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Removal of Reactive Dye from Aqueous Solution Using Physico-Chemically Treated Rice Husk

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Abstract

Dye removal onto low cost material is a suitable method for textile wastewater treatment. Rice husk was investigated for its ability to remove reactive dye from aqueous solution. Two modes of operation were performed one with physical treatment and another with physicochemical treatment. All experiments were conducted at batch system and effects of effective parameters include pH, adsorbent dose, initial dye concentration and contact time was investigated. Maximum and minimum value of 94 % and 26.41% for physicochemically and 78% and 12.35 % for physically treated rice husk was obtained. Low pH, high adsorbent dosage and high contact time favors the adsorption whereas the percent dye removal decrease dramatically with the increase of initial dye concentration. Based on the result, Freundlich isotherm (R^2 =0.986) and second order kinetic (R^2=0.985) are best modules for explanation of adsorption onto Physico-Chemically treated rice husk. The efficient parameters were applied on actual textile dye machine effluent. It was observed that the direct waste increase in dye concentration and efficient removal (91.24%) was observed for adjusted waste. In regard to cost of other methods in dye removal, Physico-Chemically treated rice husk could be suggested as relatively efficient and low cost adsorbent for dye removal from textile wastewater.

Keywords: Adsorption; reactive black 5; rice husk; batch operation

1 Introduction

Contamination of water resources by dye pollutants is considered as an environmental important problem. Due to toxicity and unpleasant appearance, discharging the dye pollutants into surface water resources is undesirable (Abraha, 2007). In many industries such as food, textile, paper, rubber carpet, plastic and cosmetic, dyes are used in manufactures process (Rehman et al., 1997). Textile and dying industries are two main sources of dye wastewater production and treatment of this wastewater is difficult due to synthetic and complex structure of dye.

Besides its great economic contribution, the textile dying industry is known by the consumption of large quantity of water and generation of huge amount of wastewater. The textile finishing sector especially the dyeing unit is the major source of polluting wastewaters in the industry [1]. To dye 1kg of cotton, which represents half of the world fiber consumption, 70- 150 liters of water is consumed and almost similar amount of wastewater will be generated after the process. Residual color is a problem with reactive dyes because, in current dyeing processes, as much as 50% of the dye is lost in the wastewater. These losses are due to the relatively low levels of dye-fiber fixation and the presence of un-reacted hydrolyzed dye in the bath. Dye hydrolysis occurs when the dye molecule reacts with water rather than with the hydroxyl groups of the cellulose [2]. The reason behind this phenomenon is that in the process of dyeing cellulosic fibers with reactive dyes, the use of alkalis are required to promote formation of covalent bonds between the dye and cellulosic substitute. However, the uses of alkalis results in hydrolysis of reactive groups in the dye, and the reaction necessary to introduce the substitute on the fiber do not go to completion. Therefore, residual reactive hydrolyzed dyes remain in the process water. These problems are compounded by the high water solubility and characteristic brightness of the dyes [3].

In many researches, different materials have been widely used as adsorbents for dye removal including orange and banana peels [4], apple peel and wood [5]. The common methods have been used for dye removal from wastewater include biological methods (anaerobic treatment) and physicochemical methods such as coagulation, electro-coagulation, floating, filtration, ion exchange, membrane filtration and advanced oxidation [6-8]. However, many of these technologies are expensive, especially when they used for treatment of large wastewater streams. Consequently, adsorption methods using low cost adsorbents have the most potential for application in industrial wastewater treatment, because their efficiency is proven in the removal of organic and mineral pollutants and economic considerations [9-11]. Rice is the second largest produced cereal in the world. In Ethiopia according to CSA (2003) report, more than 8,326.50 hectare of land was under rice cultivation in 2003 with the yield of 154,120.39 quintal owned by 30,391 holders [12]. During milling of paddy about 78 % of weight is received as rice, broken rice and bran. Rest 22 % of the weight of paddy is received as husk. The possible utilization of rice husk and rice husk ash as an adsorbent for reactive dyes from aqueous solutions can be investigated because of its effective

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adsorption properties [13]. However, the amounts of rice husk available are so far in excess of any local uses and have posed disposal problems in the world developing country concern. It was chosen because of its granular structure, chemical stability and its local availability at very low cost and there is no need to regenerate it due to their easy availability and low production costs. Various modifications on rice husk have been reported in order to enhance their sorption capacities for dye, metal ions and other pollutants [14]. Most studies indicated that the modified adsorbents are efficient in binding either the cationic or anionic species but not both.

