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FOREWORD

Welcome to the 10th volume and 1st issue of the ESTEEM Academic Journal (EAJ), an online peer-refereed academic journal of engineering, science and technology.Since the beginning of this year, a number of articles have been sent to us; some of which still being under review in their first or second phase, and the first eight of them are being published now, others following in the subsequent issue. Article submissions came from different UiTM branch campuses across the country and the manuscripts covered a wide range of engineering, science and technology topics, all of them being interesting and innovative.

First and foremost, we would like to extend our sincere appreciation and utmost gratitude to Associate Professor Dr. Ngah Ramzi Hamzah, Rector of UiTM (Pulau Pinang), Dr. Mohd Mahadzir Mohammud@Mahmood, Deputy Rector of Academic Affairs and Dr. Mohd Subri Tahir, Deputy Rector of Research, Industry, Community & Alumni Network for their generous support towards the successful publication of this issue. Not to be forgotten also are the constructive and invaluable comments given by the eminent panels of external reviewers and language editors who have worked assiduously towards ensuring that all the articles published in this issue are of the highest quality. In addition, we would like to thank the authors who have submitted articles to EAJ, trusting Editor and Editorial Board and thus endorsing a new initiative and an innovative academic organ and, in doing so, encouraging many more authors to submit their manuscripts as well, knowing that they and their work will be in good hands and that their findings will be published on a short-term basis. Last but not least, a special acknowledgement is dedicated to those members of the Editorial Board who have contributed to the making of this issue and whose work has increased the quality of articles even more. Although there will always be cases in which manuscripts will be rejected, our work so far has shown that the board members' motivation has been, and will be, to make publications possible rather than to block them. By means of intensive communication with authors, academic quality is and will be guaranteed and promising research findings are and will be conveyed to the academia in a functional manner.

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EFFECT OF CATIONIC AND ANIONIC DYE ADSORPTION BY BASE-MODIFIED PAPAYA SEED (FIXED-BED SYSTEM)

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ABSTRACT

Fixed-bed adsorption studies were conducted to evaluate the efficiency of Modified Papaya Seeds (MPS) and Natural Papaya Seeds (NPS) as adsorbents for the removal of Methylene Blue (MB) and Congo Red (CR) from aqueous solution under the effect of various process parameters namely bed depth (15-30 mm), flow rate (15-35 mL/min) and initial concentrations (15-35mg/L). The results showed that the total adsorbed quantities and equilibrium uptake decreased with increasing flow rate and increased with increasing initial MB and CR concentration. Breakthrough time and exhaustion time increased with increasing bed depth.

Keywords: chemical modification; papaya seed; adsorption; fixed-bed system.

1. INTRODUCTION

Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable. Besides, it was found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity design, ease of operation and insensitivity to toxic pollutants (Uddin, Rukanuzzaman, Khan, & Islam, 2009).

Commercial activated carbon is the preferred adsorbent for color removal, but its widespread use is restricted due to high cost. Therefore, alternative non-conventional waste materials from industry and agriculture can be obtained and employed as inexpensive adsorbents (Crini, 2006). Several tested low cost adsorbent, such as sawdust (Ferrero, 2007), orange peel (Namasivayam, Muniasamy, Gayatri, Rani, & Rangathan, 1996), and leaf (Bhattcharyya and Sarma, 2003) have been used for the removal of dyes from aqueous solution. To improve the adsorption ability of adsorbents towards various kinds of chemical pollutants, some more or less sophisticated pretreatment procedures have been developed which includes treatment with mineral acids, bases or their salts- HCl, NaOH, Na_2CO_3 (Kumar & Bandyopadhyay, 2006), and H_2SO_4 (Taty-Costodes, Fauduet, Porte, & Delacroix, 2003).

