Rice Husk is a Natural Low-cost Adsorbent for Reactive Dyes

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Abstract— *Reactive Dyes are widely used in textile industries and one of the major chemical which is responsible for water pollution all over the world specially third world countries where appropriate water treatment process do not use because of high costing. This study showed that rice husk can be used as a low cost natural adsorbent for adsorption of reactive dyes from aqueous solution. The whole process was endothermic in nature. Rice husk has great potential to adsorb reactive dyes.*

Keywords— *Adsorption, environment, effluent, langmuir, low-cost material, reactive dyes, removal, rice husk.*

I. INTRODUCTION

Without proper treatment, releases of wastewater to environment are a serious problem for marine environment and human health. For that reason, treatment of colored waste is indispensable. Usual treatment methods are often unable to remove certain forms of color, particularly those come from reactive dyes as a result of their high solubility and low biodegradability thus and methods for decolorizing textile effluents are of concern [1]. Many methods have been applied for the removal of dyes from wastewaters and effluents. Activated carbon is a versatile adsorbent and widely used for removal studies but it is an expensive material and its high cost scientists trying to find out its alternates. Some of the reported adsorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, modified rice husk and coconut shells), industrial waste products (waste carbon slurries and metal hydroxide sludge), biosorbents (chitosan, peat and biomass) and others (starch, cyclodextrin and cotton).Research is still going on to find out new adsorbent [2-7].

In this study unmodified rice husk was used as a low-cost adsorbent to adsorb Amaranth, Reactive blue 4 and Reactive orange 13 dyes from aqueous solution. The influence of pHs, solution and temperature, were studied in batch mode. Various models were tested to investigate the removal kinetics and equilibrium removal behaviour.

II. EXPERIMENTAL

A. Materials

Rice husk was purchased from local market and crushed them to make powder. Then washed with 0.1M HCl and washed again with distilled water. It was then oven dried at 45°C for 48 h. The dried sample was stored in a plastic bottle for later use. No other chemical or physical treatments were used prior to removal experiments.

All other reagents and solvents were commercially available and highest grade of purity; hence they were used without purification. Deionized water was prepared by passing distilled water through a deionizing column (Branstead, Syboron Corporation, Boston. USA).

B. FTIR Spectra

The Fourier transformation infrared (FTIR) spectra of Amaranth (AR), Reactive blue 4 (RB-4), Reactive orange 13 (RO-13) and rice husk before and after removal of amaranth (AR), Reactive blue 4 (RB-4), Reactive orange 13 (RO-13) were recorded in KBr with the frequency range 400-4000cm-1 using FTIR spectrometer (IR Prestige-21 FTIR Spectrophotometer, Simadzu, Japan).

C. Batch Removal Experiments

Batch mode was selected because of its simplicity and reliability. Batch sorption studies were carried out by agitating 25 mL of dye solution with desired concentration and 0.1g of the adsorbent (puffed rice powder) in 220 mL reagent bottle. Agitation was performed at room temperature (30± 0.20C) with shacking machine at a speed of 120r/min at different time intervals. The solutions pH (2-8) was adjusted either by adding micro liter quantities of 1 mol/L M HCl or 1 mole/L NaOH. The dye solution was separated from the adsorbent by centrifuging. The dye adsorption was determined spectrophotometrically (UV-160A, Shimadzu, Japan) by monitoring absorbance changes at the λmax of reactive dye. The concentration of dye in the supernatant was determined by spectrophotometric method, λmax value of of AR, RB-4 and RO-13 were found at 521nm, 595 nm and 488.0nm respectively to be constant at the pH ranging from 2 to 8. The amounts of dye adsorbed onto Rice Husk qt (μmole/g) at any time t and qe (μmole/g) at equilibrium were determined from the following relationships:

$$q_t = V(C_0 - C_t)/m \qquad (1)$$

and

$$q_e = V(C_0 - C_e)/m \qquad (2)$$

where C_0 (μ mole/L), C_t (μ mole/L), C_e (μ mole/L), are the liquid-phase concentrations of dye at initial, at any time t, and equilibrium, respectively; V (L) is the volume of AR solution and m (g) is the amount of dry Puffed rice power used. The equilibrium removals of dye onto Puffed rice in aqueous solution were also performed at temperatures 35^0, 40^0 and 45^0C. The adsorbate solutions were transferred at centrifuged repeatedly with an agitation speed 3000 rpm for 4 minutes. The supernatants were used for the analysis of the residual dye concentrations. The absorbance of supernatant solutions was measured onto UV-1601PC Shimadzu Spectrophotometer at a

definite wavelength, 521.0 nm, 595.0 nm and 488.0 nm for AR, RB-4 and RO-13 respectively.

