Effect of salts on the removal of remazol yellow by using activated charcoal prepared from sawdust

N. J. Ara*, M. A. Rahman and A. M. S. Alam

1Department of Chemistry, Bangladesh University of Textiles-1208, Bangladesh.
2Department of Chemistry, University of Dhaka-1000, Bangladesh.

Abstract

This study was to investigate the removal of Remazol Yellow dye from aqueous solutions by adsorption on activated charcoal prepared by chemical activation of saw dust. The dye removal was 85% which was increased to 94% with the addition of 1.0 g of NaCl electrolyte for 50 mL dye solution. The results indicated that the utilization of activated charcoal produced from saw dust played an important role in the removal of Remazol Yellow (RY) dye from aqueous solutions. In addition, saw dust was low cost and easily available material. It can be an alternative adsorbent precursor for more expensive adsorbents used for RY removal.

Keywords: Remazol yellow; Adsorption; Activated charcoal; Saw dust; Electrolyte

Introduction

Globally, thousands of dye stuffs are being synthesized daily and also being released in the environment in the form of effluents during synthesis and dying process. Reactive dyes are the most common dyes used due to their favorable characteristics of bright color, water fastness, simple application techniques, and low energy consumption. They exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups. They are not easily biodegradable, thus, the color may remain in the effluent even after extensive treatment. If waste products are improperly managed, public health and the environment could be threatened.

To remove dyes and other contaminants from waste water, several physical, chemical and biological methods have been developed, such as membrane separation, flocculation coagulation, adsorption, ozonation and aerobic/anaerobic treatments. However, these technologies are generally unsuccessful in colour removal, expensive, and less adaptable to a wide range of dye wastewaters. The low cost, simple design, easy handling, and sludge-free cleaning operations have established the adsorption technique as more effective and convenient in comparison to other techniques.

Adsorption now plays a key role in modern industries, mainly in the field of environmental protection engineering, with the increasing environmental consciousness of people all over the world. Adsorption processes are being employed widely for large scale biochemical, chemical, and environmental recovery and purification applications. Over the last few decades, adsorption has been recognized as an influential separation process and has become an attractive option for the removal of dyes from industrial effluents. Among various adsorbents, activated carbons are the most effective because of their excellent adsorption capacity for organic targets. Many studies have been undertaken to investigate the use of low cost adsorbents such as peat, wood shavings, silica, coir pith, sugar beet pulp, sugar cane bagasse pith, jute fiber, soybean, and wheat husk for colour removal. Unfortunately, these low cost adsorbents have generally low adsorption capacities and require large amounts of adsorbents. Therefore, a need arises...
to find new, economical, easily available, and highly effective adsorbents\textsuperscript{11}.

Wood industries in Bangladesh produce a lot of saw dust as by products. These byproducts are usually disposed of by burning or by deposition in landfills, but conversion to higher-value products would be preferable. One such product could be activated carbon. Previously, we have studied the removal of Remazol Red with activated charcoal prepared from saw dust \textsuperscript{25}. However, no information is available on removal of Remazol Yellow with activated charcoal prepared from saw dust. In this present research, the effects of salts on the removal of Remazol Yellow by activated charcoal prepared from saw dust was studied. Effects of various experimental parameters were investigated in batch mode to measure the adsorption rate. The isothermal data could be well described by the Langmuir and Freundlich isotherms. The kinetic data were well fitted to pseudo-second order model.

**Fig. 1. Chemical structure of remazol yellow**

### Experimental

#### Preparation of activated charcoal

There are two different processes for the preparation of activated carbon: physical activation and chemical activation \textsuperscript{26}. Saw dust was collected from nearby sources. This was washed with distilled water to remove water-soluble impurities and surface-adhered particles. Then, it was oven-dried at 60 °C to remove the moisture and other volatile impurities. Then, part of the dried saw dust was soaked in concentrated H\textsubscript{2}SO\textsubscript{4} in an amount sufficient to cover the raw material completely, agitated at 120 rpm in an incubator shaker for 30 min, and then left for 2 h. After being mixed, the slurry was subjected to vacuum-drying at 100 °C for 24 h. Chemical activation of the Saw dust was performed with ZnCl\textsubscript{2}. Ten grams of Saw dust was well mixed with 100 ml of a concentrated solution that contained 10 g of ZnCl\textsubscript{2}. The mixing was performed at 50 °C for 1 h. After being mixed, the slurry was also be subjected to drying at 100 °C for 24 h\textsuperscript{27}. The resulting impregnated solids were placed in a porcelain dish and heated (5 °C min\textsuperscript{-1}) to a temperature of 300 °C for 1 h. After cooling, the products were washed sequentially with 0.5 N HCl, hot water, and finally cold distilled water to remove residual organic and mineral materials and then dried at 110 °C.

