REMOVAL OF A BASIC DYE FROM AQUEOUS SOLUTION BY ADSORPTION USING RICE HULLS

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ABSTRACT

The removal of dyes from colored effluents, particularly from textile industries, is one of the major environmental concerns these days. Current methods for removing dyes from wastewaters are costly and cannot effectively be used to treat wide range of such wastewaters. This work describes the use of grounded rice hull as adsorbent material. Aqueous solutions of various methylene blue dye concentrations (5-25 mg l^{-1}) were shaken with certain amount of adsorbents to determine the adsorption capacity. Both treated and untreated rice hulls were used for methylene blue adsorption. The effects of adsorbents dose, initial pH, initial dye concentration and contact time on dye removal have been studied. Maximum dye was sequestered from the solution within 60-90 min after the beginning of every experiment. The adsorption capacity increased from 72 to 94 % with increasing the pH from 3 to 10. Pretreatment of rice hulls with citric acid did not reveal any beneficial effect. Rice hulls were more effective compared to commercial used adsorbents used. The results showed that ground rice hulls can be considered as potential adsorbents for methylene blue removal from dilute aqueous solutions.

KEYWORDS: Bioadsorbent, Rice Hulls, Methylene blue, Agriculture waste.

1. INTRODUCTION

Dyes and pigments are one of the problematic groups of pollutants. They are discharged from various industries such as dyestuff manufacturing, dyeing, printing, and textile finishing. Most of the dyes are stable against photo degradation, bio-degradation, and oxidizing agents (Ramakrishna and Viraraghavan, 1997). Several methods have been used for the removal of dyes from the aquatic environment, including physical, chemical, and biological processes. Among these methods, adsorption is a widely used for dye removal from wastewaters (Bhattacharyya and Sharma, 2005). Lignocellulosic agricultural waste materials such as rice hulls, sugarcane bagasse, and wheat straw are now regarded as abundant, inexpensive, and readily available natural resources for chemical and paper industries (Theander and Aman, 1979; Gould, 1984.). Today's, the world's industry is utilizing less than 10 % of biomass from plantations (Pauli *and* Gravitis, 1997). In Egypt, approximately 16 million tons of agricultural residues (AR) are currently disposed of every year the annual amount of rice hulls is about 3.6 million tones/year and many types of abundant AR especially from tropical plantations are waiting for effective utilization. AR are the most abundant renewable organic resource on the earth. AR have been utilized as renewable resources of energy and production of a diversity of chemicals, including ethanol (Ikeuchi *et al.*, 1999), activated carbon (Namasivayan and Kadivelu, 1999), ion exchangers (Šimkovic and Laszlo, 1997). Many others application for AR are in the process of being developed. Annual world rice production is about 577 million metric tons (Kiran *et al.*, 2000). The rice hulls which are discharged in large quantities at rice processing facilities or country elevators in rice cropping regions are utilized as farmyard compost, mulch and drainage materials, but the recycling rate of the rice hulls is about 10.0% (Woon *et al.*, 2006). However, many countries have imposed new regulations to

restrict field burning of rice hulls in response to restrictions on carbon emission due to global warning. This has helped simulate interest in the utilization of rice waste as a renewable natural resource. Various techniques have been employed for the removal of dyes from wastewaters (Choy *et al.*, 1999; Gupta and Bhattacharya, 1985; Khattri and Singh, 2000; Kun-She *et al.*, 2000; Liversidge *et al.*, 1997; McKay *et al.*, 1985; Mittal and Gupta, 1996; Perineau *et al.*, 1982; Singh *et al.*, 1984). Conventional physical and chemical methods are either costly, e.g. activated carbon, or produce concentrated sludge, e.g. Fenton's reagent, or may not be capable of treating large volumes of effluent without the risk of clogging, e.g. membrane filtration (Chuah *et al.*, 2005). Natural materials that are available in large quantities, or certain waste product from industrial or agricultural processes, may have potential as inexpensive adsorbents. Rice hulls, an agricultural waste, have been reported as a good adsorbent of heavy metals. (Suemitsu *et al.*, 1986; Marshall *et al.*, 1993) The focus of the research is to evaluate the adsorption capacity of treated and untreated rice hulls for the adsorption of methylene blue dye from aqueous solutions. Methylene blue is the most commonly used material for dying cotton, wood and silk. Methylene blue was chosen because of its known strong adsorption onto solids and it serve as a model compound for removing organic contaminants and colored bodies.