III. RESULTS AND DISCUSSION

A. Point of Zero Charge Measurement

Point zero charge of rice husk was determined and it was estimated to be 5.85. The total effect of all functional groups on rice husk determines pHPZC which means the pH at which the net charge of the surface of rice husk is zero. At pH < pHPZC, the rice husk surface has a net positive charge, while pH > pHPZC the surface has negative charge. Similar trend was found in the case of removal of Vertigo blue 49 and Orange DNA 13 by carbon slurry [8].

B. Effect of pH on the Removal Process

The effect of pH on the removal of AR, BR4 and RO13 by Rice Husk was studied in aqueous solution within pH range 2-8. It was observed that the percentage of removal of dyes increases significantly with decreasing solution pH (Fig. 1). pH of aqueous solution plays on important role on the dye removal onto Rice Husk powder. These results suggest that the removal capacity of Rice Husk is suitable at pH- 2 among the observed pH ranging from 2-8. At lower pH of the dye solution the surface of the rice become more positively charged and can attract negatively charged anion of the dye molecule. Similar trend was observed in the case of removal of Amaranth dye from aqueous solution using Pisum sativum Peels and Arachis hypogaea Shells [9].
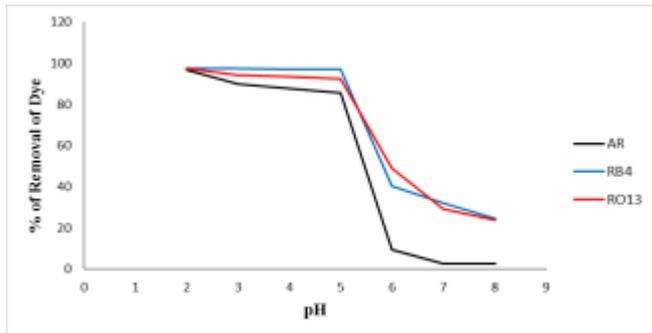

Fig. 1. pH effect on the percentage of dye removal (Initial concentration of AR, RB4 and RO13 were 110.00, 100 and 35 μmol/L respectively).

C. Effect of Temperature on the Removal Process

Temperature is an important parameter that can influence the equilibrium and rates of sorption processes. The effect of temperature on the removal process was studied at 30, 35^0, 40^0 and 45°C. When the temperature is raised from 30^{0}C to 45°C, the removal of AR, Br4 and Ro13 onto Rice husk increased (Figure: 2), indicating that the process is endothermic. This may be attributed to increased penetration of reactive dyes inside microspores at higher temperatures or the creation of new active sites. Same nature was shown in case of removal of RO13 by Jackfruit seed flakes [10].
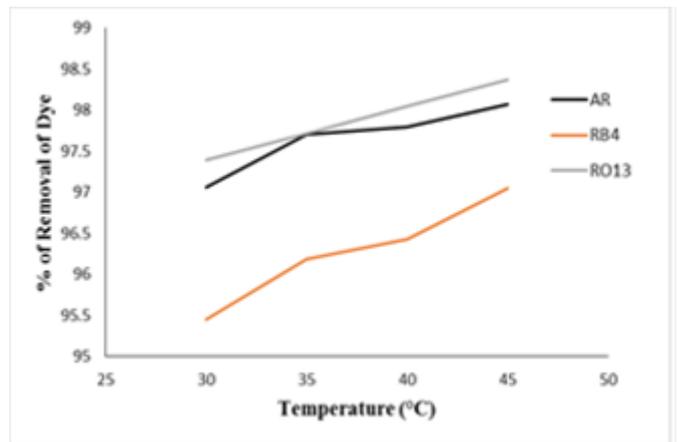

Fig. 2. Temperature effect on the percentage of dye removal (Initial concentration of AR, RB4 and RO13 were 52.00, 100 and 35 μmol/L respectively).

