COMPARATIVE ADSORPTION STUDY ON RICE HUSK AND RICE HUSK ASH BY USING AMARANTHUS GANGETICUS PIGMENTS AS DYE

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Abstract

Low cost adsorbents such as Rice Husk (RH) and Rice Husk Ash (RHA) were used for removing dyes from aqueous medium and later Linear, Langmuir and Freundlichadsorption isotherms have been verified by using adsorption data. RH was activated by treating with nitric acid and RHA wasprepared from RH by dolomite process. Natural dyes were extracted from the vegetable *Amaranthus gangeticus* by using a standard method.The removal efficiency of adsorbents was measured for the variation of parameters pH, contact time and adsorbents concentration. It has been noted that after changing time for same amount of adsorbent (1g/100ml) and dyes (10 ml) RH gave no efficiency trend but increased to 43.91% whereas for RHA efficiency was gradually increased to 59.62%. A reverse trend was noted when adsorption amounts were changed and others were put constant where RHA efficiency gradually increased to 99.30% but RH gave no trend with highest efficiency was close to 61.85%. The RH removal efficiency was good for pH 11 close to 62.86% and it was continuous from 3.95% at pH 2. Alternately, RHA gave 80.21% at pH 2 and later was decreased to 1.5% at pH 9 and again increased from pH 11. It is noted that RHA removal efficiency is better than RH and adsorptions are well fitted with isotherms.

Keywords: RHA, Spectrometer, Dyes, Isotherms, Adsorption

Introduction

Water pollution is a serious problem in some developing countries due irrational discarding of dying industries' effluents without any treatment into nearby aquatic system and this is now concerning a great majority of countries for getting ways how to prevent it. However, although a wide variety of research is going on how to remove the dyes from the waste water by using numerous low cost materials. The compounds cause serious harm to aquatic life (Gomez, 2007) and most of the dyes have complex aromatic structure and are difficult to biodegrade (Gonga, 2005). Among the various traditional water treatment methods for removing dyes from waste water, such as adsorption, ion exchange, reverse osmosis, ultra-filtration and chemical degradation etc (Bishnoi, 2004). Adsorption is a very popular and widely applied technique for removing non-biodegradable dyes ((Iqbal, 2007), (Ying, 2009)). There are many adsorbents available commercially such as activated carbon, bentonite (Vispasiriv, 2009), sepiolite, ((Gaurses, 2004), (Alkan, 2007)), zeolite, kaolin, hair and coal (Mckay, 1999), sewage sludge based activated carbon (Rozada, 2003), apple pomace and wheat straw (Robinson, 2002), banana and orange peel (Annadurai, 2002), pearl millet husk (Inbanaj, 2002), peat particles (Poots, 1976), wood (Poots, 1978), fly ash and coal (Gupta, 1990). But, activated carbon shows the good adsorption characteristics towards all types of dyes because of its large surface area and micro-porous nature. On the other hand, activated alumina exhibits good adsorption capacity for basic dye malachite green (Kannan, 2008) and the surfactant-modified alumina is used for the removal of crystal violet from water (Chao, 2005). But, the widespread use of activated carbon is restricted due to its high cost ((Venkata, 1997),(Morais, 1999)). According to one estimate up to 50% of the unused dyes may be directly lost into waterways after using reactive dyes (McMullan, 2001). The anaerobic break down of some dyes occurs in the sediments and their incomplete bacterial degradation often produces toxic materials (Weber, 1987). Recently, removing of dyes by using different adsorbents such as rice husk is becoming popular because it has many advantages such as its granular structure, chemical stability and its local availability at very low cost and they need not regenerate again due to their low production cost and affluence. The main constituents of rice husk are 64-74% volatile matters and 12-16% fixed carbon and 15-20% ash (Armesto, 2002). Practically an adsorbent needs to have some potential characteristics for acting as a good adsorbent such as (a) a large accessible pore volume (b) hydrophobicity (c) high thermal and hydro thermal stability (d) catalytic activity and (e) easy regeneration. However, the use of these materials is still limited, although they show good adsorptopn capacity, relative to that of the others expensive treatment processes (Malik, 2003). Hence, the purpose of this work is to investigate the adsorption of mixture of dyes which were extracted from natural resource like the vegetable *amaranthus gangeticus* and its pigments were adsorbed by using RH and RHA as adsorbent. This adsorption will help to remove the synthetic dyes from dying industries' effluents, which are also a mixture of profuse amount of synthetic dyes, are being discarded into water bodies without any treatment for reducing production cost and making a large amount of profit illegally. Finally, the Linear, Langmuir and Fraundlinch adsorption isotherms were fitted to understand the equilibrium condition of adsorptions.