2. EXPERIMENTAL
2.1. Materials
Rice hulls were used as precursor material of adsorbents. Rice hulls were obtained from local rice mills (Behra city-Egypt). The methylene blue dye (molecular formula: $C_{16}H_{18}N_3ClS$, λ_{max}= 655nm) used in this study was obtained from (Nice chemicals Pvt.Ltd).
Commercial adsorbents were also used for comparison (Table 1).

Table 1. Types of commercial adsorbents used

Adsorbent type	Source	Composition	Appearance	Color	Specifications
1-Adsorb-it Filtration Fabric	Eco-Tec, Inc, U.S.A.	A geo- textile quality non-woven filtration fabric manufactured from 100% recycled select fibers from the textile industry	Thin sheet, no odor	White gray	thickness 3.73 mm
2-Adsorb-it/AM Antimicrobial Filtration Fabric	Eco-Tec, Inc, U.S.A.	Fabric of Adsorb-it treated with a surface bonded non-leaching antimicrobial	Have two surfaces one is more rough than the other one, no odor, thin sheet	Dark gray	thickness 3.8 mm
3-Oil-Only sorbent	ARCUS Absorbents Inc, Toronto, Ontario Canada	It consists of a hydrophobic polypropylene product	light weight, flame resistant, non-toxic	White color	Available pad form with size 17″×19″×0.69″.

2.2. Preparation of adsorbent
Rice hulls were received grounded from local rice mills and then start to prepare samples.

Untreated rice hulls:
Rice hulls were washed four times with tap water, and then dried at 105 ^{O}C for 2h. The rice hulls were sieved to 250-500 μm, and used for the study.

Treated rice hulls:
Rice hulls were washed four times with tap water, and then dried at 105 ^{O}C for 2h. Soaking it for 2h in citric acid 0.6M at room temperature was applied to activate the rice hulls which were then

sieved to 250-500 μm. The acid- hulls slurry was dried over night at 50°C then the hulls were boiled at 100 ^{0}C for one hour and then washed with distilled water (200 ml g^{-1} of hulls) to remove any excess of citric acid followed by overnight drying at 105 ^{O}C.

2.3. Preparation of dye solution
A stock solution of the dye was prepared by dissolving 1.0 g of dye in 1000 ml distilled water to make a stock solution of 1000 mg l^{-1}. The experimental solution was prepared by diluting definite volume of the stock solution to get the desired concentration. For absorbance measurements a spectrometer UV-VIS double beam PC scanning (Lambomed. INC) was employed, the rice hulls was gravity separation before sampling .The maximum wavelength λ $_{max}$ for the methylene blue was measured at 655 nm. Concentrations during experimental work were determined from a standard calibration curve.

2.4. Adsorption Studies
Equilibrium adsorption isotherms using raw and treated rice hulls with different amount (5, 10, 15 g l^{-1}) were determined at agitation rate of 150 rpm, room temperature (26+1 ^{o}C) and with different concentrations of dye (5 - 25 mg l^{-1}). Adsorbent dosage (based on dry weight of rice hulls) was placed in a set of 100 ml beaker and different initial dye concentrations were added to each beaker. The contents were shaken for 2 hours the solution was analyzed for dye contents. The adsorption behaviors of the samples were studied by evaluating the percentage removal efficiency of methylene blue, calculated as

Removal efficiency = [(C_0 – C)/ C_0] × 100

Where C_0 is the initial concentration of methylene blue, C is the solution concentration after adsorption at any time. The effect of adsorption time on the dye removal at various predetermined intervals from (10-120 min) using spectrometer UV-VIS double beam PC scanning for measurement of concentration at λ $_{max}$= 655 nm was monitored by shaking the reaction mixture and analyzed for the dye content at the end of each contact time.