In the current study, papaya seed is utilized as the adsorbent. It has been reported that the production of papaya in Malaysia is about 50000 tonnes. Column performance of base (NaOH) modified papaya seed for the removal of MB and CR from an aqueous solution has been investigated using unmodified papaya seed as control. Breakthrough studies were carried

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out to evaluate the performance of modified papaya seed in continuous fixed-bed operation by varying the operating conditions, such as the flow rate, bed depth and feed (MB and CR) concentration.

2. MATERIAL AND METHODS

2.1 Material Development

The papaya seed used was obtained from a plantation located in Kuala Kangsar, Perak, Malaysia. The collected materials were washed several times using hot water and finally using distilled water (at room temperature) to remove any adhering dirt. The washed materials were then dried in the oven at 60 ^{o}C for 24 hours. The dried papaya seed was then ground and sieved through a sieve shaker (Retsch, AS 200) to obtain the particle size in the range of 250-355 μm.

Sodium hydroxide (NaOH) treatment process was performed in a 500 mL glass beaker. The dried papaya seed was treated in 0.05 M NaOH solution for 4 hours. The sample was then washed thoroughly with distilled water until it reached the pH level of 6-7 and dried in the oven at 60 ^{o}C for 24 hours. The samples were referred to as MPS. The resulting adsorbents, MPS, were stored in an air-tight container for further use in the adsorption experiments.

2.2 Adsorbate-Methylene Blue And Congo Red

Methylene Blue (MB), a cationic dye, and Congo Red (CR), an anionic dyes were purchased from Merck, and they were used as received without further purification. The stock solution of MB (1000 mg/L) was prepared in distilled water. All working solutions were prepared by diluting the stock solution with distilled water to the desired concentration.

2.3 Experimental Set-Up

Continuous flow adsorption studies were conducted in a glass column made of Pyrex glass tube of 1.2 cm inner diameter and 19.5 cm height. At the bottom of the column, a stainless sieve was attached followed by a layer of glass wool to prevent loss of adsorbent. The column was filled with 5 mm size glass beads in order to provide a uniformed flow of the solution through the column. A peristaltic pump (Masterflex, Cole-Parmer Instrument Co., US) was used to pump the adsorbate solutions upward to avoid channeling due to gravity and also to provide an uniformed distribution of the solutions through the column.

A known quantity of adsorbent was placed in the column to yield the desired bed height of the adsorbent. Adsorbate (MB and CR) solution of known concentration was pumped upward through the column at the desired flow rate. Samples were collected from the exit of the column at different time intervals and were analyzed for MB and CR concentration using a UV/VIS spectrophotometer (Shimadzu, UV-1601) by monitoring the adsorbance changes at a wavelength of maximum adsorbance of 668 nm. Operation of the column was stopped when the effluent MB and CR concentration exceeded a value of 99.5% of its initial concentration.

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2.4 Analysis Of Column Data

The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption fixed-bed column. The breakthrough curves show the loading behavior of dye to be removed from the solution in a fixed-bed column and is usually expressed in terms of adsorbed dye concentration (C_{ad}), inlet dye concentration (C_o), outlet dye concentration (C_t) or normalized concentration defined as the ratio of outlet dye concentration to inlet dye concentration (C_t/C_o) as a function of time or volume of effluent for a given bed height (Guo & Lua, 2003). Effluent volume (V_{eff}) can be calculated as;

$$V_{eff} = Qt_{total} \tag{1}$$

where t_{total} and Q are the total flow time (min) and volumetric flow rate (mL/min). The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration, C_{ad} (mg/L) versus t (min) plot can be used to find the total adsorbed dye quantity (maximum column capacity). Total adsorbed dye quantity q_{total} (mg) in the column for a given feed concentration and flow rate is calculated as (Goel, Kadirvelu, Rajagopal, & Garg, 2005):

