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Removal of Methylene Blue from Waste Water Using Activated Carbon Prepared from Rice Husk

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Abstract

The possible utilization of rice husk activated carbon as an adsorbent for the removal of methylene blue dye from aqueous solutions has been investigated. In this study, activated carbons, prepared from low-cost rice husk by sulfuric acid and zinc chloride activation, were used as the adsorbent for the removal of methylene blue, a basic dye, from aqueous solutions. Effects of various experimental parameters, such as adsorbent dosage and particle size, initial dye concentration, pH and flow rate were investigated in column process. The maximum uptakes of methylene blue by activated rice husk carbon at optimized conditions (particle sizes: 140 µm; Flow rate: 1.4 mL/min; pH: 10.0; initial volume of methylene blue: 50 mL and initial concentration of methylene blue: 4.0 mg/L etc.) were found to 97.15%. The results indicate that activated carbon of rice husk could be employed as low-cost alternatives to commercial activated carbon in waste water treatment for the removal of basic dyes. This low cost and effective removal method may provide a promising solution for the removal of crystal violet dye from wastewater.

Key words: Methylene blue, wastewater, activated carbon, rice husk.

I. Introduction

About 15% of the total world production of dyes is lost during the dyeing process and is released as liquid effluents[1]. Color removal from such wastes is one of the most difficult requirements, faced by the textile finishing, dye manufacturing, pulp and paper industries. Among the various types of dye, various cationic dyes, including mythelene blue, are used in dye, paint production and wool dyeing. Methylene blue is also used in microbiology, surgery, diagnostics[2,3] and as a sensitizer in photo-oxidation of organic pollutants[4].

The effluent containing dyes are highly colored, resulting in major environmental problems. As international environmental standards are becoming more stringent, these colored wastes need treatment before disposal. Several methods for the removal of dyes have been developed. Physical methods, mainly adsorption on various supports, are the most frequently used[5]. Biological methods such as biodegradation have been proposed. However, due to the low biodegradability of dyes, conventional biological waste water treatment processes are not very efficient for the treatment of dyeing wastes[6]. Chemical treatment processes (ozonation and chlorination) are more effective[7, 8]. The photocatalytic degradation over solid support is an interesting recent proposition[9-11]. M. Bielska et al. and S. Wang et al. studied the removal of methylene blue using micellar enhanced ultrafiltration, fly ash and red mud and coal respectively[12-15]. However, adsorption is one of the promising methods to remove the dye pollutants from aqueous system completely[16-17].It was, therefore, thought worthwhile to develop highly efficient and effective adsorbents for the removal of dye from the textile effluents.

In the present investigation, attempts have been made to explore for the removal of methylene blue (MB) with activated carbon prepared from rice husk.

II. Experimental

Preparation of activated charcoal from rice husk

Rice husk was collected from Comilla district, Bangladesh. Then it was washed and oven dried. Then, part of the dried rice husk was soaked in concentrated H_2SO_4 in an amount sufficient to cover the raw materials completely, mixed vigorously for 30 min, and then left for 2 h. After mixing, the slurry was subjected to drying at 100°C in an oven for 24h. Chemical activation of the rice husk was performed with $ZnCl_2$ as well. Ten grams of rice husk was well mixed with 100 mL of a concentrated solution that contained 10g of $ZnCl_2$. The mixing was performed at 50 °C for 1h. After mixing, the slurry was also subjected to drying at 100 ^{0}C for 24 h. The resulting impregnated solids were placed in a beaker and heated to a temperature of 300 °C under a nitrogen flow at a rate of 150cm^3 min^{-1} STP at 100 °C for 1h. The products were washed sequentially with 0.5M HCl, hot water, and finally cold distilled water to remove residual organic and mineral materials and then dried at 110°C[18]. The physicochemical characteristics of activated carbons prepared from rice husk was carbon; yield, 36%; ash content (3%); moisture content (4.28%); bulk density (0.84 g/mL); BET surface area (681m^2/g); total pore volume (0.42cm^3/g); mean pore radius (24.2 A°) [18].

Preparation of methylene blue solution

About 0.1 g of methylene Blue (C_{16} H_{18} N_3 SCl. 3 H_2O) was taken in a 100 mL volumetric flask and diluted up to the mark by addition of deionized water. 0.5 mL of the stock solution

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was pipetted out in a 250 mL volumetric flask and the volume was adjusted by addition of deionized water. The resulting concentration of the solution was 2.0 mg/L. Similarly 4.0, 6.0 and 8.0 mg/L dye solutions were prepared by pepetting out 1.0, 1.5 and 2.0 mL of the stock solution respectively in a number of separate 250 mL volumetric flasks.