Materials and Methods

Collection and Preparation of Adsorbents

Rice husk (RH) was collected from Jesmin rice mill is situated at kagmari in Tangail district. It was screened and washed with water to remove all dirt's and later, these were dried by sunlight. The dried rice husk was soaked in 2.0 mol/L of nitric acid for an hour. It was then rinsed with distilled water for 2-3 times and oven dried at 105°C for 2 hours. The oven dried rice husk was ground and sieved through BSS-30 mesh size particle. The name given to the adsorbent was rice husk (RH). Another adsorbent rice husk ash (RHA) was prepared by dolomite ((Regaraj, 1999), (Biswas, 2013)) processes heating at 500^oC for 3h directly. Later, RHA was collected close to ~ 0.5mm.

Preparation of dye solution

The vegetable *amaranthus gangeticus* (Figure 1) was collected from local market and to extract dyes 400g sample was collected (leaves and stems). Later, the collecting was washed to remove dirt particles and dyes were prepared ((Gins, 2002), (Khan, 2004)) and stocked for the experiment. Amaranthus is a mixture of 5-O-glucuroindoglucodides of two aglycons: Betanidin and Iso-betanidin. The Iso-betanidin is the C_{15} epimer of Betanidin. They are referred to as Amaranthine and Isoamaranthine (Figure 2) absorbed at maximum 515-537 nm. The empirical formula is $C_{29}H_{31}N_2O_{19}$ and molecular weight is 711.

Figure 1: The plant *Amaranthus Gangeticus*.

Apparatus

It was used Perkin-Elmer UV-Visible Spectrometer, Model: Lambda 25, Origin: Singapore for the measurement of adsorption. To fit desire pH Adwa, Model: AD 1000, Range: -2.00 to + 16.00, Temp: -20.0^oC to + 120.0^oC, Origin: Hungary was used and A Stuart orbital shaker, Model: SSL1, Range: 30-300 rpm, Temp: + 4^oC to + 40^oC, Origin: UK was used during conduction of research.

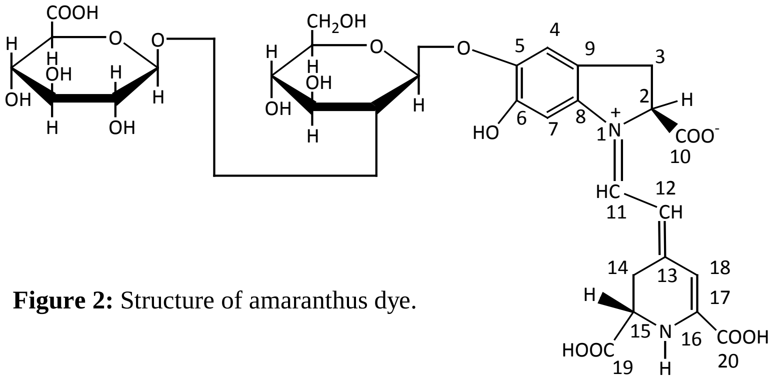


Figure 2: Structure of amaranthus dye.