2.5. Equilibrium studies

The amount of adsorption for untreated and treated rice hulls, q_e (mg g^{-1}), was calculated by

q_e = (C_0 - C_e) V / W

where C_0 and C_e (mg l^{-1}) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (l) and W is the mass of dry sorbent used (g).

3. RESULT AND DISCUSSION
Dyes are widely used in industries such as textiles, rubber, paper, plastic, cosmetics, etc. to color these products and the dyes invariably remain important source of pollution. Many of the organic dyes are hazardous and may affect aquatic life. The removal of dyes from wastewater is an essential task for environmental protection so various techniques have been employed for removal of dyes from wastewater. Natural materials or certain waste product from agricultural operations may have potential as inexpensive adsorbents, due to their low cost, while they can be disposed of without expensive regeneration.

3.1. Effect of adsorbent mass
The effect of adsorbent amount on the uptake of the dye was measured for dye concentration 10 mg l^{-1} , different shaking time (10-240 min) and different quantity of rice hulls (5,10, and 15 g) at pH 7 and room temperature (26 ±1 ºC).(Figure 1a, b). In general, it was found that by increasing the amount of the adsorbent the adsorption rate increased. This increase was most significant when the amount of adsorbent increased from (5-15 g l^{-1}). Maximum dye removal was achieved within 60-90 minutes after which a decrease in methylene blue concentration was negligible. Increase in dye removal percentage with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. At the beginning of the process the rate of dye removal by the rice hulls was fast during the first 30 min and then decreased gradually.
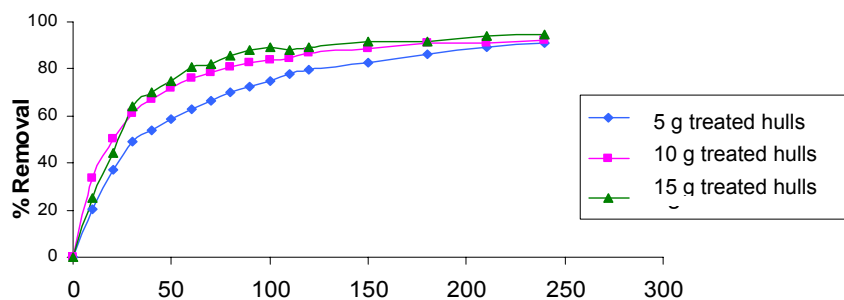
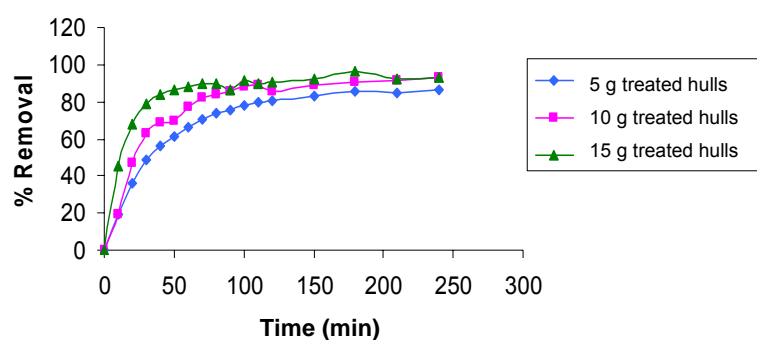*Figure 1a.* Effect of amount of untreated rice hulls on the removal of dye

