ADSORPTION STUDIES OF REACTIVE RED 195 DYE USING MODIFIED RICE HUSK

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ABSTRACT: *Adsorption has acquired huge consideration over the years. This technique is particularly appealing to treat wastewater emerging from various industries. In this research batch experimentation was carried out to check the applicability of modified rice husk (MRH) for the effective adsorption of Reactive Red (RR) 195 synthetic dye. Different operation conditions were optimized by varying RR-195 and MRH concentrations between 50-200ppm and 1-8g/150ml respectively at adsorption temperatures of 30 to 60^oC for up to 120 minutes time. Percentage RR-195 removal from lab made synthetic solution was found to be directly related to MRH concentration, adsorption time and temperature and inversely related with RR-195 concentration. Two different adsorption isotherms fitted well to experimental results for RR-195 adsorption onto MRH namely Freundlich and Langmuir isotherm. A maximum of 12.22 mg of RR-195 was adsorbed per 1gram of MRH for Langmuir isotherm and obtained equilibrium factor (R_L) was in the range of 0.52-0.81 proving favorable RR 195 molecules uptake by MRH. In present case of RR-195 adsorption onto MRH, Freundlich isotherm suited well as resulted by higher correlation coefficient value of 0.992.*

Key Words: Waste water, RR-195 Dye, Modified Rice husk (MRH), contact time, isotherm, batch process

1 INTRODUCTION

For many years, dyes utilized by various industries such as leather, cosmetics, dyeing, paper, textile, plastics, rubber, and food have been discharged to underground drinking waters and rivers without being discolored. These dyes are highly toxic because they are composed of wide range of hazardous chemicals accompanying dissolved solids, acids/bases, and hue [1]. Reactive azo dyes are often used in textile industries at commercial scale. Reactive Red 195 consists of a reactive group usually heterocyclic aromatic ring containing fluoride or chloride ions [2]. Wastewater treatment containing these dyes can be accomplished by three methods as enlisted in Table 1. Several of these techniques are not eminent due to their downsides like expensiveness and ineptitude [3].

Table 1: Wastewater Treatment Techniques

Categories	Sub-Division
Physical Methods	Screening, Sedimentation, Filtration, Flotation, Degasification, Aeration
Chemical Methods	Ion Exchange, Coagulation, Neutralization Ozonation, , Chlorination, Adsorption
Biological Methods	Aerobic/Anaerobic Digestion, Activated Sludge, Lagoons, Trickling Filtration, Septic Tanks

Adsorption technique is most preferred and practiced among all the above methods, because of its capability for adsorbing an extensive variety of the adsorbents efficiently even from the aqueous wastes containing minute amounts. Rice husk adsorbent is considered superior as it consists of grainy porous structure which enables high surface area and is stable thus stay chemically intact even in water. It is mechanically strong, economical and abundant in Pakistan which makes it suitable to remove various pollutants from wastewater streams [4]. The yearly rice generation for the most recent year in Pakistan is 6.798 million tons. As 30% of the rice production is rice husk, which infers that yearly rice husk generation in Pakistan is around 2.039 million tons [5]. Rice Husk in different ways has been studied as a one of the important adsorbent for dyes removal [6, 7, 8, 9].

2 MATERIALS & METHODS

Raw rice husk material required for the research was procured from Al-Riaz rice mills, Faisalabad at a price of 15 Rupees/Kilogram. In order to remove impurities such as dust, fine particles and color, the raw rice husk was washed with Grade 3 distilled water followed by filtration a few times till exhaust solution has no turbidity and color. This wet material was sun dried for few hours and further on in a convective oven at 110^oC till there was no moisture present. It was then cooled and milled in domestic food processor to get powder form. The particles size was retained in the range of 250 – 500 µm by passing material through sieve tray. After washing, drying and grinding procedure, this modified rice husk was stored in airtight glass jar for adsorption experimentation.

Reactive Red-195 obtained from Hilal Dyes, Faisalabad, Pakistan was utilized as it is without any additional purification. The structural properties of RR-195 are listed in Table 1 and exhibited in Figure 1.

