemical (8-10) and biological (11,12) methods were used for MB reduction from water and wastewater. At actual scale, most of them are not applicable because of the high cost and complexity instrument (13). Adsorption process has been employed for color and toxic compounds removal from wastewater, successfully (14). During the adsorption, as simple and prepare method, the pollutants are adsorbed on the surface of the adsorbent (15). Adsorption is inexpensive and has not sensitivity to the toxins and simpler implementation ability (16). The carbon, derived from low cost wastes, is important as appropriate materials for the removal of organic and inorganic contaminants from wastewater. Waste plant biomass can be utilized to produce activated carbon (17).Various low cost adsorbents for MB removal has developed such as clay (18), yeast (19), Carica papaya seeds (20), carbon Nanotubes (21), chitosan/oil palm Ash (22), leaf palm (23) raw pummelo peel (24), miswak leaves (25) and so on. Annually, high amount of walnut bark as waste evacuated. Others study shown walnut bark has functional group such OH and H that adsorb organic compounds (26).

Aims of the study:

The objective of the present study was the investigation of walnut bark granule (WBG) potential as an available adsorbent for the removal of MB from aqueous environments.

Materials & Methods

In the experimental study, initially walnut bark samples were milled and subsequently by 20-70 mesh were screened and 1-3 mm particles were separated and collected. In order to removing impurities, milled samples were rinsed times by $NaHCO_3$, 0.1 NHCl and distilled water; then, dried at 105 degrees celsius for 2 hr. Methylene blue removal by walnut bark granule was studied in discontinuous system at different contact times. Methylene blue dyes with analytical grade were purchased from Merck Co. In order to determine the pH absorbent, 5 g/L sample prepared in distilled water and preserved in laboratory conditions for 24 hours. Then, pH values of solution at 3-8 range read by pH-meter (Digimed model DM-20, Digicron AnaliticaLtda, Sao Paulo, Brazil) at six levels. In order to determine the efficiency of processed walnut bark granule in methylene blue removal, initially 5 flasks containing 100 ml of 0.1 mg/L methylene blue solution added to each flask. Then, 1-5 g/L absorbent added to flasks No. 1 to 5 respectively and stirred for 10 min at 300 rpm. After 10 min, flasks containing separately filtered by Watman filter paper and filtered solution transferred into tubes. After transferring solutions on filter paper, flasks were stirred for 10 min again. After a second stirring, flask containing was filtered. Similar steps were repeated for third, fourth and fifth 10 min (30, 40 and 50 min) and flasks residual solutions were filtered. Finally, absorption of 25 tubes measured by spectrophotometer Shimadzu Model UV-120-02 at 663 nm wavelength. In order to processing walnut bark, five dye concentrations (100, 200, 300, 400 and 500 mg/L) were utilized. Each experiment had three replications and mean of measurements were reported as final result. In the present research, effect of various parameters such as

proper contact time, absorbent dose and various concentrations of dye were studied. After determination of proper contact time and absorbent dose, properties related to absorption isotherm on processed powder of walnut bark were determined. Absorption isotherms were studied using Freundlich and Longmuir equations.

Results

The effect of pH on methylene blue removal was presented in figure 2. As can be seen in figure 2, methylene blue removal affected by pH; so, by increasing pH from 3 to 6, methylene blue removal increased on absorbent surface and at maximum pH values removal decreased. PH value of 7 was selected as optimal for the afterward experiments.

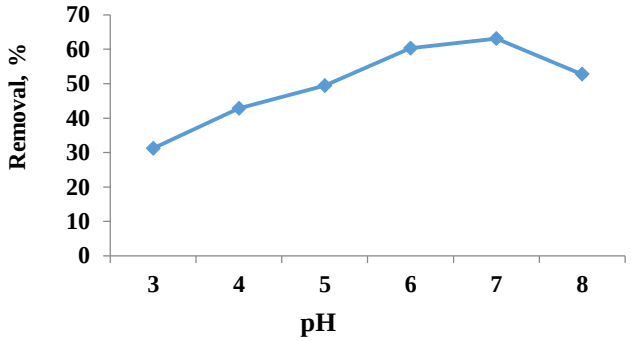

Figure 2) Effect of pH on methylene blue removal (contact time: 50 min, adsorbent dosage: 5 gr/L, methylene blue concentration: 100 mg/L)

The effect of time on methylene blue removal was presented in Figure 3. Results showed that by increasing contact time from 10 min to 50 min, methylene removal increased, so that highest removal obtained as 31.2% at 50 min time and 100 mg/L methylene blue and the lowest amount by 5% obtained in 10 min and 500 mg/L methylene blue (Fig. 3).

In order to determine the absorbent dose on methylene blue removal, various amounts of absorbent were exposed to 100-500 mg/L methylene blue (Fig. 4).