Experiment

Six sample solutions were prepared for both RH and RHA according to Table 1and Table 2 and each bottle held total 100 ml solution, where 1g adsorbent, 10 ml extracted amaranth dyes and 90 ml distilled water were present. The resulting solutions were shaken at 250 revolutions per minute (rpm) by using an orbital shaker machine. After completing their respective time intervals solutions were filtered by using ashless filter papers (Whatmann No. 40). The absorbance was measure with the help of the spectrophotometer in between 200-800 nm and later only single absorbance was taken for each solution at 525 nm. The dyes concentrations were measured by using the equation (1) where, l and ε was taken unity for simplicity. Same procedure was followed for the Table 3, Table 4, Table 5 and Table 6. But, those all were shaken for 2h at 250 rpm and to change pH standard solution of 1M, 0.1M, 0.01M and 0.001M NaOH and HNO_3 were used. Spectrometric absorbance for each sample was taken immediately for having good result. Table 1 and Table 2 were used to establish Linear but Table 3 and Table 4 were used to constitute Langmuir and Freundlich adsorption isotherms and equation (2), equation (3) and equation (4) were used for their respective calculations respectively. Adsorption tests were performed at temperature 29°C ±2. The removal efficiency was calculated by using the formula: % Removal efficiency = $(C_i\text{-}C_f)/\ C_f \times 100$ Where, C_i is the initial concentration of amaranthus pigment in solution and C_f is final concentration of amaranthus Pigment in solution. The isotherms used in this study were:

i. Beer-Lambert law,

$$A = \varepsilon c l$$

When, $\varepsilon = l = 1$, Then, A = c ……. …… ……. (1)

Where, A = Absorbance, l = Path length, c = Dyes concentration in solution and ε = Extinction coefficient.

ii. Linear Adsorption Isotherm

$C_i\text{-}C_f = Kt$ …….. ……. …….. (2)

Where, C_i is the initial concentration of amaranthus pigments in solution, C_f is the final concentration of Amaranthus Pigments present in the solution after adsorption and K is the equiliblium constant. For Linear adsorption isotherm, graphs of $(C_i\text{-}C_f)$ vst were plotted by using data from Table 1 and Table 2.

iii. Langmuir Adsorption Isotherm

$\frac{C_f}{C_i - C_f} = (b/a)\, C_a + (1/a)$ ……. ……. ……. (3)

Where, $(C_i\text{-}\ C_f)$ is the amount of amaranthus dyes adsorbed per unit weight of adsorbent, C_i and C_f are the initial and final concentration of Amaranthus pigment in liquid phaserespectively. C_a is the amount of adsorbent used. Inthe case of Langmuir adsorption isotherm, graphs of $C_f/(C_i\text{-}\ C_f)$ vs C_a were plotted. The C_i and C_f values were taken from Table 3 and Table 4.

iv. Freundlich Adsorption Isotherm

$\log (C_i\text{-}C_f) = (l/n) \log C_a + \log K_f$ …….. …….. …… (4)

Here, K_f is the equilibrium constant. For Freundlich isotherm, graphs of log (C_i-C_f) vslog C_a were plotted. The adsorption isotherms were tried to fit to the experimental adsorption data from Table 3 and Table 4. Linear regression analysis was conducted to determine the goodness of fitting for all the different types of adsorption isotherms. Based on the R-square values, the isotherms explain the experimental adsorption data are well fitted with the experiment.

Results and Discussions

Effect of different contact times

Table 1 and Table 2 are shown for 10 ml dyes, 1g adsorbent and it is observed that the RH does not give any good efficiency trend but removal efficiency increases from initial 5.12% (10 min) to final 43.91% (240 min). The removal efficiency increases with increasing in contact time for RHA, where maximum efficiency for 240 min (59.62%) and minimum adsorption at time 10 min (2.72%).