The aim of this study was to investigate the application of physically and physico-chemically treated rice husk for reactive dye removal from aqueous solution and determination of adsorption capacity in optimum adsorbent dose and reactions dynamic using common isotherms and kinetics.

2 Material and Methods

2.1 Materials

2.1.1 Rice Husk

Rice husk was collected from by-product of local rice mill factory and it was packed using sack and transported to the laboratory site.

2.1.2 Dye Solution

(a). Dye House Waste Water

The actual waste water was collected from Yirgalem Addis textile factory and Kombolcha textile factory for the purpose of simulation for the artificially constituted waste water. The wastewater was taken just from the outlet of the dyeing machine before it is mixed with other dye house wastewater streams in order not to contaminate with other source of waste waters in the dyeing section.

(b). Constituted Wastewater

According to the actual waste water from Kombolcha textile factory, laboratory constituted dye solution was prepared using Reactive Black 5 which can be representative of reactive dye groups. C.I. Reactive Black 5 was purchased from Chemical store. Reactive black 5 has chemical formula of $C_{26}H_{21}N_5Na_4O_{19}S_6$ molecular weight of 991.82g/mol with maximum absorbance of 593 nm.

2.1.3 Preparation of Adsorbent

(a). Physical treatment

The raw rice husk was washed several times with tap water until the supernatant solution was clear then the cleaned rice husk was oven dried completely at 105^0C overnight. Then it was cooled in the open air and crushed and sieved to -500/+250 µm.

(b). Chemical treatment

The physically treated rice husk was gone through further chemical treatment using nitric acid as follows. 100 gm of physically treated rice husks were soaked in 2 mole of nitric acid for 4 hours. Then it was washed several times with distilled water. Washing continues until the supernatant solution from the slurry becomes pH of 7 and clear. Finally it was oven dried overnight at 55^0C.

(c). Preparation of Adsorbate

1. An accurately weighted 1gm of the dye was dissolved in 1000ml of distilled water to prepare stock solution (1000mg/L).
2. Experimental solutions of the desired concentration were obtained by successive dilutions.
3. The pH of each experimental observations were maintained with the use of 0.1N HCl or 0.1N KOH.

2.2 Methods

2.2.1 Batch Adsorption Experiment

The batch adsorption experiment was performed as follows

1. The stock solution of dye (i.e 1gm of dye in 1 lt of distilled water) was prepared.
2. A desired amount of adsorbent (10, 30 and 50 g/l) was put in to the 250 ml flask.
3. A desired amount of adsorbate (50 , 150, 250 mg/l) was added in to the flask by adjusting the pH (2,7 and 10) while dilution.
4. The samples were shaken for a predetermined time intervals in the shaker at 150 rpm and room temperature.
5. At the end of contact time the samples were withdrawn from the shaker and filtered using vacuum filter by Whatman-42 (ø90) filter paper.
6. Finally the concentration of the remaining dye was measured using spectrophotometer.

Removal efficiency was calculated as follows

$$\% \, Removal = \frac{c_i - c_e}{c_e} * 100 \qquad (1)$$

All the experiments were done in triplicate and the average value was reported.

2.2.2 Experimental Design

The fractional factorial design (model), consisting of a four-factor and three-level pattern was used to conduct the experiment. The result of the experimental design was studied and interpreted by SPSS statistical software (13.0 Trial version for windows) to estimate the response of the dependent variable.

1 The percentage dye removal was used as response variable.
2 The potential design factors that have prime effect on the adsorption efficiency of the sorbent are initial dye concentration (mg/l), Contact time (min), Adsorbent Dose (g/l) and pH

Table 1 represents the respective level and range for selected factors. Factors those were held constant during the experiment are particle size distribution, temperature and the agitation speed at -500µm/+250 µm, 22°C and 150rpm respectively.

2.2.3 Experimental Range and Levels of Independent Variables

The initial dye concentration selected for batch experiments is within the range recommended in the actual textile effluent which was used in the light, medium and heavy shad. The levels taken for contact times are based on assumption that, the dye will have affinity for both adsorbents. The levels taken for Adsorbent dose are based on literature suggestion for other adsorbents [11]. Concerning the pH value selected, the range includes both the acidic and basic range.Design comprised of 27 runs in order; all points in coded factor levels. The combination of the four factors studied in the response experiment.