Table 2: Reactive Red-195 Dye Characteristics

C.I. Number	RR-195
Commercial Name	Synozol Red HF-6BN
Chemical Structure	Azo bonding Single
Formula	$C_{31}H_{19}ClN_7Na_5O_{19}S_6$
Molecular Weight	1136.32
λ_{max} (nm)	540

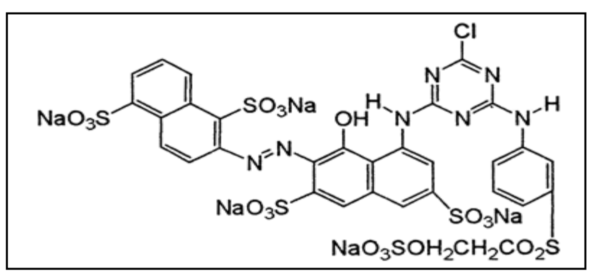

Figure 1: The structure of RR-195 dye

1000ppm RR-195 dye solution was prepared and further diluted to give seven adsorption test solutions of 50ppm to 200ppm with 25ppm gap. In order to perform all tests on similar basis no adjustment was done for solution pH so that homogeneity exists throughout the experimentation. Fixed volume of 150 ml was taken for every concentration solution in a volumetric flask. A fixed amount of 2g of modified rice husk was then mixed with above dye solutions. These adsorption experiment flasks were then subjected to shaking in an orbital shaker at 120 revolutions per minute and Laboratory temperature of 20 to 25^{o}C for a time period required to attain equilibrium which in present study was almost two hours. Then these solutions were rested for some time to settle suspended fine particles which can meddle with the outcomes. Same concentration test solutions of RR-195 without addition of MRH were run with adsorption samples. A small volume of about 20-30 ml was filtered by filter crucible from all analysis after completion of tests and spectrometer cuvettes were filled which were then analyzed for remaining RR-195 amounts utilizing UV-photometer at λ_{max}. Percentage removal was calculated.

$$\% \text{ Removal} = (C_o - C_e/C_o) \times 100 \qquad [10]$$

Here C_0 in ppm is Initial and C_e in ppm is final RR-195 concentration at time 0 and 120 minutes respectively.

For adsorbent dosage and temperature experiment, the rice husk concentration varied between 1 and 8 grams and temperature between 30 to 60°C and similar procedure was followed with the filtrate. In case of isotherm study sample solutions (50-200 mg/L) with rice husk concentration (2g/150ml) were shaken in the orbital shaker at 120 revolutions per minute and at a temperature and timing of 30^{o}C and two hours respectively. Observed absorbance readings were used to calculate C_e and Q_e values. Qe in mg/g denote RR-195 amount adsorbed onto MRH at equilibrium and obtained from the overall mass balance relationship.

$$Q_e = (C_o - C_e/M) \times V \qquad [10]$$

V is volume of RR-195 solution used in Liters and M is added rice husk in grams. Utilizing above readings, the isotherms for Langmuir and Freundlich models were plotted.

3 RESULTS & DISCUSSION

3.1 Calibration Plot

Each RR-195 dye solution in the range of 50 to 200ppm gave distinct absorbance value when measured by UV spectrophotometer at maximum wavelength of 540 nm. These values were plotted in the form of calibration curve as shown in Figure 2. Linear trend was fitted to the curve which gave calibration equation as shown below.

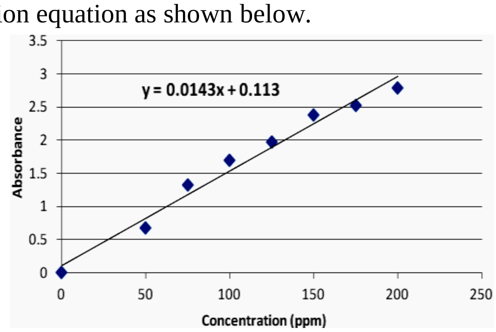

Figure 2: Calibration curve for RR-195 on Rice Husk

$$y = 0.0143x + 0.113$$

x represents concentration and y is absorbance.

This was further utilized to calculate the concentrations against various absorbance values.

3.2 Effect of Contact Time

Figure 3 illustrates relationship between percentage RR-195 removal by adsorption onto MRH particles and contact time for a time period of 120 minutes. Around 30% RR-195 dye was removed in initial 45 minutes demonstrating that adsorption is fast at first and then saturation begin to happen at different MRH sites bringing on subsequent lessening in removal percentage as just around 5 to 7% more of adsorbate was treated in next 75 minutes. In next 15 minutes just about 2% more dye was removed and this did not improve significantly and stops after half hour making total test duration of 120 minutes. Equilibrium is accepted to happen around then in all trials as available MRH sites get occupied.

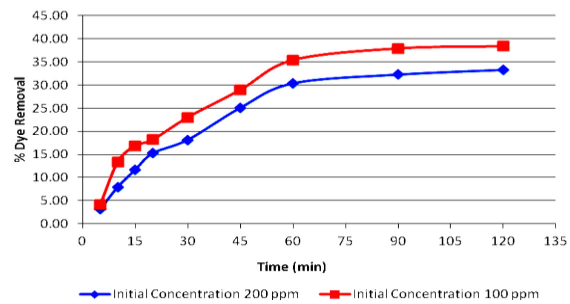

Figure 3: Effect of Contact time on RR-195 Adsorption

Figure 3 demonstrates RR-195 beginning concentration has critical impact in accomplishing adsorption equilibrium. More than 30% of dye is adsorbed for 100ppm solution in initial forty five minutes showing fast adsorption. At the same conditions, it took 1 hour in the event of 200ppm solution to achieve same 30% removal demonstrating moderate color uptake. Exterior surface of MRH was more utilized in case of 100ppm solution resulting in quick adsorption and ultimately greater removal efficiency of 39%. Dye molecules need to enter further into inside surface by the further addition of RR-195 as outside surface gets occupied. So for 200ppm, due to limited MRH available sites, adsorption required more time and outcome was lesser removal percentage of 33%.