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_{ad}\, dt \tag{2}$$

Equilibrium uptake q_{eq} (mg/g) or maximum capacity of the column in the column is defined by equation (3) as the total amount of adsorbed (q_{total}) per gram of adsorbent (w) at the end of total flow time (Aksu and Gonen, 2004):

$$q_{eq} = \frac{q_{total}}{w} \tag{3}$$

3. RESULTS AND DISCUSSION

3.1 Effect Of Inlet Concentration

The breakthrough curves obtained for MB adsorption are demonstrated in Figure 1 and 2 for different initial concentration (15, 25, 35 mg/L) of NPS and MPS respectively at 25 mL/min and 20 mm bed depth. Both figures indicated that increasing initial concentration led to decrease in breakthrough time of MB and CR-containing solution. The treated volume was greatest at the lowest inlet concentration since the lower concentration gradient caused a slower transport due to a decreased diffusion coefficient or decreased mass transfer coefficient (Vijayaraghavan, Jegan, Palanivelu, & Velan, 2004). It can be observed that, the equilibrium uptake of MB increased with increase inlet concentration from 15 to 35 mg/L and the adsorbent quickly saturated at higher inlet MB and CR concentration. As expected, a decreased amount of inlet concentration gave a later breakthrough curve and the treated volume was greatest at the lowest inlet concentration since the lower concentration gradient caused a slower transport due to a decreased diffusion coefficient or decreased mass transfer coefficient. The breakthrough time decreased with increasing inlet MB concentration as the binding sites became more quickly saturated in the system.

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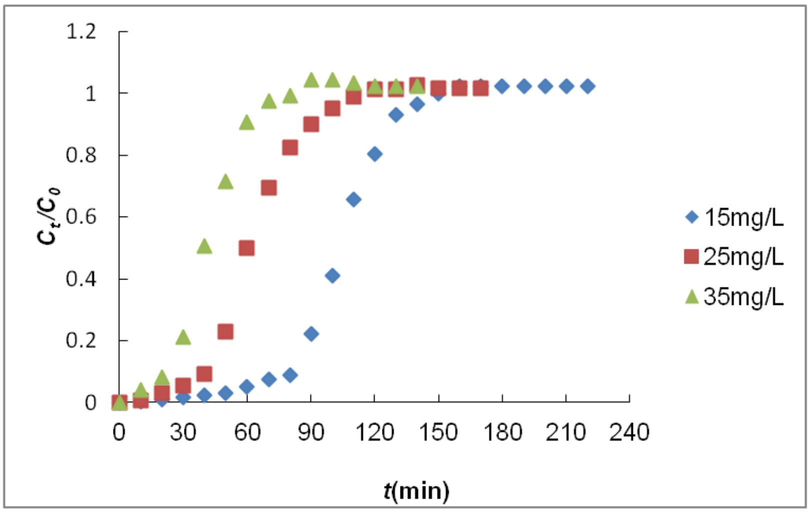

Figure 1: Effect of various inlet concentration of MB on the breakthrough curve of MB adsorption onto NPS.

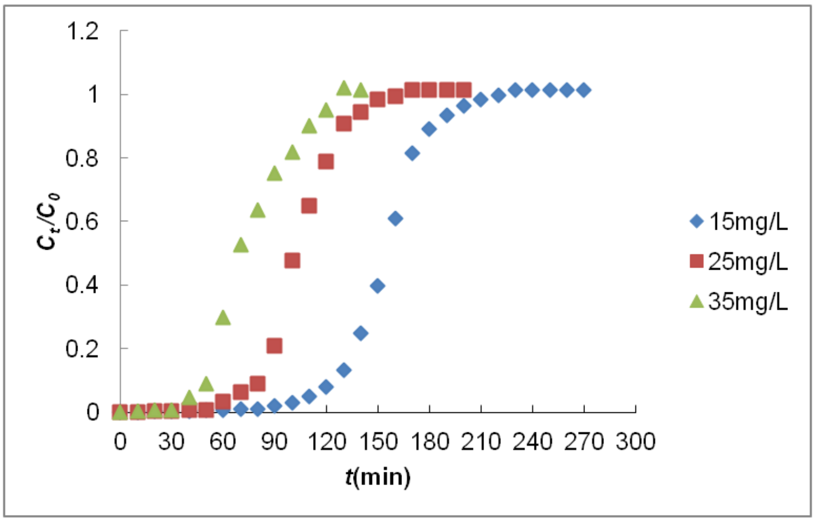

Figure 2: Effect of various inlet concentration of MB on the breakthrough curve of MB adsorption onto MPS.