Table 1: Optimum contact time of Rice Husk (RH) for 1g adsorbent

Time (t) min	Initial concentration of dyes C_i (mg/l)	Final concentration of dyes C_f (mg/l)	Amount of dyes adsorbed C_i-C_f (mg/l)	(C_i-C_f)/C_f	Removal efficiency, η = {(C_i-C_f)/C_f}100
10	3.90	3.71	0.19	0.0512	5.12
20	3.90	3.72	0.18	0.0484	4.84
40	3.90	3.56	0.34	0.0955	9.55
60	3.90	3.55	0.35	0.0986	9.86
120	3.90	3.01	0.89	0.2957	29.57
240	3.90	2.71	1.19	0.4391	43.91

Table 2: Optimum contact time of Rice Husk Ash (RHA) for 1g adsorbent

Time (t) min	Initial concentration of dyes C_i (mg/l)	Final concentration of dyes C_f (mg/l)	Amount of dyes adsorbed C_i-C_f (mg/l)	(C_i-C_f)/C_f	Removal efficiency, η = {(C_i-C_f)/C_f}100
10	3.40	3.31	0.09	0.0272	2.72
20	3.40	3.21	0.19	0.0592	5.92
40	3.40	2.95	0.45	0.1525	15.25
60	3.40	2.82	0.58	0.2057	20.57
120	3.40	2.48	0.92	0.3710	37.10
240	3.40	2.13	1.27	0.5962	59.62

For different adsorbents

From Table 3 and Table 4 it is observed that for 10 ml of amaranthus pigment with different adsorbent doses the removal efficiency increases with increasing in adsorbent doses for RHA. At adsorbent dose 2.5g efficiency is

14.00% but at the highest dose 40g the efficiency is 99.30%. Alternately, for the RH with changing adsorbents doses no good efficiency is noted but removal efficiency increases from 11.11% (2.5g) to 61.85% (40g).

Table 3: Optimum adsorbent dose of Rice Husk (RH) for shaking 2h at 250 rpm

Adsorbent dose C_a (g)	Initial concentration of dyes C_i (mg/l)	Final concentration of dyes C_f (mg/l)	Amount of dyes adsorbed C_i-C_f (mg/l)	$(C_i-C_f)/C_f$	Removal efficiency, η = $\{(C_i- C_f)/C_f\}100$
2.5	2.80	2.52	0.28	0.1111	11.11
5.0	2.80	2.41	0.39	0.1618	16.18
10	2.80	2.32	0.48	0.2069	20.69
20	2.80	2.15	0.65	0.3023	30.23
40	2.80	1.73	1.07	0.6185	61.85

Table 4: Optimum Adsorbent dose of Rice Husk Ash (RHA) for shaking 2h at 250 rpm.

Adsorbent dose C_a (g)	Initial concentration of dyes C_i (mg/l)	Final concentration of dyes C_f (mg/l)	Amount of dyes adsorbed C_i-C_f (mg/l)	$(C_i-C_f)/C_f$	Removal efficiency, η = $\{(C_i-C_f)/C_f\}100$
2.5	2.85	2.50	0.35	0.1400	14.00
5.0	2.85	2.26	0.59	0.2611	26.11
10	2.85	1.95	0.90	0.4615	46.15
20	2.85	1.52	1.33	0.8750	87.50
40	2.85	1.43	1.42	0.9930	99.30

Effect of pH

The Table 5 shows that as pH increases the removal efficiency increases for RH from 3.95% to 62.86%. Conversely, for the RHA at pH 2 removal efficiency is highest close to 80. 21%. Later, removal efficiency is decreased from 44.02% (pH 3) to 1.51% (pH 9) and again it is increased at pH 11 that is close to 26.22%. Thus, after considering only 10 ml of amaranthine pigments RH efficiency is highest at higher pH 11 (62.86%) but RHA efficiency is only 26.22% at the same pH. Moreover, at lower pH 2 the RH efficiency only 3.95% but the efficiency of RHA remarkable increases 80.21% at the same pH. So, RHA is more suitable for removing dyes from textile effluents than RH.

