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Remediation of Methylene blue and Rhodamine B using various adsorbents-A Review

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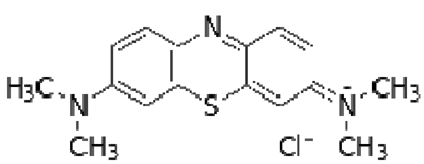
Abstract
The remediation of methylene blue dye and Rhodamine B from waste water using different adsorbents is being studied by various researchers. In recent years, the uses of various naturally available adsorbents have been widely used as a replacement for the current costly methods of treatment of waste water. In this review, a wide range of adsorbents which have been studied have been listed and there efficiency upon various parameters have been mentioned. Different kinds of adsorbents such as activated carbons from different sources, biological wastes and modern modified adsorbents have been enlisted.

Keywords: Methylene blue,Rhodamine B,Adsorbents

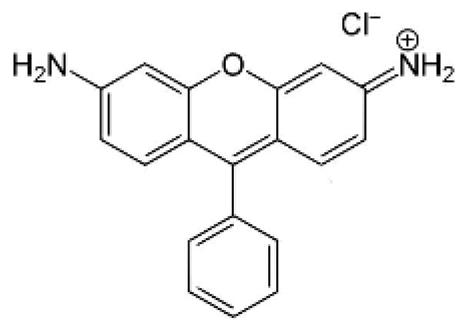
INTRODUCTION

With the advancement in technology the luxury of human life has enhanced considerably and so has the degradation of ecological systems. Instance of such advancement is the use of dyes in various fields of textiles, food, cosmetics, paper, paints, pharmaceuticals and several other industries. The effluents from these industries pose serious threats not only to human beings but also the animals, plants and aquatic life. The effluents containing dyes are difficult to be treated because of high chemical oxygen demand, color of the water which is easily recognizable and high structural stability of these molecular dyes.

Several studies have been made for the remediation of dyes. Methylene blue and rhodamine b are the two most commonly used dyes among the several. Methylene blue is a dark green powder or crystalline solid which can dissociates in aqueous solution like electrolytes into Methylene Blue cation and the chloride ion [1]. It has the IUPAC name as 3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride and the molecular structure as follows:



Rhodamine B is a chemical dye with IUPAC name [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride often used as a tracer within water and posses remarkable fluorescence property due which it finds application in biotechnological techniques. It has the molecular structure as follows:[redacted]



These have been found to be removed very effectively using activated carbon, various biosorbents chemical coagulation, and chemical oxidation methods but more research was made to develop some cost effective efficient remediation methods in the course of which adsorption emerged as a viable methods.

Activated Carbon

The commercially available granulated activated carbon provides an excellent adsorption surface but is expensive hence activated carbon manufactured from various wastes products have been employed for this purpose. In fact it is reported that at natural pH of 8.6 color removal of methylene blue by coir pith carbon was achieved to be 94% [2]. Also studies have been carried out using activated carbon derived from H_3PO_4 impregnated bagasse for the removal of methylene blue. It was observed that the rate of adsorption increases with increase in amount of adsorbent but decreases with increase in temperature. The optimum condition is 0.8 gm adsorbent, 150 min. adsorption time for 95 % Transmittance [3].

Another study depicts activated carbon was prepared using industrial solid waste called sago waste and was utilized in adsorbing Rhodamine-B from aqueous solution. The adsorption of Rhodamine-B onto carbon followed second order kinetic model. Adsorption data were modeled using both Langmuir and Freundlich classical adsorption isotherms. . A maximum removal of 91% was obtained at natural pH 5.7 for an adsorbent dose of 100 mg/50 ml of 10 mg l^{-1} dye concentration and 100% removal was obtained when

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the pH was increased to 7 for an adsorbent dose of 275 mg/50 ml of 20 mg l^{-1} dye concentration.[4]

Studies have been reported for preparation of acid activated Cynodon dactylon carbon for removal of Rhodamine B in aqueous solution. The percentage removal of Rhodamine b was found to increase with increase in concentration of both Rhodamine b cynodon dactylon. An anomaly observed during the course was the increase in rate of adsorption with the increase in temperature but decrease with increase in pH and is maximum between 3.0-5.5[5]. Another study depicted the use of activated carbon prepared from thespusia populinia. The adsorption of dye increased with temperature due to increase in availability of carbon surface and also with increase in concentration of Rhodamine [6]. Barley straw has served as another raw material for preparation of activated carbon for removal of methylene blue. The straw carbonized at 200°C was found to have maximum adsorption tendency at a contact time of 60-90min [7]. Activated carbon obtained from walnut shell also proved to be an effective adsorbent for removal of Rhodamine b. It was observed that the rate of removal of Rhodamine B increases with increase in contact time with an equilibrium of 5hrs. the removal of dye increased with pH from 6 till 9 after which it started decreasing but it stayed constant at pH less than 5.Also regular decrease in percentage of color removal was observed when the concentrations of the dye and temperature were increased.[8] Also the kinetics of adsorption of methylene blue from aqueous solution onto activated carbon prepared from palm kernel shell has been investigated which revealed that adsorption rate increased marginally after the first ten minutes to a near constant value. The maximum adsorption was obtained after 50mins at most concentrations. Whereas the percent adsorbed increased with increase in temperature at all initial concentrations reflecting the characteristic of an endothermic process. [9] The charcoal from S. persica stem was able to remove up to 97% of MB dye from solutions with maximum adsorption at the adsorbent concentration of 7g/L. The adsorption was observed to be increasing with increase in pH and was maximum at pH of 13. It followed both Langmuir and Freundlich isotherms. [10] Another study used dung ash and mustard waste ash for removal of methylene blue. It depicted the same results as other studies that the rate of adsorption increased with increase in pH. The equilibrium time for both the adsorbents was found to be 150 minutes. It was also observed that with increasing amount of adsorbent, percentage adsorption also increases accordingly because maximum surface area is available for adsorption which increases exchangeable number of sites on the surface of the adsorbent. [11]