#### Chemicals and dye solution

Deionized water and high purity reagents were used for all standard and sample solution. Remazol Yellow(RY) was used in the experiment. RY, a reactive dye supplied by dye star Ltd., Dhaka, Bangladesh. This dye form a covalent bond with the fiber, usually cotton, although they are used to small extent on wool and nylon. This class of dyes first introduced commercially in 1956, made it possible to achieve extremely high washing fastness properties by relatively simple dyeing methods\textsuperscript{8}. The chemical structure of dye is shown in Fig. 1. A stock solution of Remazol Yellow was prepared by dissolving the necessary amount of dye in water.

#### Point of zero charge

This is the point where the surface charge of adsorbent is zero. The point of zero charge (pH\textsubscript{ZPC}) for the sawdust was determined by the following procedure: 100 mL of deionized water was added to an Erlenmeyer flask, which was then capped with cotton. The deionized water was heated until boiling for 20 min to eliminate the CO\textsubscript{2} and dissolved ions in the water. The CO\textsubscript{2} free water was cooled as soon as possible, and the flask was immediately capped. Now this water is free from both cations and anions, and it is considered to be a neutral one. On the other hand, 0.5 g of activated carbon was weighed and placed in a 25 mL Erlenmeyer flask to which 10 mL of CO\textsubscript{2} free deionized water was added. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at 25 °C. The pH of the solution was measured, and this value is the point of zero charge\textsuperscript{25}.

#### Study of batch adsorption process

Equilibrium isotherms for adsorption onto the activated carbons determined by using 1 g of adsorbent per 50 ml of aqueous solution for initial dye concentrations in the range of 50-200 ppm. For these experiments, the bottles were shaken at constant temperature (25°C) with agitation speed (120 rpm), for the minimum contact time required to attain equilibrium, as determined from the kinetic measurements. The effectiveness of the treatment was evaluated by
measuring concentration by UV-Visible spectroscopic method at 590 nm. The influence of pH was studied by adjusting the reaction mixture to different initial pH values and analyzing the residual color at the equilibrium contact time.

The pH values were adjusted with dilute sulfuric acid and sodium hydroxide solutions. Then the percentage of dye removal was calculated by,

$$R = \frac{(C_o - C_e)}{C_o} \times 100\% $$  \hspace{1cm} (1)

The amount of dye adsorbed onto the activated carbons, $q_e$ (mg/g), was calculated according to:

$$q_e = \frac{(C_o - C_e)V}{W} $$  \hspace{1cm} (2)

Where $C_o$ and $C_e$ are the initial and the final dye concentrations (mg/L), respectively, and W is the amount of adsorbent (g), V is the volume of the solution (L)

**Results and discussion**

**Effect of adsorbent dosage**

Adsorbent dosage is an important parameter for the adsorption process as it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The adsorption experiments were carried out at different solid/liquid ratios for 24 h. At an initial dye concentration of 50 mg/L adsorption results obtained for various adsorbent dosages are given in Fig. 2.

![Fig. 2. Effect of adsorbent amount on the removal of remazol yellow. Particle size: 140μm; Initial concentration: 50 mg/L; Initial volume: 50 mL; pH: 7.0; Contact time: 12 h; Temp.: 25°C](image)

Fig. 2. Effect of adsorbent amount on the removal of remazol yellow. Particle size: 140μm; Initial concentration: 50 mg/L; Initial volume: 50 mL; pH: 7.0; Contact time: 12 h; Temp.: 25°C

The adsorption of Remazol Yellow was studied as a function of contact time in order to determine the equilibrium time. The experiments were conducted at 25°C in an isothermal water bath shaker with initial dye concentration of 50 mg/L. A rapid adsorption can be seen at the initial stage of the contact period. This is most likely due to a large number of surface sites for adsorption. However, it gradually slowed down until it reached equilibrium. After a lap of time, the remaining surface sites are difficult to be occupied because of the repulsion between the solute molecules of the solid and bulk phases. Thus, adsorption took long time to reach equilibrium. Form the Fig. 3, it was found that the contact time is needed for remazol yellow solution with initial concentration of 50 mg/L to reach equilibrium was 24 h. The maximum percentages removal of Remazol Yellow was found as 82%.