Table 1: Parameters with their respective level and range

parameters	levels and range		
	0	1	2
Concentration of dye (mg/l)	50	150	250
Adsorbent dose (g/l)	10	30	50
pH	2	7	10
Contact time (min)	40	80	160

2.2.4 Test on Actual Waste Water

The efficient adsorbent which is physico-chemically treated rice husk was investigated for the capacity of dye removal from the textile factory waste water. The laboratory runs was performed in two parts. It was first done without any modification on the physical and chemical appearance of the waste and another runs were conducted under the same condition by adjusting the Physical properties of the wastes. Those parameters needs adjustment was pH, dissolved solid and concentration of dye.

2.2.5 Adsorption Isotherm Study

Equilibrium adsorption isotherm for the physico-chemically treated rice husk were determined at the agitation speed of 150rpm, room temperature, 180 minutes contact time, pH 2, adsorbate dose of 150mg/l and different initial dosage (10, 20, 30, 50 g/l). The content was shaken for the specified time until equilibrium reaches. Then it was filtered using whatman filter paper in vacuum filter. The filtrate was analyzed for dye concentration to fit adsorption isotherm models. It was done in duplicate and the average value was reported.

$$\text{Amount dye adsorbed} = \frac{c_i - c_e}{m_{sorbent}} * V_{solution} \qquad (2)$$

Where, $C_i$is the initial dye con. in the liquid phase C_e is the final dye conc. in the liquid phase $m_{sorbent}$ is the mass of adsorbent, and $V_{solution}$ is the volume of experimental solution.

3 Results and Discussion

3.1 Adsorbent Characterization

The chemical composition and the physical properties of the rice husk were determined according to the methodology. The results are tabulated in Table 2. The chemical and physical property of the adsorbent is significant factor for adsorption capacity.

As compared to the maximum value of 1 the selected model is effectively correlated to the predicted value. The number of factors and 27 experimental runs has minor influence on the Adjusted R square, which is the real explanatory for the proportion of variance [15]. The values are mention in Table 5.

Table 2: Chemical composition and physical properties of rice husk used

Chemical Composition	Fresh rice husk	Physically treated rice husk	Physico-chemically treated rice husk
Moisture content (%)	8.81	5.6	4.5
Total organic carbon (TOC)	76.2	71.4	48.38
SiO_2 %	22.3	28.1	17.2
Ash content (%)	25.9	30.2	16.6
Nitrogen (%)	2.35	5.64	8.6
Cation exchange capacity (CEC)	-	30.0	44.02
Bulk density (g/cm^3)	-	0.49	0.71
Particle density (g/cm^3)	-	1.53	1.62

Dye House Wastewater Characterization***:*** The actual dye house wastewater after it has been analyzed using the analytical instruments shows the following characteristics shown in Table 3.

Table 3: Characteristics of the wastewater samples from the two textile factory

Waste water sample source	pH	COD (mg/L)	BOD (mg/L)	TS (mg/L)	Turbidity (NTU)	Concentration (ppm)*
Yirgalem Addis textile	9.9	1101.48	174	73680.2	14.23	196.32
Kombolcha textile	10.5	2408.45	186	54329.6	25.3	62.35

*Measured at absorbance of reactive black 5 λ = 593nm.

The model summary shows summaries for the selected linier model shown in Table 4.

Table 4: Model fit summary for physico-chemically treated adsorbent.

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	0.864(a)	0.747	0.701	12.46072

Table 5: ANOVA table for the physico-chemically treated rice husk

Model		Sum of squares	df	mean square	f	sig.
1	Regression	10068.628	4	2517.157	16.212	.000(a)
	Residual	3415.927	22	155.269	-	-
	Total	13484.556	26	-	-	-

The final equation for the response dependence on the four studied factors:-

Percent Dye Removal= 37.58159 + 0.323*Contact Time + 0.38*Adsorbent Dose - 2.1813*pH of Solution - 0.0419*Dye Concentration
(3)

These are the 95% confidence intervals for the coefficients.