D. Rate Constant Studies

Pseudo first-order and pseudo second-order and Elovich kinetics models were used. It was found that the experimental data (Table I) fitted well (from R2 value) to the second-order kinetics than that of other kinetics model. Same phenomenon was found in case of adsorption of Reactive Blue 4 onto acid activated Mustard Stalk [11] and adsorption of Amaranth by Alumina reinforced Polystyrene [12].

TABLE I. Comparison of calculated and experimental qe values and kinetic parameters for the AR,RB4 and RO13 adsorption onto rice husk at pH 2, initial concentrations of AR, RB4 and RO13 was 110,105.00 and 35.00μmol/L respectively.

Dye	q_e(exp.) (μmol/g)	Pseudo-First-Order Kinetic			Pseudo-Second-Order Kinetic			Elovich Kinetic Model		
		k_1 (min^{-1})	q_e (cal.) (μmol/g)	R^2	k_2 (g/μmol/min)	q_e (cal.) (μmol/g)	R^2	α (μmole/g/min)	β (g/mole)	R^2
AR	25.70	0.0159	5.44	0.874	0.0146	25.77	0.999	2.69E+04	0.58	0.971
RB4	24.44	0.078	2.73	0.953	0.1072	24.45	0.999	9.12E+09	1.12	0.750
RO13	8.31	0.0396	2.03	0.951	0.3286	8.33	0.999	4.28E+23	7.35	0.952

E. Adsorption Isotherms

Tempkin, Freundlich and Langmuir isotherm models were used to describe the equilibrium characteristic of removal. Experimental RL values are listed in table II which shows type of removal is favorable. All constants values were listed in table II. Experimental data shows that the Langmuir removal isotherm provides a good description of data for AR, RB-4,

RO-13 dye over the whole temperature range studied in single systems since R2 values from Langmuir isotherms (Table II) are always greater than that of Freundlich isotherms and Tempkin isotherm. Thus, it can be concluded that monolayer removal is occurred in this study. This also suggests that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of

the adsorbate at the outer surface of the adsorbent. Water Thus, the equilibrium constants or binding constants (aL) obtained from Langmuir isotherms are used to calculate the

thermodynamic parameters for the removal process. Similar nature was shown in case of removal of Reactive Blue 4 onto puffed rice [13].

TABLE. II. Tempkin, Freundlich and Langmuir isotherm constants at different temperatures for the adsorption of AR, RB4 and RO13 onto rice husk from aqueous solution at pH 2.

Tempkin												
Temperature (^{o}C)	30			35			40			45		
Dye	AR	RB4	RO13	AR	RB4	RO13	AR	RB4	RO13	AR	RB4	RO13
K_T (µmole/L)	14.45	2.59	5.55	8.38	3.61	3.71	4.50	8.09	6.61	3.58	7.66	4.8
bT (J/mole)	0.002	0.003	0.006	0.002	0.003	0.008	0.002	0.003	0.008	0.002	0.003	0.01
R^2	0.933	0.842	0.852	0.959	0.885	0.904	0.966	0.905	0.913	0.967	0.899	0.902
Freundlich												
K_F ((µmol/g)(µmol/L) -1/n)	12.59	1.41	34.67	12.30	1.55	36.31	12.02	1.82	42.66	12.02	1.82	43.65
b_F (J/mole)	0.56	0.57	0.21	0.55	0.57	0.23	0.57	0.55	0.22	0.57	0.56	0.25
n	6.19	1.77	4.80	5.60	1.77	4.29	5.01	1.81	4.46	4.76	1.789	3.99
R^2	0.856	0.842	0.725	0.881	0.843	0.777	0.903	0.886	0.791	0.914	0.906	0.81
Langmuir												
K_L (L/g)	0.95	8.10	8.14	1.17	9.28	13.25	1.55	11.60	23.26	1.82	12.58	30.40
a_L (µmole/L)	0.024	0.123	0.059	0.027	0.128	0.081	0.032	0.147	0.133	0.036	0.155	0.149
q_m (µmole/g)	39.84	65.79	136.99	43.48	72.46	163.93	47.62	78.74	175.44	50.25	81.30	204.08
R_L	0.0006	0.00005	0.00006	0.00005	0.00004	0.00004	0.0004	0.00003	0.00002	0.0003	0.00003	0.00002
R^2	1.00	0.999	0.999	1.00	0.999	0.999	1.00	0.999	0.999	1.00	1.00	0.999

F. FTIR Analysis

FTIR analysis for Rice husk (before used)

The peaks at 3414.67 cm-1 for surface –OH stretching, peak at 2923.37 cm-1 for aliphatic C-H stretching, peak at 2852.62 cm-1 for aldehyde C-H stretching, peak at 1653.98 cm-1 for unsaturated group like alkene, peak at 1560.17 cm-1 for aromatic C-NO2 cm-1 stretching, peak at 1077.57 cm-1 for Si-O stretching [14]. (Figures are not shown).