![Fig. 3. Effects of contact time on the removal of remazol yellow. Particle size: 140μm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH: 7.0; Temp.: 25°C](image)

**Effect of pH**

The pH of the dye solution plays an important role in the adsorption capacity, where it affects both the degree of ionization of the dye as well as the surface properties of the adsorbent. In this work, the influence of pH on the dye adsorption was studied as presented in Fig. 4. The effect of
pH on adsorption of dye was studied within pH range 2-10. The pH was adjusted by adding a small amount of 0.1 M HCl and/or 0.1 M NaOH. After 24 h equilibrium at various pH values illustrated that the percentage adsorption decreased for Remazol Yellow when pH increased from 2 to 8 (Fig. 4). Thus the pH value of 2 was selected as the optimum for performing the adsorption studies. The pH\textsubscript{pzc} value of the activated carbon was determined which was 5.5. At lower solution pH (less than pH\textsubscript{pzc}), the activated carbon may get positively charged, which enhances the negatively charged reactive dye anions through electrostatic forces of attraction and hence increase the adsorption capacity 23.

![Graph showing Effect of pH on the removal of remazol yellow.](image)

**Fig. 4. Effect of pH on the removal of remazol yellow.**
Particle size : 140µm ; Adsorbent amount : 1.0 g; Initial conc.: 50 mg/L ; Initial volume: 50 mL ; Contact time: 24 h; Temp.: 25°C.

**Effect of temperature**

To determine the equilibrium temperature for the maximum uptake of dye solution (Remazol Yellow), the adsorption onto activated carbon was studied for the above optimized condition as a function of temperature (20, 30, 40 and 50 °C). A study of the temperature dependence of adsorption process gives valuable information about the enthalpy change during adsorption. Fig. 5 indicates that removal efficiency increases with increasing temperature from 20° C to 40° C. The improvement of adsorption with temperature may be related to an increase in the number of active surface sites available for adsorption on adsorbent, in the porosity, and the total pore volume of the adsorbent. In addition, this can be a result of an increase in their kinetic energy and the enhanced rate of intraparticle diffusion of sorbate with the rise of temperature 28. The results indicated that the adsorption reaction of Remazol Yellow adsorbed by activated carbon prepared from saw dust was an endothermic process in nature.

**Effect of various electrolytes**

Reactive dyes are the major cause for complaint. Exhaust reactive dyeing required high salt concentration (up to 80 g/L of Na\textsubscript{2}SO\textsubscript{4}, NaCl); salt is added to shift the equilibrium of dye from the aqueous phase to solid (fiber) phase 29. Thus, effects of different electrolytes (NaCl, KCl, CaCl\textsubscript{2}, AlCl\textsubscript{3}, etc.) on the adsorption kinetics were investigated as shown in Fig. 6. It was found that the addition of these electrolytes to dye solution increased the percentage of dye removal compared to Fig. 5. The colour removal was also dependent on the concentration of added electrolytes. From the Fig. 6, it was found that the removal efficiency gradually decrease with increasing of salt’s concentration from 0.01-0.05M. The removal efficiency was highest (94%) with 0.01 M NaCl compared to without Salt (83% in Fig. 5). It can be preferred that the salt cations neutralize the negative charge of the carbon surface enabling the adsorption of more molecules or the cations to act directly on the negative adsorbate ion 30. As seen from the Fig.5. The removal efficiency increases in the order of NaCl < KCl<CaCl\textsubscript{2}, < AlCl\textsubscript{3}. Removal efficiency decreases as in the case of divalent and trivalent salt. Therefore, considering the cost and efficiency NaCl is the best electrolyte for the removal of remazol yellow.

**Effect of NaCl**

From the Fig. 6, it was found that, NaCl is the best electrolyte for the removal of Remazol Yellow. Presence of NaCl shows significant effect on removal efficiency of RY, where the removal efficiency was 94% with 0.01 M NaCl but without salt it was 84% (Fig. 7). Here the salt ions force the dye molecule to aggregate and migrate towards the adsorbent surface which increases removal efficiency.

**Adsorption isotherm**

The adsorption isotherm used to show the adsorption molecules distribute between the solid phase and liquid phase at adsorption equilibrium state. The Langmuir and Freundlich
isotherms are the most frequently employed models. The linear regression is used to determine the best-fitting isotherm and the pertinency of isotherm equations is compared by evaluating the correlation coefficients, $R^2$. Langmuir’s isotherm model is based on the theory that adsorption energy is constant and uptake occurs on homogeneous surface by monolayer adsorption. When the surface is covered by monolayer of adsorbate, the adsorption goes on localized sites with no interaction between adsorbate molecules and that maximum adsorption occurs. The linear form of Langmuir isotherm equation is given as:

$$
\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m}
$$

(3)

Where, $C_e$ (mg/L) is the equilibrium concentration of remazol yellow and $q_e$ (mg/g) is the amount of remazol yellow adsorbed per unit mass of adsorbent. $q_m$ (mg/g) is the Langmuir constant related to adsorption capacity and $K_a$ (L/mg) is rate of adsorption. The values of $q_m$ and $K_a$ were calculated from the intercept and slope of linear plot and are presented in Table I.

