2012 3rd International Conference on Chemistry and Chemical Engineering
IPCBEE vol.38 (2012) © (2012) IACSIT Press, Singapore

Utilization of Chemically Modified Rice Hull for the Treatment of Industrial Wastewater

Siew-Teng Ong [1,2 +] and Weng-Nam Lee [3]

[1] Faculty of Science, [2] Centre for Biodiversity Research, Universiti Tunku Abdul Rahman, Jln Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia

[3] Department of Science, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Jln Genting Kelang, Setapak, 53300 Kuala Lumpur, Malaysia

Abstract. Effectiveness of using chemically modified rice hull (MRH) in the treatment of industrial wastewater was investigated. The optimised chemical modification process was preformed by treating 1.00 g of rice hull with 0.02 mol of ethylenediamine (EDA) in a "well stirred" water bath at 80 °C for two hours. Batch and column studies were performed under various experimental conditions and the parameters studied included pH, contact time and bed depth. The experimental results revealed that the optimum pH for the treatment of wastewater from textile industry was in the range of 2 to 5. Uptake of dye under both batch and continuous flow conditions shows similar behavior as in synthetic solutions.

Keywords: Wastewater; Dyes; Sorption; Batch Study; Column Study

1. Introduction

Colorants are characterized by their ability to absorb or emit light in the visible range (400-800 nm). The term colorant is frequently used to encompass both dyes and pigments. These two terms are often used indiscriminately; in particular, pigments are sometimes considered to be a group of dyes. Indeed, these two groups of colouring materials are quite similar chemically. However, they are distinctly different in their properties and especially in the way they are used. The major characteristic of pigments is their insolubility in the media in which they are applied, especially water. Pigments have to be attached to a substrate by means of additional compounds, e.g., polymers in paints, plastics, or melts.

In contrast to pigments, dyes are coloured substances that can be applied to various substrates (textile materials, leather, paper, hair) from a liquid in which they are completely, or at least partly, soluble. In other words, the substrate has a natural affinity for appropriate dyes and readily absorbs them from solutions or aqueous dispersion.

The usage of these dyes has continuously increased in many industries such as textile, paper, plastics and cosmetics [1]. It has been reported that approximately 10,000 different types of dyes and pigments are used in industries and over 7×10^5 tons of these dyes are being produced annually [2]. Effluents containing dyes from these industries show low level of biodegradability because of high molecular weight and complex chemical structures. Many dyes are difficult to degrade, as they are generally stable to light and oxidizing agents, and are resistant to aerobic digestion [3]. Hence, the presence of dyes even in trace quantities is very undesirable in aqueous environment.

The conventional treatment methods for color removal from industrial effluents are divided into three categories which include physical, biological and chemical [4]. For physical treatment, this normally includes filtration, ion exchange, adsorption and membrane process. As for biological treatment, it involves the usage of bacteria or microorganisms to decompose the waste while chemical treatments are often associated to the addition of oxidizing or reducing agents, coagulants and other chemicals.

+ Corresponding author. Tel.: +605-4688888; fax: +605-4661676
E-mail address: ongst_utar@yahoo.com, ongst@utar.edu.my

However, when biological and chemical treatments are being employed, the accumulation of concentrated sludge creates a disposal problem. The ultimate disposal of these wastes may be very expensive and indirectly increase the cost of treatment. As such, the application of adsorption techniques using low cost material can be seen as an attractive way to remove dyes from wastewater. It is hoped that information gathered in this research project will allow us to produce an economical and efficient sorbent material for wastewater treatment via chemical modification of an agricultural waste material, thus leading to a zero waste situation.

2. Materials and Methods

2.1. Sorbent

Rice hull was collected and washed several times to ensure the removal of dust and ash. It was subsequently rinsed several times with distilled water and dried overnight in an oven at 50 °C. The dried rice hull was ground to pass through a 1 mm sieve and labeled as natural rice hull (NRH). Modification of NRH was optimized by varying the treatment temperature and the ratio of NRH to EDA. Consequently ethylenediamine modified rice hull (MRH) was prepared by treating NRH with EDA in a ratio of 1.00 g rice hull to 0.02 mole of EDA in a well-stirred water bath at 80 ^{o}C for two hours.

2.2. Experimental

The study on the efficiency of MRH on the removal of colour from industrial wastewater was carried out using textile wastewater, obtained from a textile factory located in Kluang, Johor. This wastewater contained mainly reactive, vat and direct dyes. The wastewater was filtered using membrane filter, 22µm, before the experiments were carried out. The absorbance of the wastewater was analyzed using UV-vis spectrophotometer at λ_{max} of 486 nm.

2.2.1 Effect of pH

The effect of pH on the sorption efficiency of MRH in industrial wastewater was studied. The pH of the wastewater was adjusted to the range of 2 to 10 from its original pH, 11.5 by adding HCl. MRH (0.05 g) was shaken with 20 ml of wastewater. The mixture was equilibrated for four hours at 150 rpm.