3.2 Effect of Parameters on Percentage Dye Removal

3.2.1 Effect of Contact Time

The contact time between dye and adsorbent is significant parameter in waste water treatment using adsorption methods. A rapid removal of pollutants and establishment of equilibrium in a short period signifies the efficacy of that adsorbent. As can be seen in Table 4, contact time is significant factor with coefficient of 0.33. Fig.1 gives the relation between agitation time and percent dye removal for the adsorption of dye onto rice husk.

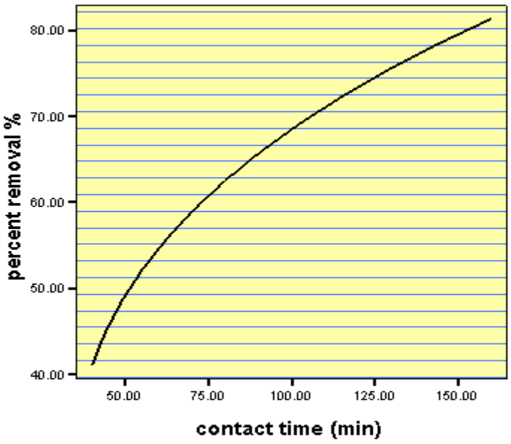

Figure1: Relation between contact time and percent dye removal

Color removal was rapid at initial stage but the rate decreased with the increase in time was shown in Fig. 1. Similar trends of bioadsorption were reported for three similar reactive dyes for EDTA modified rice husk by Ong et al., in terms of dye adsorption ratio. Initially rapid increase was due to the presence of large number of vacant sites and with the passage of time, number of active sites starts to decrease which is responsible for the reduction of adsorption rate.

3.2.2 Effect of pH

The pH value of the solution is process controlling parameter in the adsorption study since it determines the surface charge of sorbent. pH plays a major role in removal of reactive dye. $P < 0.05$. Its correlation with the response variable is in negative magnitude (-2.13) which means increase in pH decrease in percentage dye removal. Fig. 2 shows the relation between pH of the solution and percent dye removal.

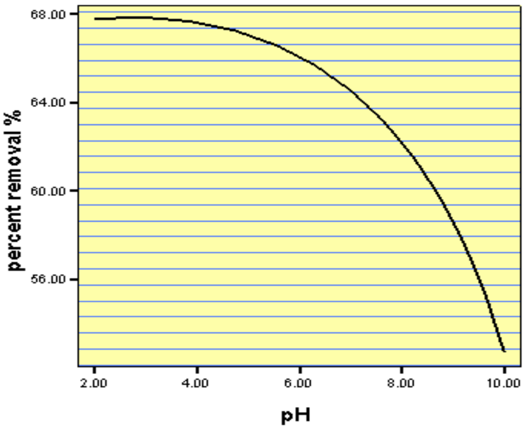

Figure 2: Relation between pH and percent dye removal

Increase in pH from 2 to 7 decreases the adsorption efficiency by about 21.33% and further decrease in adsorption rate observed when pH increase to 10. Low pH favors adsorption of reactive black 5 dyes on rice husk treated with nitric acid. Similar behavior was obtained for the rice husk treated with EDTA for reactive dye solutions. The reversed trend was also reported using removal of Metaylin Blue 2 where the percentage of uptake was more favorable in high pH [16]. As the pH of the system increases, this lead to the deprotonation of surface groups and the presence of excess OH^-, results in the electrostatic repulsion between the anionic dye and negatively charged sites.

3.2.3 Effect of Dye Initial Concentration

In batch absorption systems, available adsorbate initial concentration in solution plays an important role as a driving force which overcomes mass transfer resistance of adsorbate between aqueous and solid phase. Dye concentration is significant and it has negative correlation with percent dye removal (Table 3). The graphical relation between dye initial concentration and percent dye removal is shown in Fig.3.

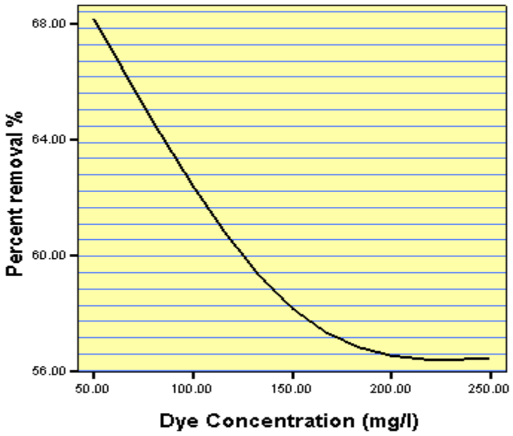

Figure 3: Relation between the percent dye removal and initial dye concentration

The result in Fig.3 shows that with increase of initial dye concentration from 50 to 150 mg/l, the removal efficiency decreases from 87 % to 65.43% (average value). The decrease in removal efficiency can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration.