It was also illustrated in Figure 3 and 4 that the breakthrough time decreased with increasing influent CR concentration. At lower influent CR concentrations, breakthrough curves were dispersed and breakthrough occurred slower. As influent concentration increased, sharper breakthrough curves were obtained. These results demonstrated that the change of concentration gradient affected the saturation rate and breakthrough time (Goel et al., 2005). This can be explained by the fact that more adsorption sites are being covered with the increase in CR concentration. The larger the influent concentration, the steeper the slope of the breakthrough curve and smaller the breakthrough time. These results demonstrated that the change of concentration gradient affected the saturation rate and breakthrough time, or in other words, the diffusion process was concentration dependent. As the influent concentration increases, CR loading rate increases, so does the driving force for mass transfer.

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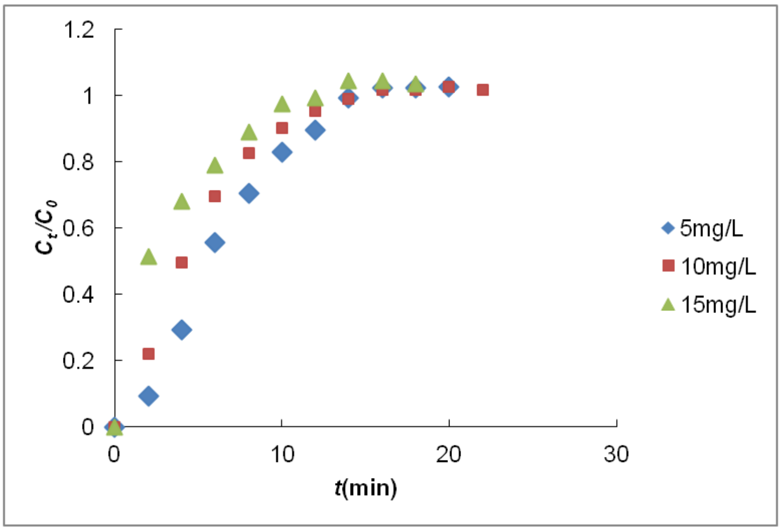

Figure 3: Effect of various inlet concentration of CR on the breakthrough curve of CR adsorption onto NPS.

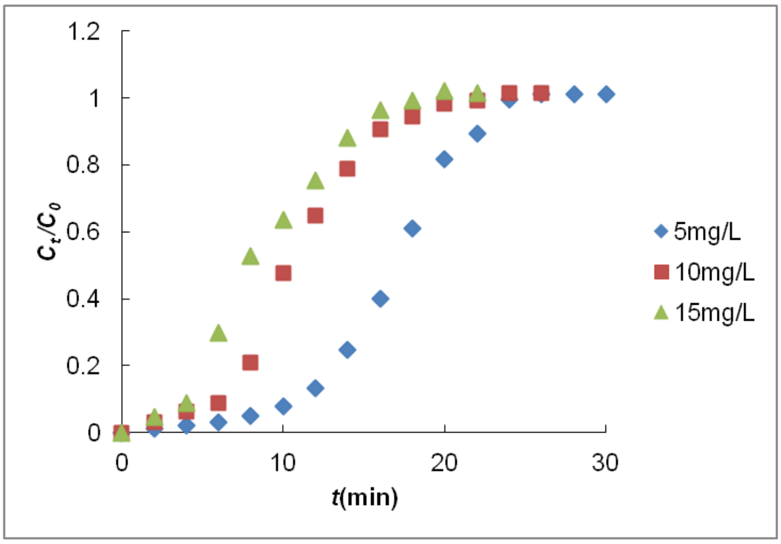

Figure 4: Effect of various inlet concentration of CR on the breakthrough curve of CR adsorption onto MPS.

