Photocatalytic degradation of Textile Dye Remazol Red 133 by activated Charcoal

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Abstract

During the last decade the Sanganer (Jaipur) has developed into a leading place in the textile industry. Sanganer is the hub of Textile industries in the State of Rajasthan. The textile industry is one of the most water-intensive and chemical-intensive industries on the earth. About 300-500 litres of water is needed to produce 1 kg of textile fabric in textile factories. Textile manufacturing or conversion of raw material/fabric into finished cloth requires a number of processes/operations, absorbs a lot of water, and creates highly polluted waste effluents. Textile effluent is usually coloured due to the presence of residual dyestuffs and contains both inorganic and organic compounds in dissolved, colloidal, or suspended forms. As a consequence, depending on the characteristics of textile wastewater, different physical, chemical, and biological methods are used to treat it.

In the present work, the Photolytic degradation of Commercial Azo Dye (Ramazol Red 133) was examined by using U-V light in Photochemical Reaction with activated charcoal. The effects of various operational parameters such as Catalyst , Mass , type of Catalyst , Type of Dye and Dye concentration were also investigated. For the Ramazol Dye Solutions, a 120- min treatment resulted in 97.9% decolourisation and 87.6% degradation at catalyst loading of 3gm/L experiments using real Textile Waste Water were also carried out. Textile Waste water degradation was enhanced at acidic conditions .thedecolourisation and degradation efficiencies for Textile waste water were 97.8% and 84.9% at pH 3.0 , Catalyst loading of 3gm/L and Treatment time of 120 min

<u>Keywords</u> : Photochemical Treatment , TiO_2 Catalyst , Remazol Red 133 Azo Dye , Textile Wastewater

Introduction

Textile Dyeing processes are the main cause of contamination of Water. Volume of Wastewater containing processed textile dyes is ever increasing over 7×10^5 ton and roughly 10,000 different types of dyes and pigments are produced world wideannually .it is estimated that 10-15% of the Dye is lost in the effluents during the dying processes . water pollution control has importance for both organism which live in water and those who benefit from water. Many dyes reaching the water source are difficult to decompose and cause many problems due to their carcinogenicity .consequently , it is important to remove these pollutants from waste water before their final disposal

The azo dyes represent approximately 50-70% of the dyes available in the market. They are known as monoazo, diazo, or triazo based on the presence of one or more azobonds (N=N) and can be contained in a number of categories, including acid, simple, disperse azoic, and pigments. Several studies have shown that azo dyes are toxic and carcinogenic. Furthermore, because of their high molecular weight and complex structure, Azo dyes are immune to oxidative catabolism in aerobic environments due to electronic impairments induced by the electro-attraction of azo groups . the presence of these dyes in drinking water with concentration greater than $3.1ugL^{-1}$, generates health problems for the human being.The various conventional processes , used for decontamination of these wastewater that is either of the processes physical , chemical and or biological , present a major disadvantage in transforming the pollution of an aqueous

phase toward a new phase , by the formation of concentrated sludge , thus creating a problem of secondary waste , or leading to a regeneration of materials , often very expensive.

Vinyl sulfone dyes are a class of reactive dyes .these effectively used for cotton , silk and wool. After the trademarked name under which they were first launched, they are also known as remazol dyes. Since vinyl sulfone dyes are less reactive than other dyes, the majority of them stay in the dyeing bath or are discharged as industrial effluents. It has been stated that after the dying processes, up to 30% of the used dyestuff remains in the spent dye-bath. (Ozacar et al. , 2005). The presence of such dyes in effluents pollutes water significantly. Attempts have been made to eliminate these toxic dyes from agricultural waste through a variety of challenges. (Ho et al. , 2005)

Adsorption is one of the most cost-effective and efficient methods. Adsorbents such as alumina, crushed bricks, peat, sand, charcoal bentonite, silica, and others are used to remove dyes from aqueous solutions. The most commonly used adsorbent for dye removal is charcoal, which is made from saw dust and is inexpensive and readily available. As a result, there is an increasing interest in seeking an alternative adsorbent to industrial charcoal. The effects of remazol red adsorption onto sawdust are compared to those of industrial charcoal.