FTIR analysis for Amranth

Broad intense band (Figures are not shown) at 3444.87 cm-1 attributed to hydrogen bonded –OH vibration [15]. The in-plane OH deformation vibration appears in the IR spectra as strong band at 1496.76 cm-1 corresponding to in-plane-bending vibration of OH. Peaks in the region 520-702 cm-1 for associated -OH [16]. The medium strong band at 740.67 cm-1 for in the IR spectra corresponds to out-of-plane bending mode of hydroxyl vibrations. The band occurring between 1435.04 cm-1 and 1339.60 cm-1 corresponds to the stretching mode of an azo-compound [17]. C-N stretching vibrations of azo-compounds appear in the 1197.79 -1139.93 cm-1 region (IR) [18, 19]. Asymmetric vibrations of SO3- group of sulfonic acid salts usually occur in the IR at 1250-1140 cm-1.The band due to the symmetric stretching vibration is sharper and occurs at 1130-1080 cm-1. SO3- symmetric deformation modes give strong bands in the 550-660 cm-1 region (IR) [20]. Naphthalene ring stretching vibrations are expected in the region 1580-1300 cm-1 whereas naphthalene CH bending modes give rise to bands in the region 1230-970 cm- [21, 22]. These vibrations are mixed with in–plane-bending vibration of OH group, coupled with C-N stretching vibration or with SO3- vibrations. Peaks at 1197.79 cm-1 and 1041.56 cm-1atributed for S=O stretching as sulfonate salts.

FTIR analysis for Rice husk (after removal of AR)

The peaks (Figures are not shown) at 3414.67 cm-1 for surface –OH stretching shifted to 3442.94cm-1, peak at 2922.16 cm-1 for aliphatic C-H stretching, peak at 2852.72 cm-1 for aldehyde C-H stretching, peak at 1653 cm-1 for unsaturated group like alkene, peak at 1558.48 cm-1 for aromatic C-NO2 cm-1 stretching, peak at 1077.57 cm-1 for Si-O stretching shifted to 1082.07cm-1, sharp peak at1197.79 cm-1 in amaranth for S=O stretching is absent in the FTIR spectra of rice husk after removal and peak at 1041.56 cm-1 shifted to 1055.06 cm-1.

FTIR analysis suggested that there is some sort of interaction among protonated -OH and Si-O groups of rice husk and -SO3H groups of dyes.

FTIR analysis for Reactive Blue 4

In the spectrum (Figures are not shown) the broad region around 3450.68 cm-1 can be assigned to overlapping of -OH stretch and -NH functional groups. The peak at 2924.89 and 1654 cm-1 (not marked) which corresponds with C-H and C=O stretch, respectively. The band at 1290.89, 1224.13 and 1188.84 cm-1 correspond to the S=O stretching, peaks at 796.46 cm-1, 765.20 cm-1 for –C-H stretching, 617.94 cm-1 – C-Cl stretching.

FTIR analysis for Rice husk (after removal of RB4)

Band at 3414.89 cm-1 attributed to O-H stretching and (Figures are not shown) the band at 1290.89, 1224.13 and 1188.84 cm-1 correspond to the S=O stretching in the RB4 FTIR spectrum were absent in FTIR spectrum of rice husk after removal of RB4. Peak at 1077.57 cm-1 for Si-O stretching in the spectrum of rice husk shifted to 1042.86 cm-1 after removal of RB4.

This analysis concluded that the removal due to the interaction of protonated Si-O groups of rice husk with –SO3-groups of RB4.

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TABLE. III. Thermodynamic parameters.