Figure 1b. Effect of amount of treated rice hulls on dye removal

3.2. Comparison of treated and untreated rice hulls

The effect of treating the rice hulls was studied at fixed adsorbent dose 10 g hulls, temperature (26 ±1 ℃) , with initial concentration of methylene blue 10 mg l^{-1} and pH neutral for different time intervals. It is evident from Figure 2 that the adsorption of the dye with treated hulls was higher than the untreated and equilibrium was established in about 90 min.
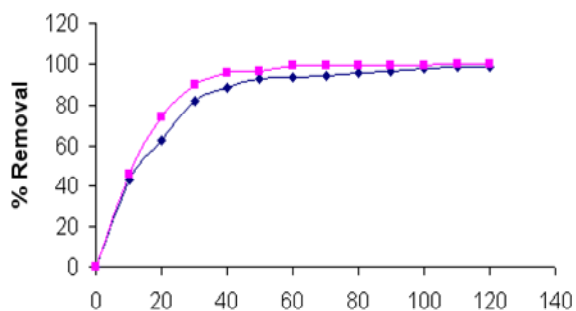

Figure 2. Effect of chemical treatment of rice hulls on methylene blue adsorption

3.3. Effect of initial dye concentration

The influence of the initial concentration of methylene blue (5-25 mg l^{-1}) on the adsorption rate using untreated and treated rice hulls was studied. The experiments were carried out at fixed adsorbent dose (10 g), at room temperature (26 ±1 ℃), neutral pH (7.0) for 30 min.

Dye removed by treated and untreated rice hulls were about 90% after 30 min. The removal efficiency of the two adsorbents decreased with increasing initial dye concentration. Table 2 shows that the percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of adsorbent increased with increase in dye concentration in the test solution for different concentrations (5-25 mg l^{-1}) at the same time (min).

Table 2. Effect of methylene blue concentration on dye adsorption

Initial dye concentration (mg l⁻¹)	Percent dye removal with time(min)					
	10	20	30	40	50	60
Untreated rice straw						
5	65.46	80.22	82.86	98.23	90.2	98.84
10	42.9	62.18	82.1	88.23	92.9	98.59
15	41.97	53.57	67.63	74.84	80.19	86.38
20	41.16	58.82	70.185	75.23	79.69	85.37
25	38.67	56.96	62.98	66.23	66.99	72
Treated rice straw						
5	81.1	85.2	89.98	96.35	98.8	98.97
10	46.2	73.9	89.85	95.7	96.25	97.8
15	36.63	65.89	78.57	80.01	86.32	90.65
20	29.04	48.46	68.92	73.43	78.25	80.22
25	32.01	54.51	71.28	75.60	78.06	79.34

The unit adsorption for untreated rice hulls increased from 0.41 mg g⁻¹ to 1.57 mg g⁻¹ as the methylene blue concentration in the test solution was increased from 5 to 25 mg l⁻¹. Similarly, unit adsorption for treated rice hulls increased from 0.45 mg g⁻¹ to 1.78 mg g⁻¹ as the methylene blue concentration in the test solution increased from 5 to 25 mg l⁻¹. Maximum dye was sequestered from the solution within 15 min (30 or 90 as previously) after the beginning for every experiment. Thereafter, the decrease of methylene blue concentration was negligible.