3.2.4 Effect of Adsorbent Dose

Adsorbent dose is one of the important factors because it is used to determine capacity of an adsorbent for initial concentration of adsorbate. By monitoring the amount of adsorbent, it is possible to study the effects of adsorption process to attain maximum adsorption capacity of the adsorbent. The relation between the adsorbent dose and percent dye removal is explained in Fig. 4.

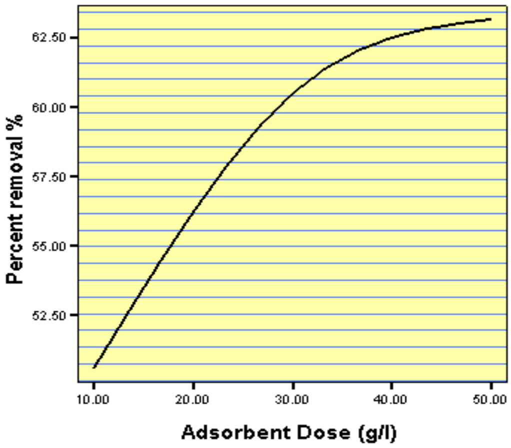

Figure 4: Relation between the percent dye removal and adsorbent dosage

The increase in adsorbent dose accompanied with the increase in percent dye removal. This is mainly because increase in adsorbent dose means adding more extra adsorption sites for the adsorbate. Roughly linear relation can be observed in Fig. 4. A similar result for direct F. Scarlet dye was observed by Abdel *et al.* (2005), it was reported that an incremental of 10% was observed for every 2.5g/l increase biomass for citric acid treated rice husk [11].

The selected model is effectively correlated to the predicted value as compared to the maximum value of 1. R square is the proportion of variance in the dependent variable (percent removal) which can be explained by the independent variables, the overall selected parameters can explain 42.5 % of the percent dye removal, shown in Table 7

Table 6: The model fit summary for physically treated adsorbent

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.652(a)	.425	.320	15.866

*Predictors: (Constant), dye concentration, solution pH, adsorbent dose, contact time.

Table 7: ANOVA table for physically treated rice husk

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	4092.680	4	1023.170	4.065	.013(a)
	Residual	5538.049	22	251.729	-	-
	Total	9630.728	26	-	-	-

*Predictors: (Constant), dye concentration, solution pH, adsorbent dose, contact time

Dependent Variable: Percent dye removal the final equation of the response dependence on the four studied factors

$$\text{Percent Dye Removal} = 40.115 + 0.1499 * \text{Contact Time} + 0.31386 * \text{Adsorbent Dose} - 1.2720 * \text{Ph Of Solution} - 0.08312 * \text{Dye Concentration} \quad (3)$$

The confidence intervals are related to the p-values such that the coefficient will not be statistically significant if the confidence interval includes 0 which is the null hypothesis value (coefficient = 0) is correct. These confidence intervals can help to put the estimate from the coefficient into perspective by seeing how much the value could vary.

3.3 Effect of Parameters on Percentage Dye Removal

3.3.1 Effect of Contact Time

The effect of contact time (agitation time) was investigated for the given time range of 40 to 160 minutes. It is main parameters for the design of adsorption process. It was described in Table 4.9 that time is significant factor with coefficient of 0.15. Fig. 5 shows the relation between agitation time and percent dye removal.

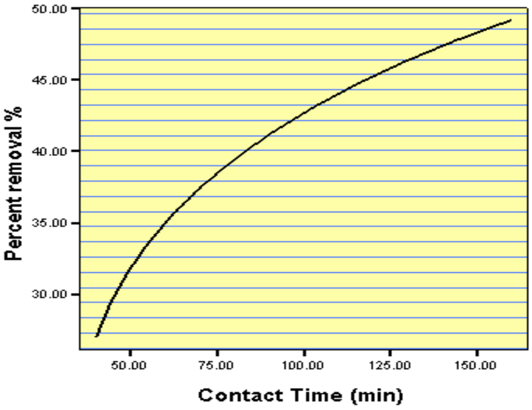

Figure 5: Relation between contact time and percent removal

As can be seen from Fig.5 the amount of percent dye removal increases with agitation time. This is because the agitation of the solution facilitates the rate of transport of the adsorbate species from the outer sites to the interior site of the adsorbent. As the vacant sites are occupied the rate of adsorption becomes decrease.