Analysis of crystal violet solution

Crystal violet solution was analysed by using UV-Visible spectrometer (UV-160A, Shimadzu, Japan) at a wavelength of 665.0 nm.

Preparation of column

For the treatment of single adsorbent, firstly glass wool was inserted into the column which acted as a support for the adsorbent**.** The soaked adsorbent with water was poured into column and the water was then allowed to pass through the column. In this way dissolved materials and coloured substances were washed out form the adsorbent. Further few milliliter of deionized water was added to complete removal of these unwanted substances. This water was then drained out

Adsorption and analytical procedures

The adsorption experiments were carried out in columns that were equipped with a stopper for controlling the column elute flow rate (treatment rate) as represented in figure 1. Adsorption factors including the amount of each adsorbent (2.0-6.0) g, particle size (90-425) µm, treatment flow rate (1.0-2.2) mL/min, initial sample concentration (2- 1000) mg/L, and pH (1-12) were evaluated. After the pH had been adjusted to the desired value with HCl and NaOH solutions, the sample solution (50 mL) was passed through the adsorption column at a given flow rate. The treatment flow rates of 1.4 mL/min correspond to retention times of, 109 s, 58 s and 29 s, respectively. The packing density of the treatment column was 0.32 g/cm^3. The flow rate was kept constant by controlling the stopper valve. The removal treatment was performed at ambient temperature. The number of experiments for the removal of methylene blue was greater than five. The removal (adsorption) efficiency was calculated using the equation:

Removal efficiency (%) = $[(C_0-C_e)/C_0] \times 100$

Where, C_0 = Concentration of methylene blue in the sample solution before treatment

C_e= Concentration of methylene blue in the sample solution after treatment.

III. Results and Discussion

Optimization of particle size

Effect of particle sizes on removal of methylene blue was investigated. Column adsorption experiments were carried out for the removal of methylene blue from aqueous solution using three particle sizes 140 µm, (141-355) µm and (356-425) µm. The results are shown in Fig. 1. It shows that removal efficiency of methylene blue was decreased with increasing particle size of AC (activated carbon). About 94.10% of methylene blue was removed with particle size 140 µm, whereas 92.30% removal efficiency was found with particle size 141-355µm and 90.20% with particle size 356-425 µm. From the above findings, it is clear that methylene blue removal efficiency increases with decreasing particle size. Therefore particle size 140µm was chosen for next experiments. The removal efficiency increasing with decreasing particle size is was probably due to the fact that, with the decrease of particle size, the surface areas of the adsorbents were increased, which provide greater number of sites for adsorption.

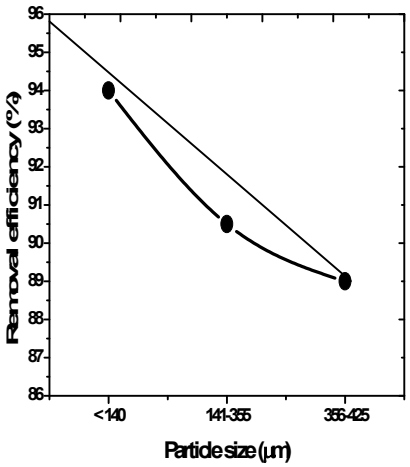

Fig. 1. Effect of particle size on the removal of methylene blue by adsorption on acid activated carbon. Initial MB concentration: 4 mg/L; Amount of AC: 2 g; Volume of methylene blue solution: 50 mL; Flow rate 0.6 mL /min.

Optimization of amount of adsorbent

The effect of the amount of adsorbents on the removal of methylene blue was investigated. For all the experiments, initial concentration of methylene blue solution was kept constant at 4 mg/L, initial volume was 50 mL and particle size was 140 µm. The results were depicted in Fig. 2 shows that removal efficiency was increased sharply with increasing amount of activated carbon up to 3.0 g. Then removal efficiencies were not changed significantly with increasing amount of adsorbent. It shows that removal efficiency was 74.36% when the amount was 2.00 g. For 3.00 g, it was 93.70% and 97.15% for 4.00 g.