Materials and methods

Reagent

The various reagents used in this study were used without prior purification .theRemazol red 133 is an azo dye synthetic organic used in the textile industry , which is provided by the firm Sigma – Aldrich . its chemical structure are as following . the following table summarizes the main physic- chemical characteristics of the dye used in this work
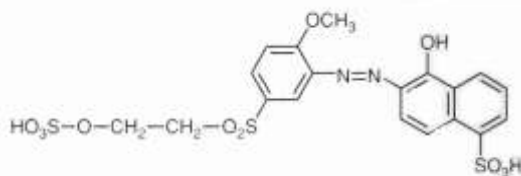
structure of Remazol Red 133 dye

Physic-chemical properties of the Remazol Red 133 dye

Dye	Remazol Red 133
Family	Reactive dye
Brute formula	$C_{19}H_{18}S_3O_{11}N_2$
Molecular weight (g/mol)	546
λ_{max} (nm)	510
Origin	Sigma-Aldrich
Purity (%)	99.9

Preparation of dye solution:

Remazol Red (RR) was used in the experiment. It is reactive dye supplied by firm Sigma- Aldrich .this dye form covalent bond with the fiber , usually cotton , although it is used to a 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 . a stock solution of 1000 ppm RemazolRed was prepared by dissolving appropriate amount of dye in water. Dilution was used to prepare the necessary concentration for the different stages of the investigation.

Preparation of activated charcoal:

Physical activation and chemical activation are the two methods for making activated carbon. (Ho et al., 2005).

Chemical activation, as opposed to physical activation, has a range of benefits. The process of dye removal was applied in batch mode. Adsorption tests were carried out by suspending sawdust in the effluent and spectroscopically examining the supernatant.   Sawdust was collected from nearby Sawmill (Sanganer Jaipur, Rajasthan). To extract water-soluble impurities and surface-adhered particles, this was

washed with double distilled water. The moisture and other volatile impurities were then separated by oven drying the adsorbent at 60°C. The dried sawdust was then soaked in concentrated H_2SO_4 in an amount sufficient to fully cover the stuff, agitated for 30 minutes at 120 rpm in a shaking incubator, and then left for 2 hours. The slurry was vacuum-dried at 100°C for 24 hours after it had been mixed. Chemical activation of the sawdust was performed with $ZnCl_2$. 10grams of sawdust was mixed well with 100 ml of 10% of $ZnCl_2$ solution. The mixing was performed at 50°C for 1 hour. After mixing, the slurry was subjected to vacuum drying at 100°C for 24 hour (Mohanty et al., 2006; Ahmadpour et al., 1997).　The resulting impregnated solids was placed in a stainless steel tubular reactor and heated (5°C min-1) to a temperature of 300°C under nitrogen flow at a rate of 150 cm^3 min- 1 at STP for 1 hour. Nitrogen entering the reactor was first heated to 250-300°C in a preheater. The products were washed sequentially with 0.5 M HCI, hot water and finally with cold distilled water to remove residual organic and mineral materials and then dried at 110°C. The heating rate and nitrogen flow were kept constant during all of the experiments.

Experimental setup

Equilibrium isotherms for adsorption onto the selected carbons determined by using 1 gram of adsorbent per 50 ml of aqueous solution for initial dye concentrations in the range of 50200 ppm.
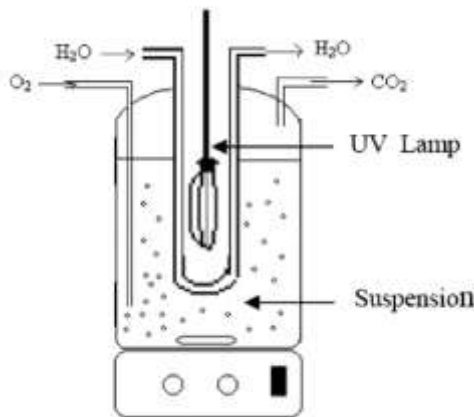
Photocatalytic reactor used for degradation of textile dyes

The bottles were shaken for the minimum contact time needed to achieve equilibrium, as determined by the kinetic measurements, at a constant temperature (25°C) and agitation speed (120 rpm). The treatment's efficacy was assessed using a UV-Visible spectroscopic procedure at 541.5 nm to measure concentration. By adjusting the reaction mixture to various initial pH values and evaluating the residual colour at the equilibrium contact time, the effect of pH was investigated. Dilute sulfuric acid and sodium hydroxide solutions were used to change the pH levels. Then the percentage of dye removal was calculated by,

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \qquad ………………. (1)$$

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

$$q_e = \frac{(C_0 - C_e)V}{C_0} \qquad …………………..(2)$$

where C_0 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).