3.3 Effect of initial dye concentration

Adsorption capacity MRH vary considerably by changing the starting solution concentration of RR-195 dye. As dye particles in adsorption media increase the resistance due to mass transfer between the RR-195 molecules and the MRH particulates enhance. 50, 75, 100, 125, 150, 175, 200ppm of RR-195 solutions were subjected to same adsorption treatment as described in method and resultant effect on % removal has been depicted in the Figure 4 below. About 42% removal occur for 50ppm solution of RR-195 in two hours and a 3% decrease is observed for 75ppm solution for which 39% adsorption of available dye molecules was observed. This similar decline trend continued and about 33% of dye molecules were taken by MRH at 200ppm initial concentration which corresponds to about 10% less removal than 50ppm.

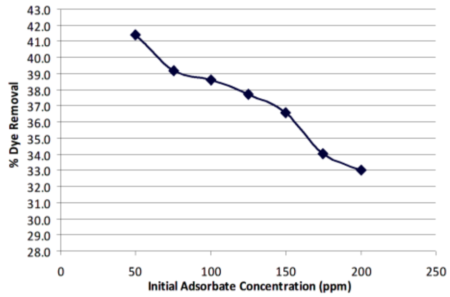

Figure 4: Effect of initial concentration on RR-195 Adsorption

3.4 Effect of adsorbent dose

RR-195 adsorption is critically dependent on MRH dosage. The adsorbent MRH was employed in different quantities varying between 1 gram to 8 gram for two different RR-195 starting solutions of 100 and 200ppm. A graph shown in Figure 5 depicts relationship between RR-195 removal and MRH dose.

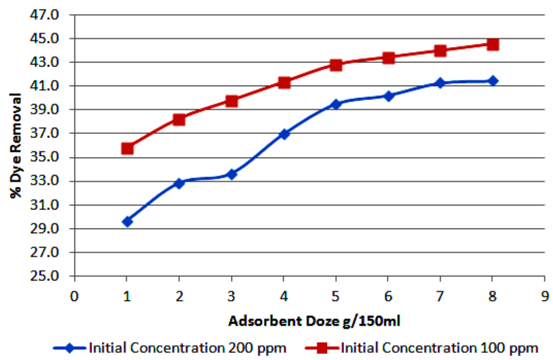

Figure 5: Effect of adsorbent dose on RR-195 Adsorption

At a dose of 1gram MRH, 35% and 29% RR-195 removal was achieved for 100ppm solution and 200ppm solution respectively. After adding more MRH at a dosage of 5 grams per 150ml volume solution, the removal percentage was raised to 43% for 100ppm and 39% for 200ppm solution. This almost 10% more dye removal observed for both cases was result of an increase in available MRH sites to adsorb RR-195 molecules. Easy availability of sites enhances surface adsorption thus molecules have no need to penetrate in interior structure which is slow and complicated process. The percentage removal was improved for about only 2% with the addition of 3 more grams of MRH. This scenario may be caused by increased resistance in mass transfer between MRH particles and RR-195 molecules making it impossible for some sites to be utilized as they become unreachable. To optimize adsorption capacity, cost and rice husk wastage no more than 5 grams/150ml of MRH should be utilized.

3.5 Effect of Temperature

For RR-195 adsorption onto MRH, the overall % removal was not considerably influenced by changing temperature from 30 to 60°C. Figure 6 shows a plot representing relationship between % removal and time at various temperatures for 100ppm solution of RR-195. It was indicated by test results that MRH has capability to adsorb about 23% of RR-195 dye at a temperature of 30°C in initial half hour. After increasing temperature up to 60°C a removal percentage of about 27% was achieved in same time period. High temperatures causes fast RR-195 ions mobility and dispersion which in turn reduce resistance in mass transfer thus ease adsorption process as these ions has already attained required energy from heating. Also MRH molecules swell thus reduce RR-195 ions effort to penetrate in interior structure. 38% removal achieved after 2 hours for all temperatures.