3.4. Effect of pH

The pH value of the solution is an important parameter for the adsorption processes, and the initial pH value of the solution has significant influence compared to than the final pH (Hem *et al.*, 2007). To study the effect of pH on methylene blue adsorption, the experiments were carried out at 10 mg l⁻¹ initial dye concentration with 10 g l⁻¹ adsorbent dosage at (26 ±1 ºC). In general, initial pH value may enhance or depress the uptake. This is attributed to the charge of the adsorbent surface with the change in pH value. Figure 3 shows the relationship between the pH value and the removal of methylene blue. It can seen from the figure that as the solution pH increases, the adsorption capacity increases. Increasing solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites and enlarges the attraction between dye and adsorbent surface' (Lai and Chen, 2001). Generally, the net positive charge decreases with increasing pH value lead in the decrease in the repulsion between the adsorbent surface and the dye thus, improving the adsorption capacity.
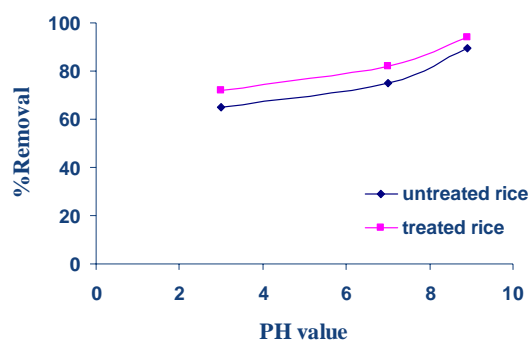

Figure 3. Effect of pH on methylene blue adsorption

3.5. Isotherm analysis

The purpose of the adsorption isotherms is to relate the adsorbent concentration in the bulk solution and the adsorbed amount at the interface (Eastoe and Dalton, 2000). The equilibrium isotherms in this study have been described in terms of Freundlich isotherms.

The Freundlich isotherm (Freundlich, 1906) is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the

concentration of methylene blue dye at equilibrium. A linear form of the Freundlich equation is generally expressed as follows:

$$\ln q_e = \ln K_F + (1/n) \ln C_e$$

where K_F (mg g^{-1} (l mg)$^{-1/n}$) is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption condition (Treybal, 1968). The plot of ln q_e versus ln C_e (Fig. 4-5) is employed to evaluate the intercept K_F and the slope $1/n$. The values of K_F, n and the linear regression correlation (R^2) for Freundlich are given in Table 3.
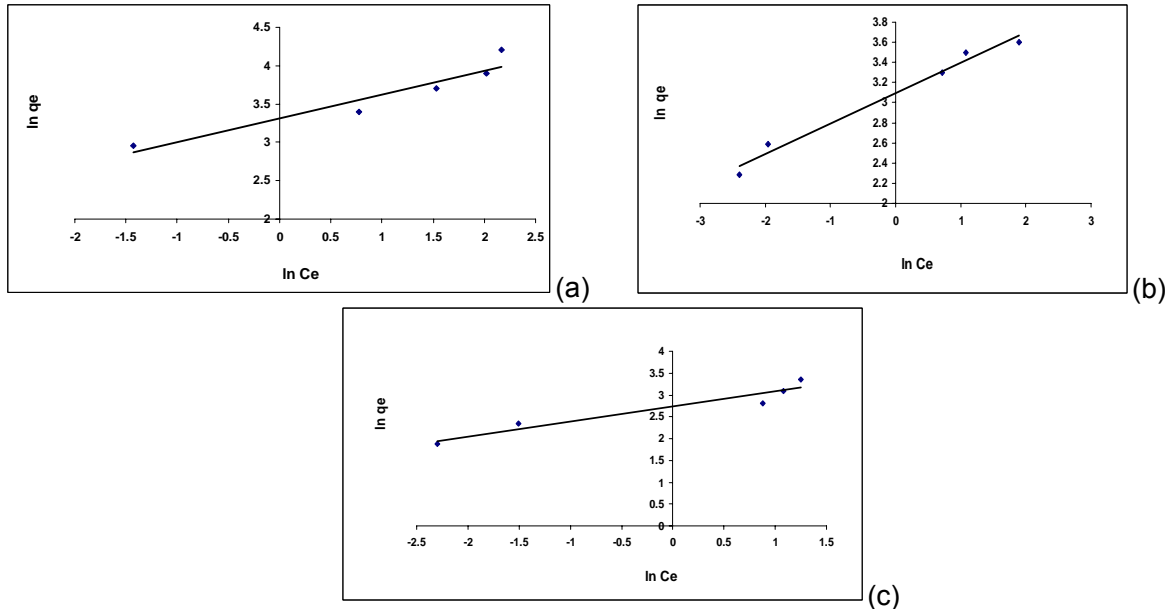