3.3.2 Effect of Adsorbent Dose

The effect of adsorbent is determinant factor to consider while assessing the possibility of using the adsorbent for large scale process. The positive effect to the percentage dye removal and it is significant parameter shown in Fig. 6.

The amount of dye removal was increased with increasing the adsorbent dose up to 30 mg/l and after that the rate becomes more pronounced as it goes to final. Increase of adsorbent dosage from 10 to 30 g/L increases adsorption rate by ≈ 4.7% and increase of adsorbent from 30 to 50 increases the percent dye removal by ≈18%. This is due to the fact that, increase in adsorbent dosage increase area available for adsorption.

3.3.3 Effect of Solution pH

The physically treated rice husk goes through further chemical treatment as the pH of the solution changes. The change in pH affects the adsorption process because the pH of the solution affects the charge in the surface of the adsorbent where the ions concentration may react with the functional groups on the active sites of the adsorption surface. It can be recalled that the effect of treatment was to activate the surface functional group. It is correlated negatively with magnitude of -0.222 and a negative coefficient of -1.272. The relation between solution pH and percent dye removal is presented in the Fig. 7.

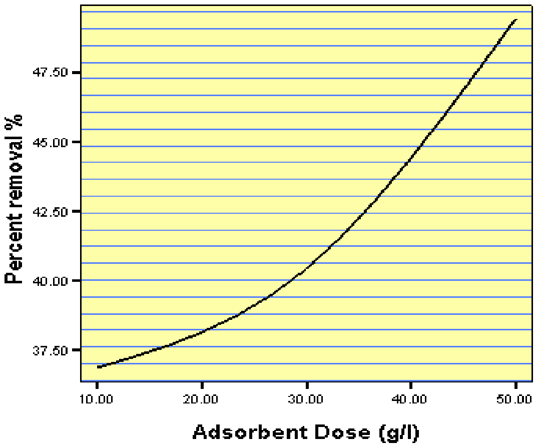

Figure 6: Relations between adsorbent dose and percent removal

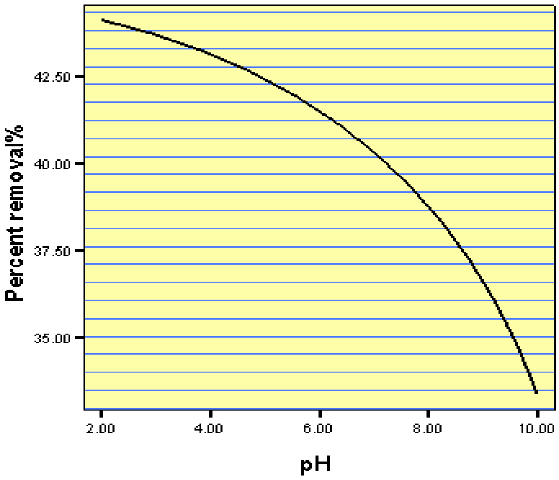

Figure7: Relations between solution pH and percent removal

From the Fig.7 it can be seen that the effects of pH is positive at the initial stage and after neutral condition the percentage removal sharply decrease up to pH of 10. Low pH favors adsorption of reactive black dye on physically treated rice husk.

3.3.4 Effect of Dye Concentration

The value for dye concentration was 0.025 which is significant and inversely correlated to percentage dye removal. The relation between initial dye concentration and percentage dye removal is presented in Fig.8.

A smooth plot of initial dye concentration and percentage dye removal was obtained. As in Fig. 8 the average percentage dye removal was decreased ≈ 12% for addition of 100 mg/l dye. This effect was due to the increase in dye concentration occupy the adsorption site and saturation of all adsorption sites reaches easily.