Table 5: Optimum pH for adsorbent Rice Husk (RH) for shaking 2h at 250 rpm.

pH	Initial concentration of dyes C_i (mg/l)	Final concentration of dyes C_f (mg/l)	Amount of dyes adsorbed C_i-C_f (mg/l)	$(C_i-C_f)/C_f$	Removal efficiency, η = $\{(C_i- C_f)/C_f\}100$
2	3.42	3.29	0.13	0.0395	3.95
3	3.42	3.21	0.21	0.0654	6.54
5	3.42	2.99	0.43	0.1438	14.38
7	3.42	2.68	0.74	0.2761	27.61
9	3.42	2.50	0.92	0.3680	36.80
11	3.42	2.10	1.32	0.6286	62.86

Table 6: Optimum p^H for adsorbent Rice Husk Ash (RHA) for shaking 2h at 250 rpm.

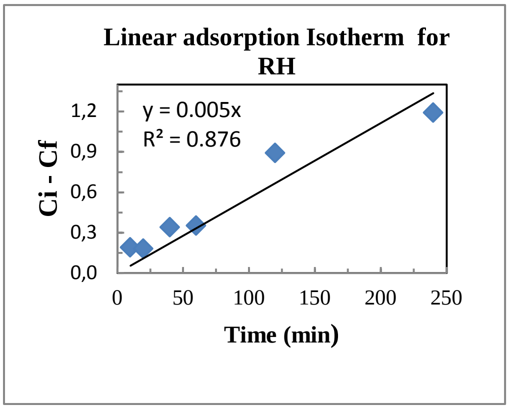
pH	Initial concentration of dyes C_i (mg/l)	Final concentration of dyes C_f (mg/l)	Amount of dyes adsorbed C_i-C_f (mg/l)	$(C_i-C_f)/C_f$	Removal efficiency, $\eta = \{(C_i-C_f)/C_f\}100$
2	3.37	1.87	1.50	0.8021	80.21
3	3.37	2.34	1.03	0.4402	44.02
5	3.37	3.03	0.34	0.1122	11.22
7	3.37	3.32	0.05	0.0151	1.51
9	3.37	3.32	0.05	0.0151	1.51
11	3.37	2.67	0.70	0.2622	26.22

Application of adsorption isotherm

The linear regression is performed and used to determine whether the isotherms are fitted with experimental adsorption data or not by knowing the R-square values. The R-square values, which are close to 1, are clearly indicating that all isotherms are matched with the experimental data.

Linear Adsorption Isotherm

By using the Table 1 and Table 2 and after suitable calculation from the equation (2) Linear adsorption isotherms are plotted and shown in the figure 3, where R-square values are 0.876 for RH and 0.833 for RHA. The isotherms are fitted well with the experimental data. The equilibrium constant values are 0.005 and 0.006 for RH and RHA, respectively.



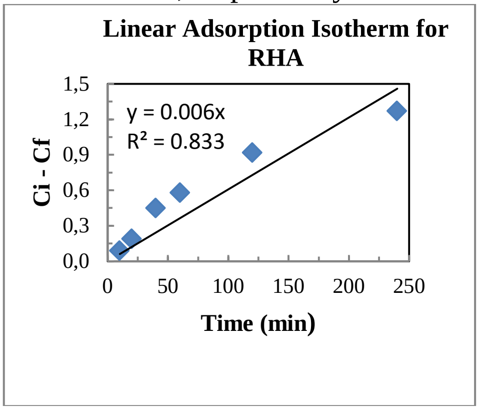


Figure 3: Linear adsorption isotherms of amranthus dyes for RH and RHA.

Freundlich Adsorption Isotherm

Figure 4 is showing Freundlich adsorption isotherms for RH and RHA where R square values are 0.977 and 0.948, respectively. These isotherms are also fitted well with the experimental data in Table 3 and Table 4. According to equation (4) the equilibrium constants are 0.13 and 0.07 for

RH and the RHA, respectively, where values of *n* are 2.17 for RH and 0.55 for RHA.