(a)

(b)

(c)

Figure 4. Freundlich isotherm of methylene blue adsorption onto untreated rice hulls
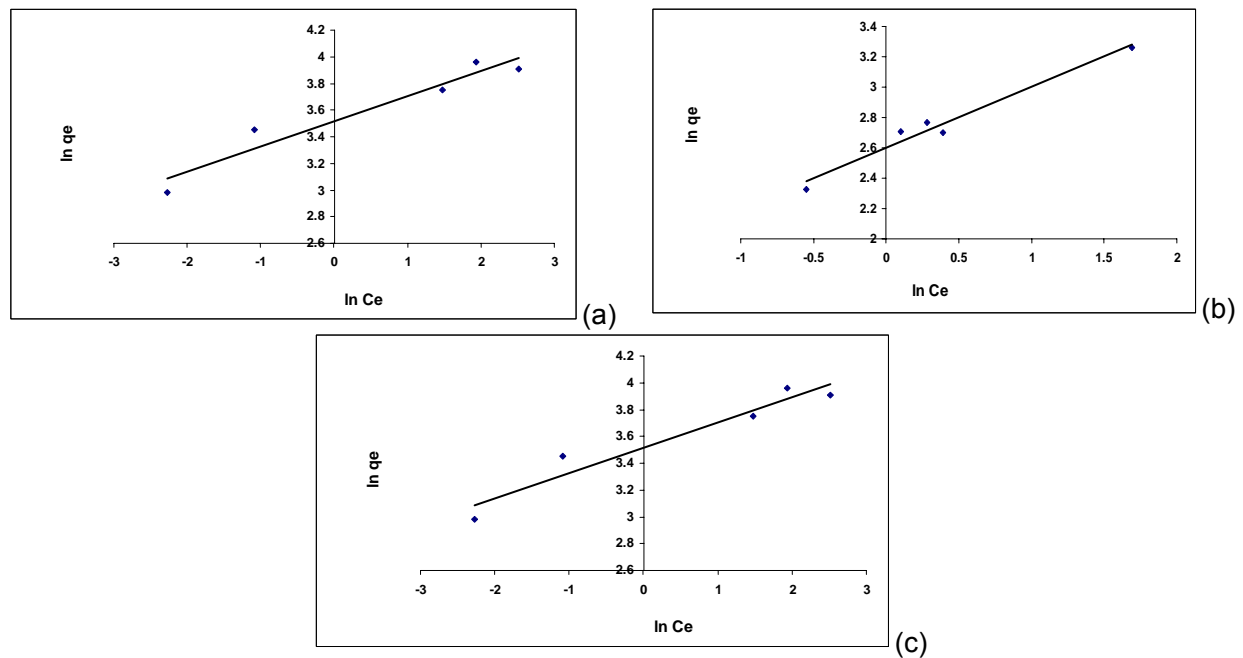(a) 5 g, (b) 10 g, (c) 15 g

(a)

(b)

(c)

Figure 5. Freundlich isotherm of methylene blue adsorption onto treated rice hulls
(a) 5 g, (b) 10 g, (c) 15 g

Table 3. Isotherm parameters for removal of methylene blue by untreated and treated rice hulls

Isotherm	Parameters	
	Untreated rice hulls	**Treated rice hulls**
5g		
n	3.2	5.32
K_F	27.54	33.56
R^2	0.9075	0.9306
10 g		
n	3.32	4.67
K_F	22.1	15.5
R^2	0.9803	0.979
15g		
n	2.9	2.49
K_F	15.44	13.5
R^2	0.9167	0.9677