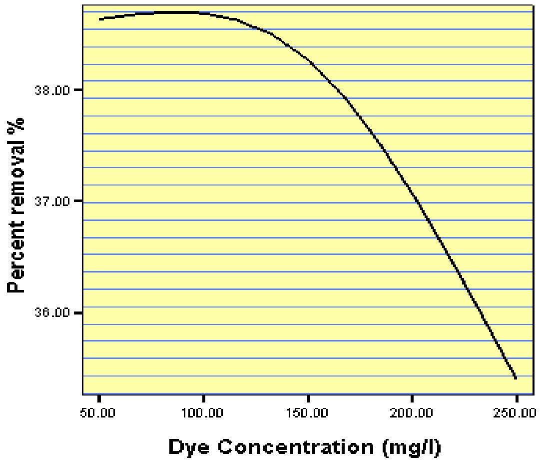

Figure8: Relations between dye concentration and percent removal

3.4 Adsorption Isotherms

3.4.1 Langmuir isotherm

The plot of specific sorption (Ce/qe) against the equilibrium concentration (Ce) for the dye is shown in Fig.9. Linearized form:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e \qquad (4)$$

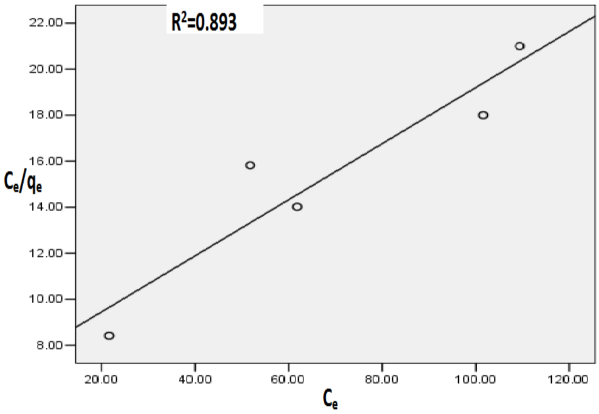

Figure 9: The plot of (Ce/qe) against the equilibrium concentration (Ce)

3.4.2 Freundlich Isotherm

The experimental data were fitted to the Freundlich isotherm and correlation coefficients were obtained by plotting log (qe) vs. log (Ce) in Fig.10. Linearized form of Freundlich equation is

$$\log q = \log K + \frac{1}{n}\log C_e \qquad (5)$$

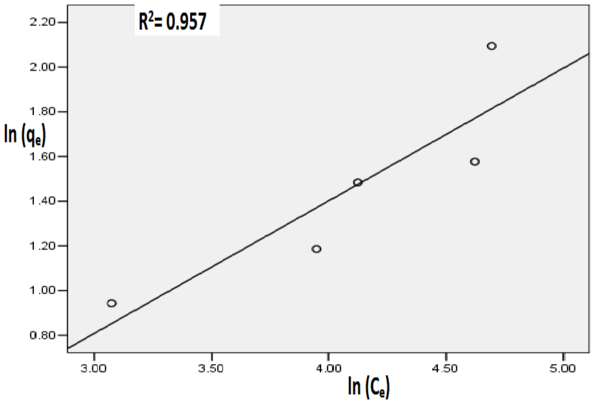

Figure 10: The Plot of (Ce/qe) against the equilibrium concentration (Ce)

3.4.3 Temkin Isotherm

Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbate, shown Fig. 11. Linearized form

$$q_e = \frac{RT}{b_T}\ln KT + \frac{RT}{b_T}\ln C_e \qquad (6)$$

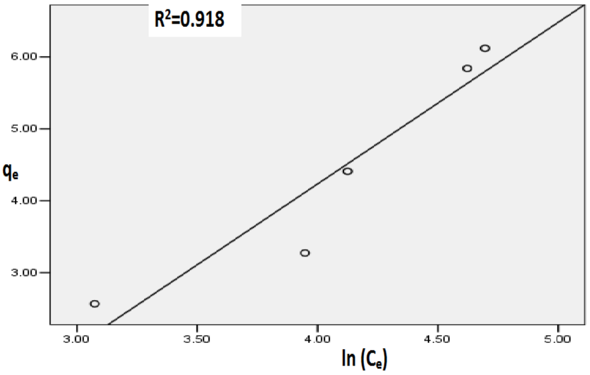

Figure 11: Temkin equilibrium isotherm model for the adsorption of reactive black 5 onto the physico-chemically treated rice husk

Table 8: Langmuir, Freundlich and Temkin isotherm constants for the adsorption of reactive black 5 on physico-chemically treated rice husk.