Tem. ((K)	303			308			313			318		
Dye	AR	BR4	RO13	AR	BR4	RO13	AR	BR4	RO13	AR	BR4	RO13
ΔG (kJ/mole)	-25.40	-29.53	-27.69	-26.11	-30.11	-28.94	-27.03	-30.97	-30.69	-27.75	-31.59	-31.49
Dye	AR	BR4	RO13									
ΔH (kJ/mole)	23.05	13.24	23.35									
Δ S(J/mole/K)	159.81	141.03	168.85									
R^2	0.988	0.947	0.901									

FTIR analysis of Reactive Orange13 (RO13)

The FTIR spectrum(Figures are not shown) displays peak at 3440.1 cm-1 for the intramolecular hydrogen bonding aromatic –OH and –O-H stretching, peak at 1622.7 cm-1 and 1555.4 cm-1 for –C=C stretching of aromatic rings, 1466.5 cm-1 and 1394.6 cm-1 –C-H stretching of alkyl acetals, peak at 1329.8 cm-1 and 1187.5 cm-1 for –C-N stretching due to amines, peak at 845.2 cm-1, 799.9 cm-1, 763.3 cm-1 for –C-H stretching, 617.8 cm-1 –C-Cl stretching.

FTIR analysis for Rice husk (after removal of RO13)

The peaks (Figures are not shown) at 3414.67 cm-1 for surface –OH stretching shifted to 3422.55cm-1, peak at 2923.11 cm-1 for aliphatic C-H stretching, peak at 2852.66 cm-1 for aldehyde C-H stretching, peak at 1653.33 cm-1 for unsaturated group like alkene, peak at 1560.38 cm-1 for aromatic C-NO2 cm-1 stretching, peak at 1077.57 cm-1 for Si-O stretching shifted to 1050.77cm-1, sharp peak at 1253.62 cm-1, 1185.99 cm-1 and 1140.66 cm-1 in reactive orange 13 (RO13) for S=O stretching is absent in the FTIR spectra of rice husk after removal.

FTIR analysis suggested that there is some sort of interaction among the protonated OH and Si-O groups of rice husk and -SO3H groups of dyes.

G. Thermodynamic parameters

Thermodynamic parameters are very important to understand the removal process. Van't Hoff equation was used to calculate the values of thermodynamic parameters (ΔH, ΔS and ΔG). As we saw the Langmuir isotherm was best fitted with the experimental data (Table-II).

$$\ln a_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (3)$$

The equilibrium constants or binding constants (a_L) obtained from Langmuir isotherms are used to calculate the thermodynamic parameters for the removal process.

The values of ΔH, ΔS were calculated from the slope and y-intercept of Van't Hoff plot of $\ln a_L$ vs. 1/T (Figure is not given).

Equation-3 was used to determine all the values of ΔH and ΔS are presented in table-III. The results show that the changes in enthalpy, ΔH for the removal of AR, RB4 and RO13 by Rice Husk were 23.05, 13.24 and 23.35kJ/mol respectively. A positive enthalpy change, ΔH suggests that the interaction of dye adsorbed by Rice Husk is endothermic which is supported by the increasing removal of the dye with the increasing in temperature while a negative removal standard free energy change (ΔG) and a positive standard entropy change (ΔS) indicate that the removal reaction is a spontaneous process. Generally, a value of ΔH in between 5-40 kJ/mol is consistent with electrostatic interaction between removal sites and adsorbing ion (physical removal) while a value ranging from 40-800 kJ/mol suggests chemisorption [23].

IV. CONCLUSION

Present study shows that the Rice Husk can be used as an adsorbent for the removal of Amaranth (AR), Reactive Blue 4 (RB4) and Reactive Orange 13 (RO13) from its aqueous solution. FTIR analysis suggested that -OH and Si-O groups of rice husk and -SO3H groups of dyes are mainly involved in removal process. The amount of dye sorbed was found to vary with pH and temperature. The amount of dye uptake (µmol/g) was found to increase with increase with solution temperature. The results demonstrate that the removal system studied belongs to the second-order kinetic model, based on the assumption that the rate-limiting step may be chemical removal. Thermodynamic activation parameter shows that the process is endothermic. The negative value of the Gibbs energy change of the removal indicates that the removal is spontaneous. The positive value of the enthalpy change of the removal shows that the removal is an endothermic process. RL (Table-II) values show the removal process is favourable. Rice husk has a high potential to adsorb AR, RB4 and RO13 from aqueous solutions. Therefore, rice husk can be effectively used as an adsorbent for the removal of the used dyes from waste waters.

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