2.2.2 Effect of Contact Time

Contact time experiments were performed using the wastewater with the pH adjusted to 5. MRH (0.05 g) was shaken with 20 ml of wastewater on orbital shaker at 150 rpm for predetermined durations (5, 10, 15, 30, 60, 120,180, 240, 300, 360, 420, 480 minutes).

2.2.3 Effect of Bed Depth

The column was packed with MRH to a height of 11.8, 18.3 and 21.2 cm using 2.0, 3.0, 3.5 g of MRH, respectively. The flow rate was adjusted to 10 mL/min and the eluants were collected in 50 ml fractions. The feed concentration of textile wastewater was kept constant and the pH of the wastewater was adjusted to 5 prior to the experiment.

3. Results and Discussion

As demonstrated from both batch and column studies, under controlled laboratory conditions an appreciable amount of both dyes could be removed by MRH [1,5]. But the ultimate test of its usefulness is its application to a sample of industrial textile wastewater. Due to the complexity of wastewaters, and in particular the presence of the problematic azo-reactive dyes, colour removal is a major concern for the textile industries [6]. Thus, the capability of MRH to remove colour from an untreated textile waste consisting of a variety of reactive, disperse, direct and sulphur-vat dyes was investigated.

3.1. Effect of pH

It has been suggested that the adsorptive treatment of wastewater containing dyes is pH dependent [7]. Hence, the effect of pH in the colour removal efficiency of MRH from the textile waste was studied. With the initial pH of 11.5, the pH of the wastewater was adjusted to the range of 2 to 10. Percent removal (%

Removal) was defined as $(Abs_o - Abs_t / Abs_o) \times 100$ where Abs_o is the initial absorbance of wastewater and Abs_t is the absorbance at time t.

Figure 1 shows that the percentage of colour removal from industrial wastewater decreased from 100% to 3.7% with an increase in pH from 2 to 10. This phenomenon is closely related to the influence of pH on the surface charge of MRH and the charges of dye groups in the wastewater. It appears that most of the dyes are present as anionic species in the wastewater. Thus, at high pH, there is an increase of negatively charged sites on the sorbent and this does not favour the sorption of anionic dye due to electrostatic repulsion. Besides, the presence of excess OH^- ions in the solutions would compete with the dyes for sorption and lead to lower colour removal efficiency. Coulombic interaction appears to play an important role in the colour removal by MRH.

Similar observation was reported by Ozacar and Sengil in the removal of metal complex dyes by sawdust [8]. They reported that the adsorption capacity increased significantly with a decrease in the pH and was due to both aqueous chemistry and surface binding sites of the adsorbents. In acidic conditions, the positively charged species are dominating and the adsorbent surface tends to acquire positive charge while the adsorbate species are negatively charged. As the adsorbent surface is positively charged, the increasing electrostatic attraction between negatively charged adsorbate species and positively charged adsorbent particles would lead to increased adsorption of the metal complex anions [9]. Precipitation occurred below pH 5 on standing. Thus for all the subsequent studies, the pH of the wastewater was adjusted to pH 5 prior to experimentation.

3.2. Effect of Contact Time

The effect of contact time in the colour removal by MRH from wastewater is presented in Figure 2. MRH showed a rapid sorption from 5 to 120 minutes with percentage colour removal increasing from 12.4 to 50.1 %; this was followed by a sudden and abrupt increase at 130 minutes time interval where 100% of colour removal occurred. This phenomenon was rather unusual but was similar to the uptake of RO16 in synthetic binary dye solution at low concentration. This indicates that most probably more than one process is involved in the removal of colour from wastewater by MRH.

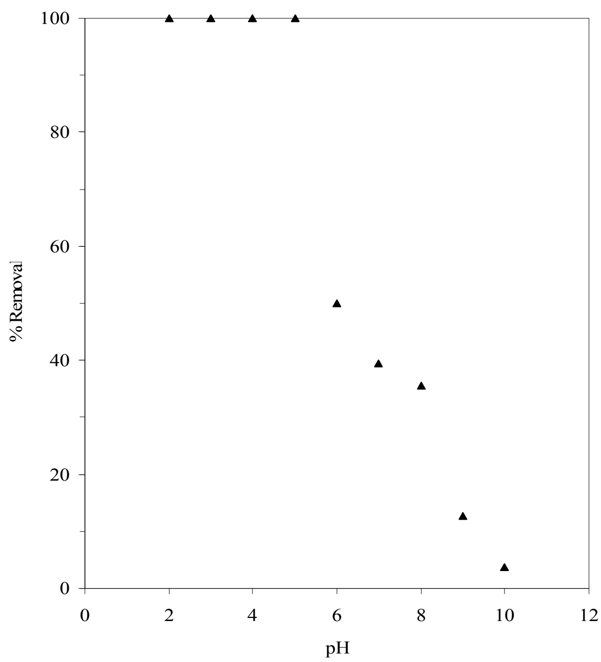

Fig. 1: Effect of pH in the colour removal by MRH from textile wastewater

3.3. Effect of Bed Depth

The effect of bed depth in the breakthrough time of the column was studied by varying the bed depths of the column from 6.0 to 18.3 cm at a constant flow rate. The breakthrough curves of wastewater obtained at different bed depths are shown in Figure 3. Clearly the breakthrough curves did not exhibit a typical 'S' shape of a packed-bed sorption system. Breakthrough was rapid and 50% breakthrough occurred at 150, 350, 600 and 950 ml of dye solutions for bed depths of 6.0, 9.5, 11.5 and 18.3 cm, respectively. At the lowest bed depth (6.0 cm), breakthrough occurred almost immediately but with increasing bed heights, with larger number of sorption sites, a longer service time before breakthrough occurred was observed.