Adsorbent	Langmuir			Freundlich			Temkin		
	Qm (mg/g)	K_L (Lmg^{-1})	R^2	N	K	R^2	R^2	K_T	b_T
Physico-chemically treated	8.34	0.061	0.914	0.60	0.000575	0.956	0.918	0.992	42.3R

4 Conclusions

The effect of treatments was discussed using the parameters such as agitation time, initial concentration of dye, solution pH and adsorbent dosage. It was observed that the maximum percent dye removal was 94% at 160minute, pH 2, adsorbent dose 50g/l, dye concentration 100 mg/l for physico-chemically treated rice husk and 73 % at 80minute adsorbent dose 50 g/l, pH 2, dye concentration 50 mg/l for physically treated rice husk. These figures show that chemical treatment enhance the adsorption of reactive dye on rice husk. According to statistical result from SPSS, time and pH have high significant followed by dose and dye concentration on the percent dye removal. For the selected isotherm models a regression coefficient of 0.893, 0.957 and 0.918 was calculated for Langmuir, Freundlich and Temkin isotherms respectively. The experimental data yielded excellent fit with Freundlich isotherm equation. Rice husk is a by-product from rice milling industries and abundant material available with low cost, the treatment of reactive dye using it as adsorbent is expected to be economical. The result based on actual textile waste water gives rice husk as a good treatment option especially for Kombolcha textile factory and it needs further work to reach the industry. In the visited textile industries, they fail to meet the effluent discharge standards set by regulatory bodies.

Reference

1- Christie RM, Environmental Aspects of Textile Dyeing. *Woodhead, Boca Raton Cambridge,* 2007.

2- Berger RR, Fiber Reactive Dyes with Improved Affinity and Fixation Efficiency, *M.Sc thesis North Carolina State University*, 2005.

3- Maelign A, Removal of textile reactive dye from waste water by using nanofiltration *Addis Ababa University*, 2010.

4- Wan WA, Ngah MAKM, (2012). Hanafiah, Biosorption of copper ions from dilute aqueous solutions on base treated rubber (Hevea brasiliensis) leaves powder: kinetics, isotherm, and bioadsorption mechanisms. *Egypt Journal of Aquatic Research*, 2012: 5(12):111-354.

5- Kumar R, Sridhari MNV, Trends in color removal from textile mill effluents, *Colorage*, 1998; 40:25-34.

6- Robinson T, McMullan G, Marchant R, Nigam P, Remediation of dye in textile effluent: a critical review on current treatment technologies with a proposed alternatives. *Bioresource Technology*, 2001; 77:247- 255.

7- Safa A, Bhatti S, Removal of dyes from effluents using low-cost agricultural by-products, *Science of Total Environment*, 2011; 79:271-279.

8- Teshome A, Removal of textile reactive dye from aqueous solution by Using charcoal based bottom ash and coffee husk Adsorbonts, *Addis Ababa University*, 2011.

9- Annadurai G, Chellapandian M, Krishnan MRV, (1999). Adsorption of reactive dye on chitin. *Environmental Monitoring Assessment of Science and Technology*, 1999; 59:111-120.

10- Daifullah AAM, Girgis BS, Gad HMH, Utilization of agro- residues (rice husk) in small wastewater treatment plans. *Material letters*, 2003;57:1723-1731.

11- Abdel AW, Wahab PK, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of acid yellow 36. *Dyes and Pigments*, 2003; 56:239-249.

12- CSA, Statistical report on area and production of temporary crops. FDRE Centeral Agricultural Census Commission, Ethiopian Agricultural Sample Enumeration. Results at Country Level. Part I. *Addis Ababa*, 2003; 375.

13- Ong, Lee WN, Equilibrium studies and kinetics mechanism for the removal of basic and reactive dyes in both single and binary systems using EDTA modified rice husk. *Dye and pigments*, 2012; 59:265-283.

14- Hongquan Xu, A Catalogue of Three-Level Regular Fractional Factorial Designs Department of Statistics, *University of California*, CA 90095-1554, U.S.A, 2012.

15- Ho YS, McKay GA, A comparison of chemisorptions kinetic models applied to pollutant removal on various sorbents. *Process Safety and Environmental Protection*, 1998; 76(4):332-338.

16- Robert L, Mason RF, Hess GML, Statically design & Analysis of experiment 2nd edition, *Willy*, 2003.