The study of methylene blue removal using activated carbon obtained from jackfruit peel waste showed that adsorption was a pseudo second order reaction with a large equilibrium time of 3000mins. Another important result obtained was that the adsorption was monolayer. Also the adsorption of the cationic dye was found to be more favorable at higher pH increasing from 78 to 98 % when pH range was raised from 1.5 to 10[12]. The monolayer sorption capacity of activated carbon was also observed for activated carbon prepared from pea shell on methylene blue dye. The adsorption was found to be 246.91 mg g^{-1} at 25 °C with an equilibrium contact time of 180min. Observation was made that with increase in adsorbent concentration, removal percentage also increases from 33.58% to 99.41%. An anomaly observed in the study was the increase in the percentage of removal of methylene blue by both increasing and decreasing pH. At pH values of 2.0 and 11.5, the maximum percentage of dye removal was found to be 97.30%. As the temperature increased from 25°C to 55°C, the removal of dye percentage also increased due to the increase of the rate of diffusion of the adsorbate molecules. An additional finding done was the effect of presence of surfactant. The percentage of removal in the presence of anionic surfactant sodium dodecylsulfate increased to 99.38% [13]. Another adsorbent prepared from an indigenous waste Azadirachta indica bark by acid treatment was tested for its efficiency in removing Rhodamine B. The equilibrium time found was 60mins. The adsorption capacity of the carbon increased with increase in the temperature of the system from 30-60 °C. The adsorption increased with increase in pH after 7.5 but at 7.5 it was the minimum and a maximum uptake was obtained at pH 3.0 – 6.0 [14].

Biological wastes

Other than activated carbons several adsorbents prepared from biological wastes have also found to be effective. The removal of methylene blue was carried out using leaves of psidium guajava (guava). It was observed that the adsorption is maximum at natural pH of 7.5 n low at low pH. An adsorbent dosage of 1.5gm/dm^3, temperature of 303°K and concentration of 500 gm/dm^3 was found to be the optimum condition with contact time of 120mins. Another observation made was that the powdered adsorbent is more effective than the granular one due to increased surface area [15]. Fruit waste digested with phosphorous (V) oxy chloride was used as adsorbent in removing Rhodamine B and Methylene blue. The results reveal that, percent adsorption decreased with increase in initial dye concentration and increased with increase in the adsorbent concentration for both methylene blue and Rhodamine B. Also the percent removal increased with increase in pH and temperature which indicated that the adsorption is spontaneous and endothermic nature and the study suggested that the adsorption followed pseudo second order kinetics [16]. Study conducted using grewia orbiaculta leaves as adsorbent revealed that one gram of leaf powder of 82.5µm size is found to remove 90% of 20 mg/l methylene blue from 30ml of aqueous solution in 30min. These results indicate that adsorption of methylene blue is increased with an increase in adsorbent dosage, decrease in adsorbent size and increase in pH value from 4 to 7.28[17]. Another effective biosorbents was prepared using shell of Limonia Acidissima fruit for methylene blue for which study carried out was done for untreated and treated material. The percentage removal of dye is maximum at 35°C for treated material and at 25°C for raw material which indicated that physisorption process occurs in raw adsorbent whereas chemisorptions takes place in treated one[18]. The use of jackfruit leaves as adsorbent revealed that the uptake of methylene blue increases after pH of 4 till 10 but increases marginally after 7. The removal of color increased from84.64 to 00.46 for increase of adsorbent from .1 to .8 gram. The adsorption density was further found to increase with increase in concentration of methylene blue dye [19]. Other low cost adsorbents for the removal of methylene blue were prepared using orange peel and neem leaves and showed up to 95% of removal within 15-20mins also reflecting the characteristics of a pseudo first order reaction [20]. Ashoka(Polyalthia longiflolia) seeds served as another low cost adsorbent for methylene blue which revealed that the equilibrium sorption capacity is increased from 4.40 to 8.90 mg/g as the methylene blue concentration increased from 20mg/L to 50mg/L and attains equilibrium after 30 minutes. The common observation made was that the amount of dye sorbed per unit mass of sorbent decreased with increase in sorbent dose and temperature but was maximum in the pH range of 6 to 8. The kinetics of pseudo second order reaction were reflected from the data [21]. Rice husk was also found to be good adsorbents, to remove Rhodamine B at pH 6 with maximum of 77% removal at pH 3[22]. Waste tuberose sticks were investigated for the removal of methylene blue from water and showed that the dye removal increased with increase in dye and adsorbate concentration. The equilibrium time was found to be 30 min for 20, 30, 40 and 50 mg/L of the dye concentration. With increase in pH from 2 to 6, the percent removal increased from 35 to 70. With further increase in pH to 11 there was a slight increase in percent removal (80%) [23]. A comparative study was carried out on the use of sawdust(SDZ) and walnut shell(WNSZ) carbon for the removal of methylene blue which were treated with zinc oxide. The adsorption characteristics indicated a rapid uptake of the adsorbate. The adsorption rate however decreased to a constant value with increase in contact time. The study shows that with increase in dye concentration the rate of dye removal decreases due to lack of adsorption site. The % MB removed by SDZ decreased from 100-99.85 % while that of WNSZ fluctuate between 99.70 and 99.97 % and finally decreased to 98.80 % [24].