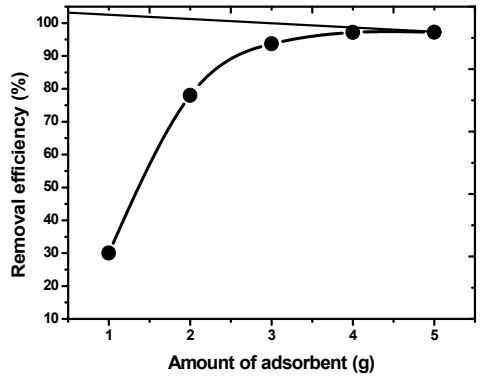

Fig. 2. Effect of adsorbent amount on the removal of methylene blue by adsorption on acid activated carbon. Initial MB concentration: 4 mg/L; particle size: 140 µm; Volume of methylene blue solution: 50 mL; Flow rate 0.6 mL /min.

That is adsorption efficiency increased due to the increased number of adsorption sites. Therefore, removal efficiency reached in equilibrium with the amount of 3.0 g of activated carbon.

Optimization of flow rate

The effect of the treatment flow rate on the removal of methylene blue was investigated. It is presented in Fig. 3. It could be clearly understood from the figure that removal efficiency decreases with increasing flow rate. About 98.43% of methylene blue was removed at flow rate 1.0 mL/min, where as 96.81% of methylene blue was removed at flow rate 1.4 mL/min and similarly 91.86% of methylene blue was removed at flow rate 1.8 mL/min. These phenomena might be due to the fact that when the flow rate was slow methylene blue in the sample solution got more contact time with the active surface of the adsorbents. However flow rate 1.4 mL/min was chosen for the next experiments because it makes the removal process faster.

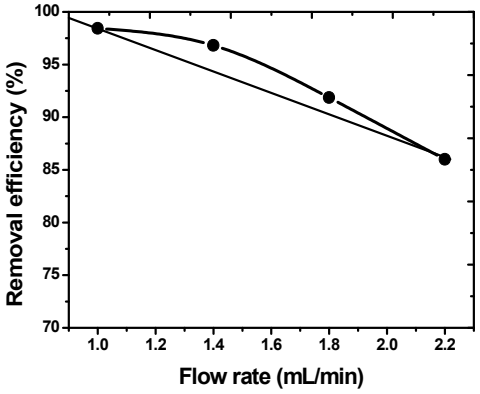

Fig. 3. Effect of flow rate on the removal of methylene blue by adsorption on acid activated carbon. Initial MB concentration: 4 mg/L; amount of adsorbent:2g; particle size: 140 µm; Volume of methylene blue solution: 50 mL.

Optimization of initial concentration

Removal efficiency is greatly depended on the initial concentration of solution of adsorbate. For the evaluation of the effect of initial concentration, 50 mL solution of different initial concentrations was treated onto the adsorbent. Initial concentration was varied from 2 mg/L to 8 mg/L. The results were illustrated in Fig. 4.

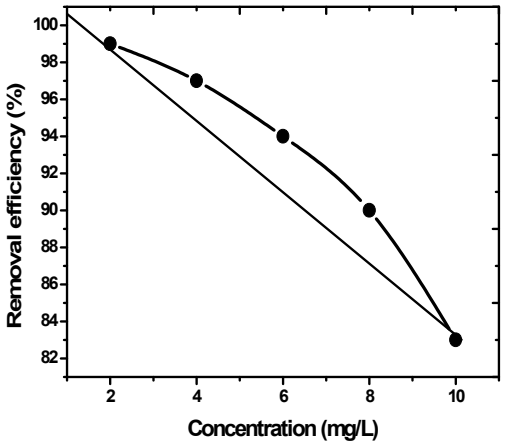

Fig. 4. Effect of initial concentration on the removal of methylene blue by adsorption on activated carbon. Amount of adsorbent: 3g; particle size: 140 µm; Volume of methylene blue solution: 50 mL; flow rate: 1.0 mL/min.

It shows that removal efficiency was decreased with increasing of initial concentrations, although the amount of total methylene blue accumulation increased. The total accumulation of methylene blue increased with increasing initial concentration was probably due to more contact of adsorbent sites with methylene blue. The removal efficiency decreased with increasing adsorbate concentration in the solution. From this experiment it was observed that about 99% methylene blue was removed using 2 mg/L. In addition, 98.5% methylene blue was removed at initial concentration 4 mg/L. For initial concentration 6 mg/L removal efficiency was 89.81%. Therefore, initial concentration 4 mg/L was chosen for the next method optimization work. At low concentration, most of methylene blue in the sample solution might contact with active sites of adsorbent and when the concentration is increased all methylene blue species will not be available to contact with the active surface due to active sites are already filled up.