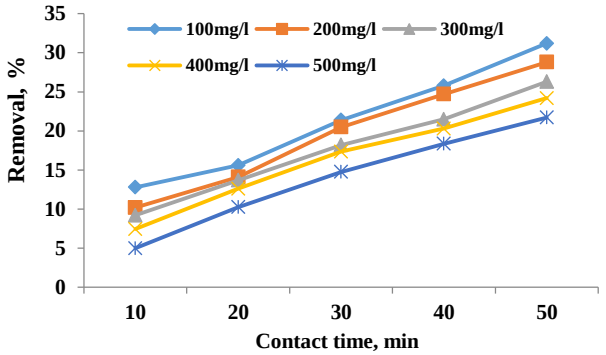

Figure 3) Effect of contact time on methylene blue removal (pH: 7, adsorbent dosage: 5 gr/L)

Finding showed that increasing absorbent dose from 1 to 5 gr resulted to increase in methylene blue removal; so, the highest removal by 41% obtained in adsorbent dose, 5 gr, methylene blue concentration, 100 mg/L, the lowest amount obtained by 1 gr absorbent and 500 mg/L methylene blue as 5.88%. Absorption isotherms are mathematical equation for explaining the equilibrium state of absorbate between solid and liquid phase. Experimental data for absorption equilibrium were studied by Freundlich and Longmuir absorption isotherms. Results showed that methylene blue absorption on studied absorbent follows Freundlich isotherm (R^2= 95%).

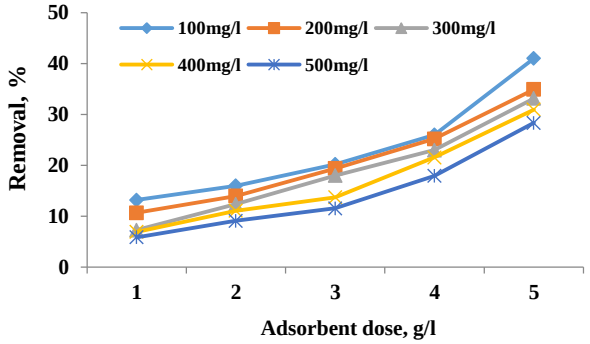

Figure 4) Effect of adsorbent dosage on methylene blue removal (pH: 7, contact time: 50 min)

Discussion

Various factors such as pH, contact time, initial dose of pollutant and absorbent dose affect sorption process. Therefore, in the present study the impacts of above mentioned factors on methylene blue removal via walnut bark

granules were evaluated. pH is an important factor which affects sorption process through affecting pollutant structure and absorbent surface charge. Sorption process affected by initial pH of the solution; so, as pH increased to 7, removal efficiency increased but in higher pH values, we observed decreasing in removal efficiency. The reason for decreasing methylene blue removal at higher pH values than 7 could be attributed to increasing OH ion which results in decreasing electrostatic bonding power between methylene blue molecules and absorbent surface (27). One of the other effective parameters on sorption is absorbent dose. In the present study, by increasing absorbent dose from 1 to 5 g/L in standard solution, methylene blue removal efficiency increased. Increasing the removal efficiency resulted from increasing absorbent dose could be explained such that by increasing absorbent dose; there is more surface area which could be resulted to increasing removal efficiency (28). Initial dye concentration provided a considerable motive power for overcoming to resistance resulted from mass transfer among solid and liquid phases. Results of studying the methylene blue concentration showed that methylene blue removal efficiency decreased by increasing initial concentration which is due to this fact that absorbents have limited sorption sites which will be more saturated by increasing the initial concentration and removal efficiency would be decreased (29). Contact time is one of the main effective parameters in practical applications in sorption process. As can be observed in the present study, surface sorption capacity and methylene blue removal percent via absorbent rapidly increased at initial stages; then, increased slower according to increasing time up to reaching to equilibrium within 50 min. The highest methylene blue removal efficiency obtained at 50 min contact time by 41 percent. Generally, pollutants removal rate initially was rapid and gradually decreased by the time and eventually reached to equilibrium. This event resulted from this fact that at initial stages there are so many sorption sites which are empty for absorption, while by increasing the process time, the void sites in the absorbent surface will saturated which could be due to inhibitory powers among absorbed molecules on solid and liquid absorbent surface (30). In this research, 5 g/L absorbent dose, contact time of 50 min and 100 mg/L methylene blue concentration were selected as optimum conditions. Absorption isotherms show absorbent molecules fraction in equilibrium state among solid and liquid phases (31). In Long-Muir model, a layer of dissolved molecules absorbed on absorbent surface and at all surfaces, the similar absorption energy and reversible absorption bonds were assumed and in Freundlich model, areas on absorbent surface are not uniform and have different sorption power (32). Results of isotherm researches showed that correlation coefficient of Freundlich isotherm equation was very high (R^2=0.95). Therefore, it can be stated that methylene blue removal was not a one-layer reaction and follows Freundlich equation.

Conclusion

Present study showed that use of walnut bark granule as an absorbent could be utilized in methylene blue removal. In colored wastewaters containing methylene blue, studied absorbent could be utilized in small water treatment facilities as supplemental stage. Walnut bark provides well sorption active sites through an appropriate porosity.

Footnotes

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Conflict of Interest:
The Authors have no conflict of interest.

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