Result and Discussion

The physical properties of treated sawdust:

Table 1 shows the physical properties of the sawdust that has been cleaned. The BET surface area (Rabolli et al., 2010) is 5.69 m2/g, and the average pore diameter is 99.60 A0, according to the table. The above-mentioned adsorbent's point of zero charge (pzc) is 5.5.

Table 1.Physical properties of treated sawdust.

Properties	Value
Particle size (µm)	<140
BET surface area (m2/g)	5.69
Average pore diameter (A°)	99.60
Micro pore volume(cc/g)	0.014
Micro pore area (m2/g)	2.37
Bulk density (g/ml)	0.84
Point of zero charge	5.5

Optimization of contact time:

In waste water treatment by adsorption methods, the contact time between dye and adsorbent is critical. The adsorbent's effectiveness is determined by how easily contaminants are extracted and equilibrium is restored in a short period of time. At 25°C, the effect of shaking time on dye adsorption onto sawdust-based charcoal was investigated.

The fixed concentration of RemazolRed was shaken after adding 1gram of adsorbent in each time. Colour removal was rapid at initial stage but decreased with the increase of time (Fig. 2). The rapid rise was initially attributed to the presence of a large number of vacant sites, but as the number of active sites decreased over time, the adsorption rate decreased. For all of the advertisements, the ideal
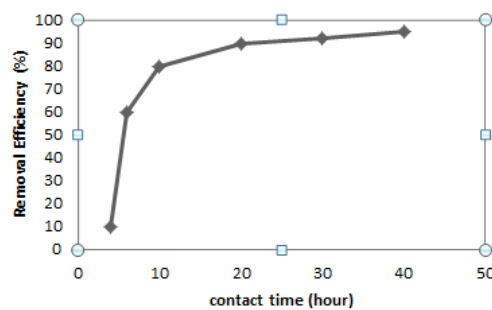
communication time was found to be 12 hours.

Figure 2.Effect of contact time on the removal of RR. Particle size: 140µm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/l; Initial volume: 50 ml; pH: 7.0; Temp.: 25°C.

Optimization of adsorbent amount:

For optimizing the amount of adsorbents,experiments were performed using 50 ml aqueous solution of RemazolRed and was shaken for 120 minutes after adding different amount of adsorbents (0.5-3.0 g). Absorbance of the filtrate was noted using spectrophotometer at λ_{max} of the dye. It was discovered that as the amount of adsorbents increased, dye adsorption increased as well, eventually reaching a constant value at equilibrium (Fig. 3). The optimum amount of 1.0g was discovered and used in all subsequent adsorption studies.
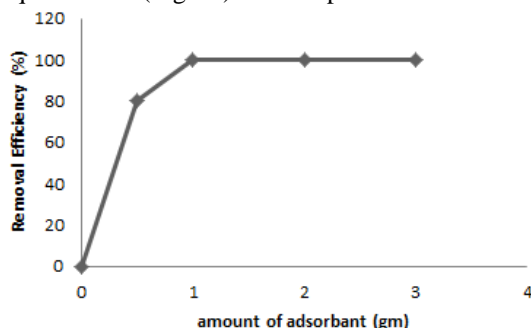

Figure 3.Effect of adsorbent amount on the removal of RR. Particle size: 140 µm; Initial concentration: 50 mg/l; Initial volume: 50 ml; pH: 7.0; Contact time: 12 hours; Temp.: 25°C.

Influence of initial pH:

Due to its smaller size than the dye molecules, hydrogen and hydroxyl ions are usually very strongly adsorbs on the surface of the adsorbents and thus the adsorption of other ions by pH in the solution is affected. The pH affects primarily the degree of ionization of the thread and adsorbent surface characteristics. RR adsorption decreased in pH (Figure 3). This can be explained by the fact that the surface of adsorbents at a lower pH of positive charges is formed by adsorption of hydrogen ions on an adsorbent surface.
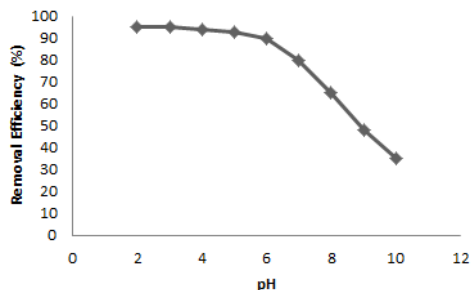