Optimization of initial volume

It is desired to obtain the optimum condition for the development of a noble method for a methylene blue removal. It is also required to investigate the effect of initial volume. Different initial volumes with optimized concentration of 4 mg/L were treated onto activated carbon prepared from rice

husk. It shows that removal efficiency decreases with increase of initial volume. The removal efficiency was 100% when the volume of methylene blue solution was 50.0 mL. For initial volume 100 mL, the removal efficiency was 98.70% and for 150 mL, the removal efficiency was 80.16% and similarly decreased for successive higher initial volumes. This removal efficiency decreases probably due to increased contact of adsorbate with available sites of adsorbent.

Effect of pH on the removal of methylene blue

Fig. 5 indicates the effect of pH on the removal of methylene blue in the presence of activated carbon. When initial pH of the dye solution was increased from 3 to 11, the percentage removal increased from lower to higher. The increasing trend of removal of the methylene blue with increasing pH is dependent on the nature of the adsorbent. At lower pH, the percentage of the removal of methylene blue was 40%. Interestingly, at higher pH, the trend of the removal was increased.

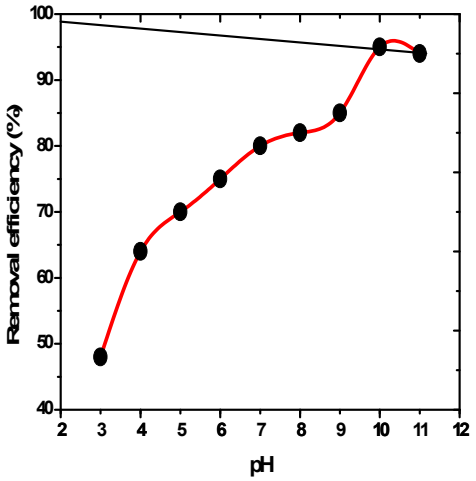

Fig. 5. Effect of pH on the removal of methylene blue by adsorption on acid activated carbon. Amount of adsorbent: 3 g; particle size: 140 µm; Volume of methylene blue solution: 50 mL; flow rate: 1.0 mL/min.

More significant enhancement in the adsorption of dye is reached at pH 10. This variation is quite similar to the previous reports[13].

Application of the Developed Treatment System

The utility of the activated carbon prepared from rice husk was evaluated for the treatment of methylene Blue contaminated waste water samples collected from Gazipur industrial area, Dhaka. The concentration of total methylene blue in the samples was 2.28 mg/L. pH of the samples was 7.4. The treatment results are presented in Table 1.

Table1. Removal and Desorption of Methylene Blue from the waste water by the Developed Method*

Sample no	pH	Initial MB concentration (mg/L)	Final MB concentration (mg/L)	Removal (%)	Desorption (%)
1	7.49	2.28	0.22	87.50	85
2	7.5	2.20	0.21	87.40	84
3	7.45	2.02	0.20	87.00	85

*Amount of activated rice husk: 3.0 g; Particle size : <140 µm; Flow rate: 1.4 mL/min; Desorption: 4 M NaOH, 100 mL; Standing time: 20 minute

The concentration of methylene blue in the treated sample water could be lowered to 0.22 mg/L. Desorption of methylene blue from the activated carbon was also studied. The desorption efficiency of 100 mL MB solution was 85% with 4 M NaOH. These results indicate that the adsorbed methylene blue could be recovered from the surface of activated carbon.

Probable removal mechanism

It is known that ionic dyes upon dissolution release colored dye anions/cations into solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge of the adsorbent which is in turn influenced by the solution pH. Methylene blue is a basic dye. In water it produces cation (C+) and reduced ions (CH+). If the solution pH is above the zero point of charge the negative charge density on the surface of the activated carbon increases, which favors the sorption of basic (cationic) dyes[18]. In addition, the basic dye will become protonated in the acidic medium and the positive charge density would be located more on the dye molecules at low pH results the lower uptake.

IV. Conclusion

From the results of this study it may be concluded that the utilization of activated carbon prepared from rice husk materials in a column system may offer a practical mean for an effective treatment of wastewater contaminated with methylene blue. Further investigation is required to study the removal mechanism of methylene blue by activated carbon.

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