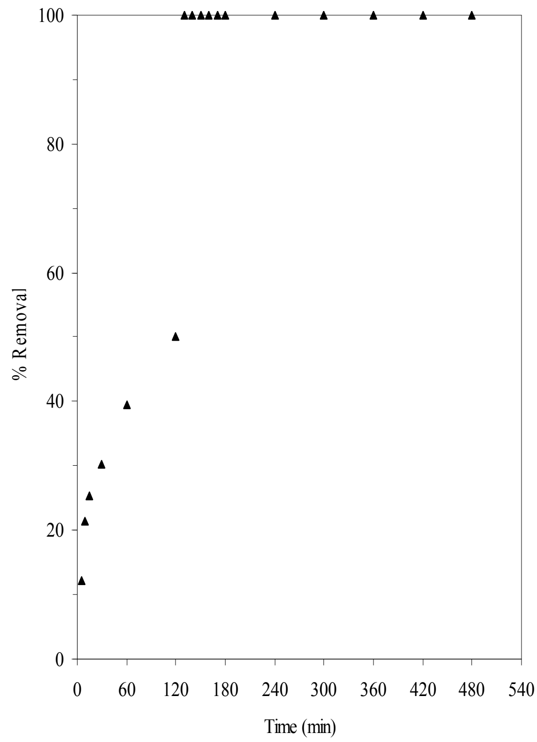

Fig. 2: Effect of contact time in the colour removal by MRH from textile wastewater.

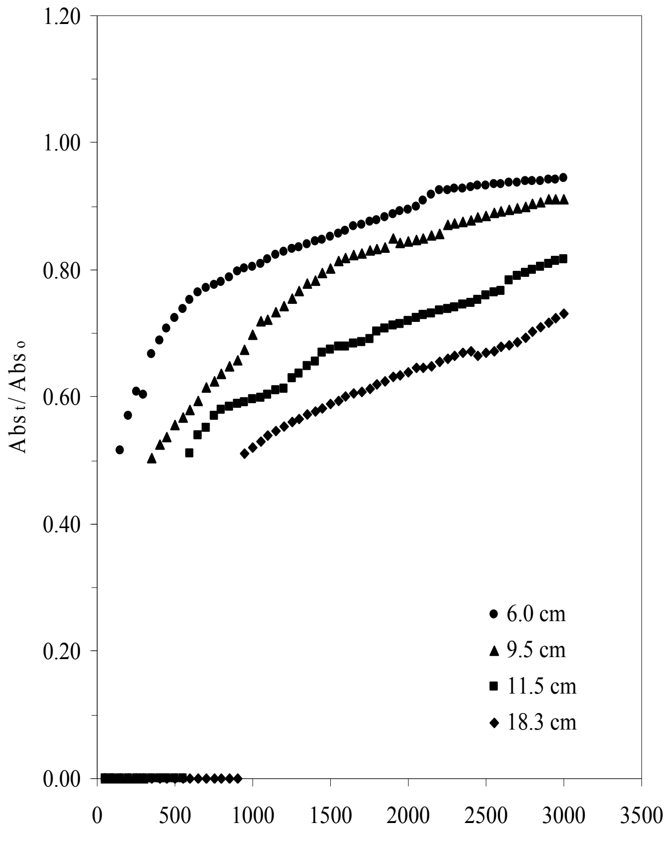

Fig. 3: Breakthrough curves of textile wastewater at different bed depths at a flow rate of 10 mL/min.

4. Conclusions

The present study shows that modification of rice hull with EDA under the optimum conditions (in a ratio of 1.00 g of NRH to 0.02 mole of EDA in a well stirred water bath at 80°C for 2 hours) resulted in the formation of a sorbent (MRH) that could be used successfully to dyes from textile wastewater. The optimum pH for the sorption of dyes using MRH was in the range of 2 to 5. The uptake of dyes was very rapid during the first 120 minutes, followed by an abrupt increase. This is similar to the phenomenon observed in the uptake of 50 mg/l of RO16 in synthetic binary dye solution. Continuous flow study indicated that increasing bed depth increased the service time of the column. All the breakthrough curves showed similar trend: efficient sorption at the beginning followed by a sudden breakthrough.

5. Acknowledgements

The financial supports by the International Foundation of Science, Stockholm, Sweden and research facilities from Universiti Tunku Abdul Rahman are gratefully acknowledged.

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