Fig. 6. Effect of various salt on the removal of remazol yellow. Particle size: 140μm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH:2; Contact time: 24 h;

Freundlich isotherm of remazol yellow

Freundlich model is an empirical expression that is the earliest known relationship describing the adsorption equation. This isotherm takes into account a heterogeneous surface and multilayer adsorption to the binding sites on the surface of the adsorbent. The Freundlich model is expressed in the following equation:

$$
\log(q_e) = \frac{1}{n} \log(C_e) + \log(K_F)
$$

(4)

Where, $K_F$ and $n$ are indicative isotherm parameters of adsorption capacity and adsorption intensity, respectively. Generally, $n>1$ illustrates that adsorbate is favorably adsorbed on the adsorbent. The higher of $n$ values favors the adsorption process as well as intensify the adsorption.

Fig. 8. Freundlich isotherm of remazol yellow

Fig. 9. Langmuir isotherm of remazol yellow
From the Freundlich and Langmuir plot (Fig. 8 and Fig. 9), the isotherm results are presented in Table I. From the Table I, it was found that Freundlich model gave higher R² values (without salt: 0.991; with salt: 0.995) than Langmuir model (Without salt: 0.978; with salt: 0.989), which indicate that remazol yellow adsorption by activated carbon in presence of electrolyte was made up of heterogeneous surface and multilayer adsorption. This result is similar to other works on reactive dye adsorption by activated carbon prepared from coir pith.

Adsorption kinetics

Kinetic adsorption data of DY dye on activated charcoal was analyzed using two kinetic models: pseudo-first-order and pseudo-second-order. The pseudo-first-order kinetic model is shown by the following equation:

\[ \frac{\log(q_e - q_t)}{q_e} = \frac{\log q_e}{k_1} - \frac{k_1}{q_e} t \]  

(5)

Where, q, is the amount of dye adsorbed at time t (mg g⁻¹), qₑ is the amount adsorbed at equilibrium (mg g⁻¹), k₁ is the pseudo-first order rate constant (min⁻¹) and t is the contact time (min).

The values of the constants, k₁ and qₑ for the adsorption of dye on the adsorbents were determined from the slopes and intercepts of the plots \( \log(q_e - q_t) \) against t, respectively and their values are given in Table III.

Pseudo-second order model can be represented in the following form:

\[ \frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{1}{q_e} t \]  

(6)

Where, k₂ is the Pseudo-second order rate constant (gmg⁻¹min⁻¹). The values of the qₑ and k₂ were determined by plotting a graph between t/qₑ and time. The applicability of the pseudo first order and pseudo second order model can be examined by linear plot shown in Fig. 10 and 11. The linearity of this plot indicates the applicability of the two models. However the correlation coefficient, R² shows that second order model fits the experimental data better than the pseudo first order model.

![Fig. 10. Pseudo first order Kinetics of remazol yellow](image)

![Fig. 11. Pseudo second order Kinetics of remazol yellow](image)
Table II. Pseudo first order & second order rate constants, calculated & experimental \( q_e \) values for Adsorption of remazol yellow on treated sawdust at 298K.

<table>
<thead>
<tr>
<th></th>
<th>Pseudo first order Kinetic model</th>
<th>Pseudo second order Kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_e (mg/g) )</td>
<td>( K (h^{-1}) )</td>
</tr>
<tr>
<td>Without Salt</td>
<td>2.62</td>
<td>0.25</td>
</tr>
<tr>
<td>With Salt (NaCl)</td>
<td>3.75</td>
<td>0.655</td>
</tr>
</tbody>
</table>

Conclusion

Activated charcoal produced by chemical activation of sawdust with an activation agent NaCl was capable of removing Remazol Yellow dye molecules from aqueous solutions. The removal was an adsorption process which was favored at acidic medium with pH value 2 and adsorption efficiency (removal efficiency) % was also found to increase with increase in adsorbent dosage, contact time, temperature, and addition of electrolyte. Addition of electrolyte is a new dimension for removal of dye. The kinetic study showed that dye-activated charcoal adsorption systems followed by pseudo-second-order model with high correlation coefficients and the process was endothermic. The equilibrium data was in good agreement with the Langmuir model and dimensionless separation factors (R, values) within the range of zero to one showed that the adsorption favorable. Therefore, this successful adsorbent could be considered as an alternative to commercial activated charcoal for the removal of Remazol Yellow dye from aqueous solutions.

References


Amin NK (2008), Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith, Desalination, 223(1–3): 152–161.


Qada EN, Allen SJ and Walker GM (2008), Adsorption of


Mbolekwa Z and Buckley C (2006), The impact of inadequate wastewater treatment on the receiving water bodies – Case study: Buffalo City and Nkokenbe Municipalities of the Eastern Cape Province, Industrial Wastewater Treatment, WISA, pp 111-112.