Figure 3 .effect of pH on the adsorption capacity of saw dust for Remazol red at 25°C

It has been discovered that positively charged ions prefer higher pH values whereas negatively charged ions prefer lower pH values for adsorption. The number of positively charged sites on the surface of adsorbents decreases as the pH of the device grows. The anion (Equation 3) is dissociated from the dye, and as a result, dye adsorption is reduced at higher pH values.

$$ASO_2 \ Na \xrightarrow{\ H^+ - OH^-\ } ASO_2^- \ Na^+ \dots..(3)$$
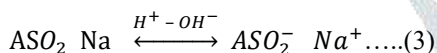
The amount of dye adsorbed on the surface of the adsorbents decreases as pH increases, which is consistent with previous findings. (Ahmadpour et al., 1997)

Adsorption isotherms:

In each case, the RR adsorption isotherms on sawdust were found to be L-type (Ho et al., 2005). The availability of higher adsorption sites on the surface of the adsorbents induces the initial sharp increase in the degree of adsorption with rising dye concentration. Adsorption sites decrease as the concentration of dye solution rises. As a result, the dye molecules have a hard time getting to the remaining empty surface. The adsorption of RR is found to increase slightly with rising temperature before staying nearly constant (Figure 4). This suggests that the desorption process is more favourable at lower temperatures, and that it is an endothermic process.
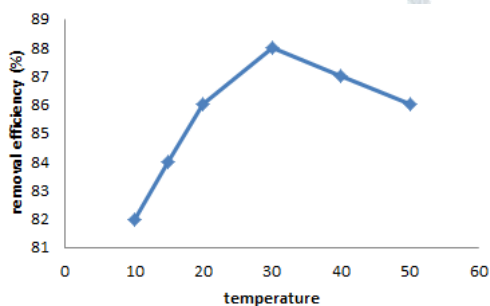

Figure 4 .effect of temperature on the removal of RR . particle size : 140 um ; adsorbent amount: 1.0 gm ; initial concentration : 50 mg/L ; initial volume: 50 ml : pH : 7; Contact time : 12 hours

The linear forms of Freundlich (4) and Langmuir (5) equations were used to fit Remazol Red adsorption data onto activated sawdust.

$$log(q_e) = \frac{1}{n}\log(C_e) + \log(K_F)\dots\dots\dots(4)$$

Where q_e(mg/g) is the amount adsorbed per unit mass of the adsorbent,Ce is the equilibrium concentration, K_F and 1/n are constants, being indicative of the extent of adsorption and the degree of non-linearity between the concentration of the solution and the amount of dye adsorbed.

The constants K_f and n are determined from the intercepts and slopes of linear plots of $log(q_e)$ versus log(Ce) from the Freundlich plot (Figure 5), and their values are given in Table 2. If n = 1,adsorption is homogeneous and there is no interaction between the adsorbed species. If n < 1, the adsorption is unfavourable and ifn > 1, then theadsorption is favorable. In present studies, we have found that n is

greater than unity for the given adsorbents which indicates that adsorption is favorable. It has also been reported that the value of K_f gives rough estimation about the degree of adsorption. In the present studies it was observed that the value of K_f for the adsorption of RR onto saw dust (1.71 mgg⁻¹) is greater than those for charcoal (5.91 mg g⁻¹) (Table 2). Greater value of K_f for activated sawdust reflects that it is better adsorbent for the removal of RemazolRed than commercial charcoal.
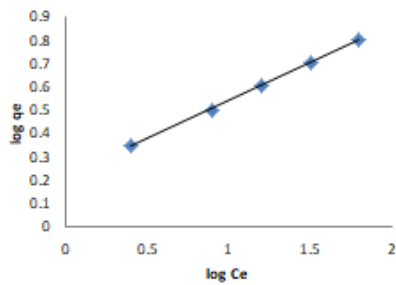

Figure 5.Freundlich isotherms of Remazol red on saw dust at 25°C

Table 2.Freundlich parameters for Remazol red on sawdust and commercial charcoal at 25°C

Adsorbents	n	K_F	R²
Prepared activated saw dust	2.85	1.71	0.991
Commercial activated carbon	1.79	5.91	0.998

Langmuir equation is given as

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \ldots\ldots(5)$$

A straight line with a slope of $1/q_m$ and an intercept of $1/(K_a q_m)$ should appear on a plot of Ce/qe versus Ce, where Ce is the equilibrium concentration (mg/dm3), q_e is the sum of dye sorbed (mg/g), q_m is q_e for a full monolayer (mg/g), and Ka is the sorption equilibrium constant (dm3/mg). The separation factor RL (Rao et al., 2008.) can be used to express the critical characteristics of the Langmuir equation. Where RL = 1/(1+Ka.Co)

* $R_L > 1$; Unfavorable.