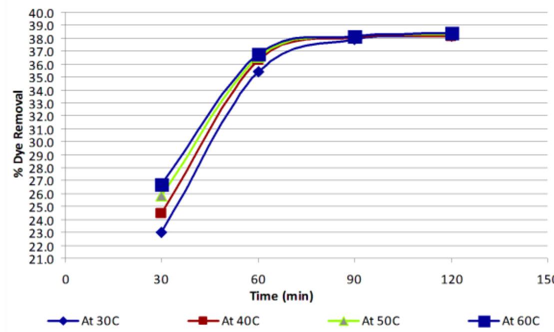

Figure 6: Effect of temperature on RR-195 Adsorption

3.6 Isotherms studies:

The data obtained by RR-195 adsorption study was then fitted to the Langmuir and Freundlich adsorption isotherm equations and results were compared.

Langmuir isotherm:

$$Q_e = Q_m K_a C_e / (1 + K_a C_e) \quad \text{Or}$$

$$C_e / q_e = C_e/Q_m + 1/K_a Q_m \qquad [10]$$

Q_m represents maximum rice husk adsorbing capacity in mg/g and K_a constant in L/mg denote adsorption equilibrium.

Freundlich isotherm:

$$Q_e = K_F C_e^{1/n} \quad \text{Or}$$

$$\ln q_e = \ln K_F + (1/n) \ln C_e \qquad [10]$$

K_F in mg/g is known as the Freundlich isotherm constant and n which is Freundlich exponent should have a value more than 1 for adsorption to be favorable. Ce/Qe values were plotted against Ce for Langmuir isotherm and $\ln Q_e$ values were plotted against lnCe for Freundlich isotherm.

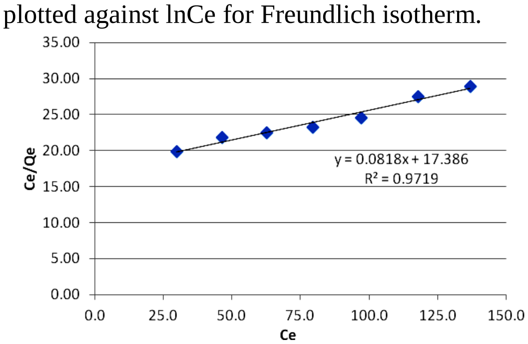

Figure 7: Langmuir isotherm at 30°C for RR-195

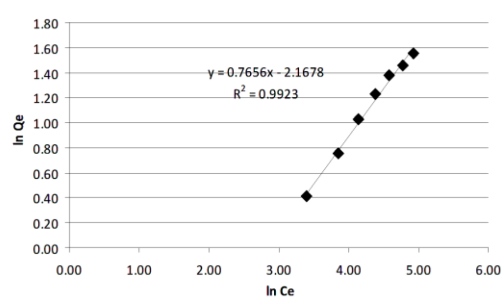

Figure 8: Freundlich isotherm at 30°C for RR-195

Linearity and higher R^2 values showed that the experimental data fitted better to Freundlich model then Langmuir. Isotherm slope and intercept gave the value of constants. Values obtained for isotherm constants and correlation coefficients for both isotherms listed in Table 3.

Table 3: Isotherm Constants

Sr #	Langmuir Model	
1	Q_m	12.22
2	K_a	0.005
3	R^2	0.972
	Freundlich Model	
4	n	1.306
5	K_F	8.739
6	R^2	0.992

Langmuir isotherm practicability for RR-195 adsorption onto MRH particles can be assessed by numerical values of a constant conventionally called as dimensionless separation/ equilibrium factor R_L. Its values must be in 0 to 1 range to ensure good applicability and are listed in Table 4.

$$R_L = 1/\ 1 + K_a\ C_o \qquad [11]$$

Table 4: R_L Values for RR-195 at 30^oC

Sr #	C_0	R_L
1	50	0.81
2	75	0.74
3	100	0.68
4	125	0.63
5	150	0.59
6	175	0.55
7	200	0.52

The adsorption process is considered to become more permanent / irreversible when R_L values reach close to zero.

Freundlich isotherm suited better because achieved numerical value of K_f was 8.739 indicating that simple RR-195 uptake by MRH. The type and percentage achievability of the adsorption depends on n value which tells about energy level existing at different sites and 1/n which was 0.76 in current research proves that 76% of the MRH active surface was at consistent energy level.

4 CONCLUSIONS

The analysis revealed that Reactive Red 195 can be removed from aqueous effluents utilizing rice husk, with maximum removal efficiency occupying between 35-45%. The optimum adsorption conditions were discovered to occur at a temperature of 40^0C utilizing MRH amount of 6 grams for which equilibrium reached in 120 minutes.

The adsorption process was promising as variables obtained by applying Langmuir and Freundlich Isotherm models were in the range that proposes effective adsorption. Freundlich equation best fitted as achieved R^2 was 0.992 which was very near to needed value of 1 proving favorable adsorption.

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