3.6. Comparison between the raw, treated rice hulls and commercial adsorbents

The adsorption of methylene blue onto three different commercial adsorbents (as these adsorbents are used in the market for other sorption processes as oil sorption, so we choose this commercial adsorbent to evident the availability of using these in dye removal and comparing with the rice hulls and it used in pad form contain granules of the adsorbent, using this types instead of using activated carbon because many researches interested in this type of adsorbent) , treated and untreated rice hulls was studied at fixed adsorbent quantity (10 g), temperature (26 ±1 ºC) and neutral pH for a 120 min period. It is evident from Figure (6) that the adsorption capacity of the treated and untreated rice hulls is higher compared to commercial adsorbents except for oil adsorbent which revealed higher percentage removal during the first 60 minutes and following this, the adsorption of rice hulls were almost equal, which confirm that this waste can be used as an adsorbent.
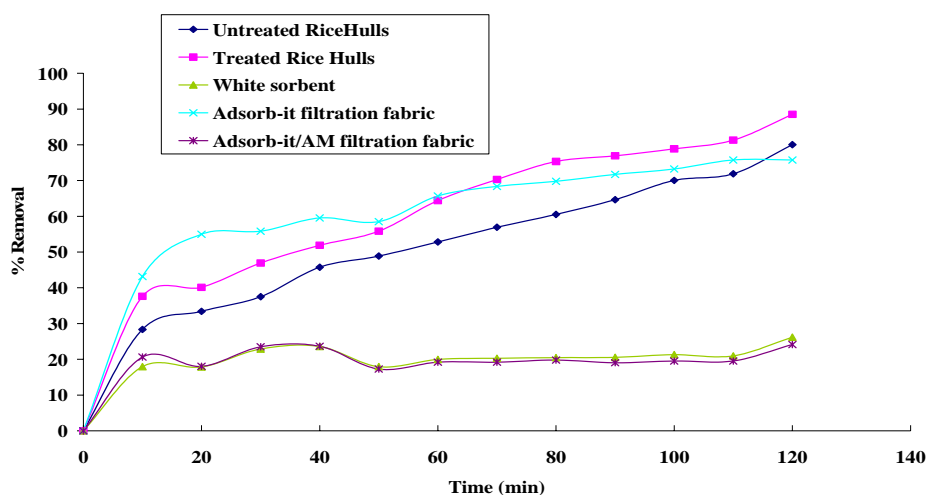

Figure 6. Comparison between commercial sorbents and rice hulls residue treated and untreated

3.7. Technology importance, separation technique and disposal

Natural fibers have little resistance towards environmental influences and show an intrinsic variability of their properties (Joseph *et al.,* 2002). Rice hulls were chosen to be applied as adsorbent material due to its fibrous structure, insolubility in water, chemical stability, high mechanical strength and its local availability at almost no cost. The advantage in the application of this waste is that there is no need to regenerate them because of their low production costs

(Daifullah *et al.*, 2003). Furthermore, separation of the rice hulls from the treated water is possible by a simple settling process. The rice husks which are discharged after dye removal can be used as insulating material (walls, floors or roofs) and for manufacture of particle boards.

4. CONCLUSIONS

Biosolid is a promising adsorbent for removal of the cationic dyes.The removal of methylene blue from wastewater using grounded rice hulls has been investigated under different experimental conditions in batch mode. The adsorption of dye was dependent on adsorbent dose and methylene blue concentration in wastewater. Initial pH of solution affected the adsorption of this dye. The optimum pH for the removal of methylene blue from aqueous solution under the experimental conditions used in this work was 10. Maximum dye removal was observed within 30 min from the beginning of each experiment. No pretreatment is necessary as sufficient dye removal is achieved by the untreated material. The present investigation showed that rice hulls can be effectively used as adsorbent comparable with the three commercial adsorbents used. Rice hulls are economically cheap and so regeneration is not necessary. Rice hulls are unwanted waste agriculture, would be useful for the economic treatment of dyeing effluent.

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