* $0 < R_L < 1$; Favorable.

* $R_L = 1$; Linear.
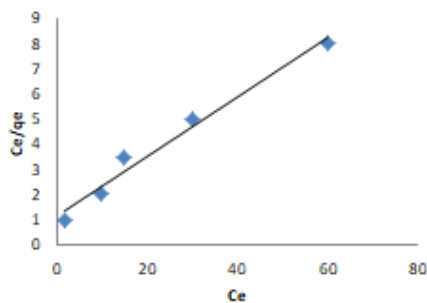
* $R_L = 0$; Irreversible.

Figure 6. Langmuir isotherms of Remazol Red on saw dust at 25°C

Table 3 . Langmuir parameters and separations factor R_L for adsorption of RR on treated sawdust

Adsorbent	K_a / dm^3 mg^{-1}	q_m/ mgg^{-1}	R^2	R_L
Prepared activated saw dust	0.105	8.00	0.988	0.045
Commercial activated carbon	7974.8	0.074	0.9448	

Adsorption kinetics:

Two kinetic models were used to study the adsorption mechanisms of Remazol Red onto sawdust. The pseudo-first order kinetic equation is as follows: (Ho et al., 2005):

$$log(q_e - q_t) = log q_e - \frac{k_1}{1.202} t \dots \dots \ (6)$$

Where q_t represents the amount of dye adsorbed at time t (mgg-1), q_e represents the amount adsorbed at equilibrium (mg g-1), k_1 represents the pseudo-first order rate constant (min^{-1}), and t represents the interface time (min). The values of the constants k_1 and q_e for dye adsorption on adsorbents were calculated using the slopes and intercepts of the plots $log(q_e - q_t)$ against t, as shown in Table 4. This is how the pseudo-second order model is expressed:

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} - \frac{c_e}{q_t} t \qquad \dots \dots \dots \ (7)$$

Where, k_2 is the Pseudo-second order rate constant ($gmg^{-1}min^{-1}$). By plotting a graph between t/q_t and time, the values of the q_e and k_2 were calculated.
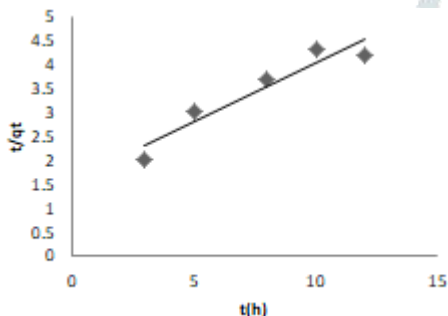

Figure 7. Pseudo- Second order kinetics plot for the adsorption of Remazol Red on saw dust at 25°

Table 4 displays the theoretical and experimental evidence for adsorption kinetics. For second order kinetics, the experimental values of q_e are similar to the measured values than for first order kinetics. As compared to first order, the value of the correlation coefficient (R^2) for second order is also similar to unity (Table 4). As a result, the adsorption of selected dye on rice husk, sawdust, and charcoal followed a pseudo second order kinetic model more closely.

Table 4.Kinetic parameters for the adsorption of remazol red on sawdust.

Pseudo first order kinetics model			q_e (mg/g)	Pseudo second order kinetics model		
q_e (mg/g)	K_1 (h , g/mg)	R^2		q_e (mg/g)	K_2 (h , g/mg)	R^2
	2.2	0.83	2.36	2.73	0.092	0.96

Conclusion

When compared to commercial charcoal, activated saw dust was found to be a stronger adsorbent for extracting Remazol Red from aqueous media in the current research. The investigated dye's adsorption decreases as the pH of the solution rises, but slightly increases as the temperature rises. It was observed that adsorption process followed pseudo-second order kinetic model. Values of q_e calculated from pseudo second order plots are in good agreement with the experimental values. Future research should focus on selectively separating the

existing dye pollutants, regenerating exhausted biomass, recovering sorbed dye, and developing continuous dye treatment systems. These studies would help to improve the economic aspects of dye wastewater treatment, giving pharmacology a better chance to address water-related contamination.

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