Modified modern adsorbents

A unique adsorbent used for the removal of methylene blue dye is multi-walled CNTs which produced in Iranian Research Institute of Petroleum Industry (R.I.P.I). It showed excellent results with removal up to 99% of the dye in a solution of 10mg/l. The isothermal data fitted well to the Langmuir model and equilibrium contact time of 2 hrs for CNTs was observed. The negative adsorption standard free energy changes and the positive standard entropy changes indicate that the adsorption reaction is a spontaneous process. A positive value for the standard enthalpy change indicates that the interaction is endothermic [25]. Another distinct adsorbent studied for the removal of methylene blue and Rhodamine b is flyash obtained as waste in thermal power plants. The studies suggested the applicability of the Langmuir adsorption model, and is indicative of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The adsorption of methylene blue and rhodamine B was maximum at high pHs (7-9) and is maximum initially but decreases with time [26]. Studies were carried on sheep wool fiber and cotton fiber as the natural adsorbent for the remediation of methylene blue. For sheep wool fiber maximum adsorption occurs in 30 minutes as 82.50% whereas in cotton fiber the maximum adsorption occurs in 10 minutes as 72.0%. Also the results indicate that maximum adsorption takes place as 94.3% at 1.0g of sheep wool fiber and 97% at 1.50 g of cotton fiber. The parameters K and 1/n were obtained from isotherms which show that with decrease in the values of K with rise of temperature which reveals that adsorption affinity of methylene blue decreases with rise in temperature showing less adsorption favorable at high temperature [27]. Another unique adsorbent that has been used to study the removal of Rhodamine blue is perlite. The equilibrium dye uptake capacity (q e) was found to decrease with an increase in the dosage of the adsorbent, and was best when using 0.05 g perlite. The maximum adsorption at pH 8-9 and at low temperature due to exothermic interaction with dye which was confirmed by negative value of enthalpy change.[34]

Table 1. Some of the low cost adsorbents used for the removal of methylene blue dye

Adsorbent	Reference
Activated Carbon	2
Ashoka(Polyalthia longiflolia) seeds	21
Barley straw	7
Bagasse	3
charcoal from S. persica stem	10
carbon nano tube	25
cotton fiber	27
coir pith carbon	2
dung ash	11
Flyash	26
grewia orbiaculta leaves	17
hazelnut shell	2
jackfruit leaves	19
jackfruit peel	12
Limonia Acidissima fruit	18
mustard waste	11
maize shell carbon	29
neem leaves	20
orange peel	20
palm kernel shell	9
pea shell	13
Psidium guajava (guava)	15
P (V) oxy chloride digested fruit waste	16
sheep wool fiber	27
Waste tuberose sticks	23
Wood	28
Zinc oxide activated walnut shell	24
zinc oxide activated sawdust	24

Table 2. Some of the low cost adsorbents used for the removal of Rhodamine B dye

Adsorbent	Reference
activated carbon of walnut shell	8
Activated alumina	33
Azadirachta indica bark	14
Cynodon dactylon carbon	5
Flyash	26
orange peel	30
P (V) oxy chloride digested fruit waste	16
Perlite	34
rice husk	22
Sago	4
teak leaf	31
thespusia populinia	6
Trametes versicolor (white rot fungi)	32
zinc oxide activated sawdust	24
Zinc oxide activated walnut shell	24

CONCLUSION

Activated carbon is an efficient means for water treatment but its use is somewhat restricted because of high cost. To replace it there are wide range of cheap and naturally available adsorbents which also have proved to be considerably efficient. However the need for such study and research still exists to develop a adsorbent which removes dye entirely, lasts long and costs nothing. Such an adsorbent needs to be developed for all and mixture of various dyes.

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