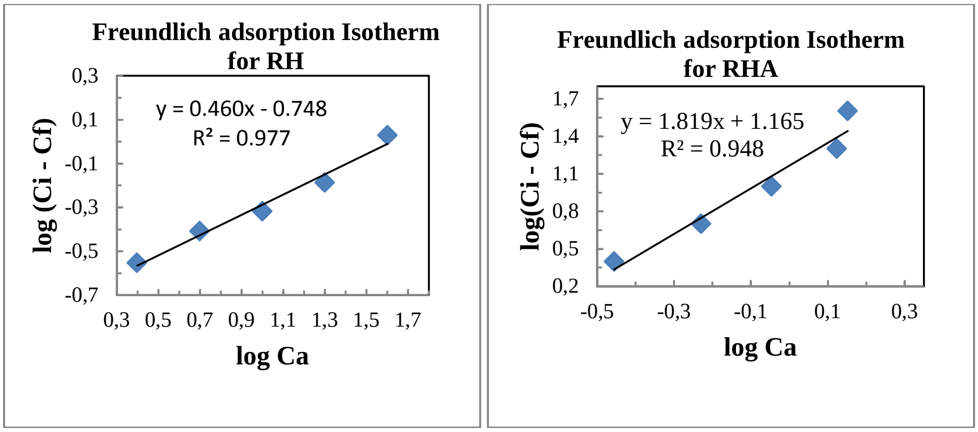


Figure 4: Freundlich adsorption isotherm of amranthus dyes for RH and RHA.

Langmuir Adsorption Isotherm

It is shown the Langmuir adsorption isotherms in figure 5 where R-square values are 0.803 for RH and 0.820 for RHA. Table 3 and Table 4 are used for sketching the isotherms and suitable calculations are done by using the equation (3). The values of Langmuir constants *a* and *b* are calculated and these are -0.03 and -0.12 for RH. Similarly, the RHA shows constants values are -0.04 and -0.16 respectively.

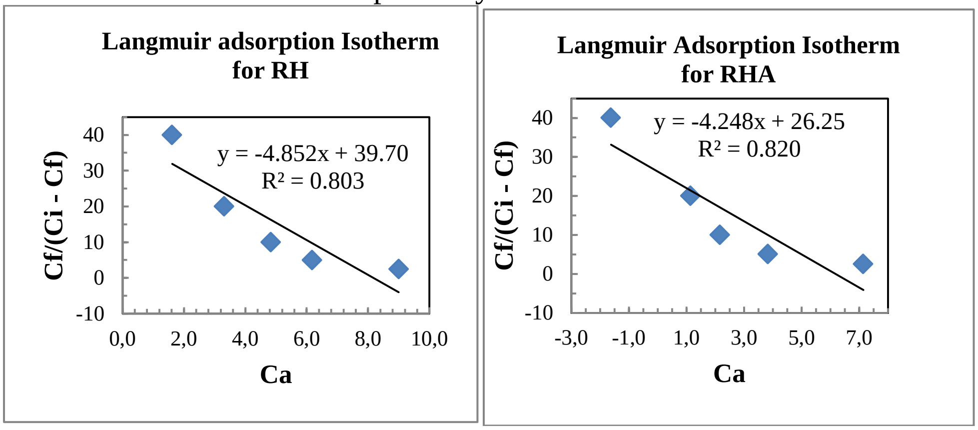


Figure 5: Langmuir adsorption isotherm of amranthus dyes for RH and RHA.

Conclusion

The result of the present study is clearly showing that acid treated both RH and RHA are effective for removing dyes from aqueous solution and the RHA is more effective than RH. In addition to that, the effectiveness increases when it is increased the contact time and the amount of adsorbents until the equilibrium is established. The adsorption isotherms and R-square values are good fit with the experimental data. So, such type of adsorbents is economically good for the removal of dyes from industries' effluents.

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