3.2 Effect Of Bed Depth

Accumulation of MB in the packed bed column is largely dependent on the quantity of adsorbent inside the column. In order to yield different bed heights, 1.0, 1.5 and 2.0 g of NPS and MPS were added to produce bed height of 1.5, 2.0 and 3.0 cm, respectively. The sorption breakthrough curves obtained by varying the bed heights 1.5, 2.0 and 3.0 cm at 25 mL/min flow rate and 25 mg/L initial MB concentration for NPS and MPS biomass are presented in Figure 5 and 6. The bed capacity and percent removal of MB were increased with increasing bed height, as more binding sites were available for adsorption. The increase in adsorption with bed depth was due to the increase in adsorbent doses in larger beds, which provide greater adsorption sites for MB. As expected, an increased bed resulted in high volume of MB solution treated and high percentage of MB removal.

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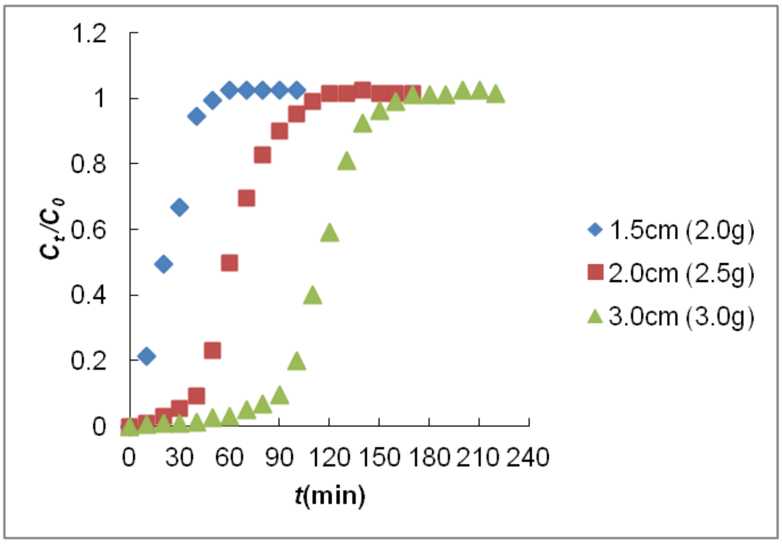

Figure 5: Effect of various bed height of MB on the breakthrough curve of MB adsorption onto NPS.

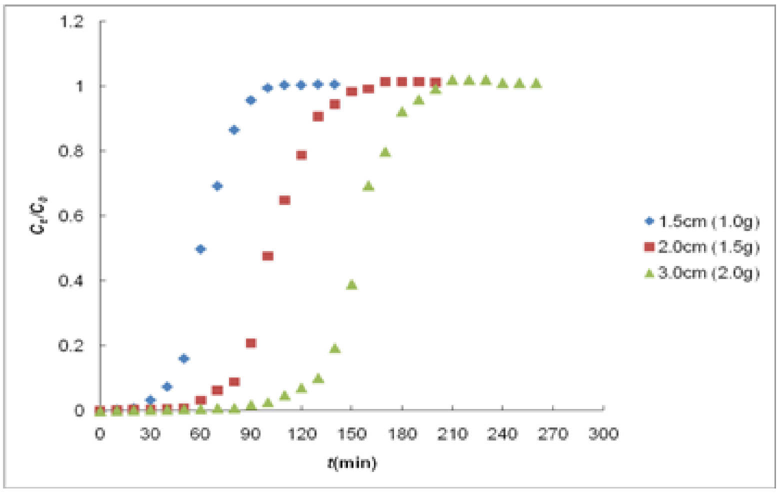

Figure 6: Effect of various bed height of MB on the breakthrough curve of MB adsorption onto MPS.

From Figures 7 and 8, it could be seen that as the bed height increased, CR had more time to contact with the NPS and MPS that resulted in higher removal efficiency of CR. So the higher bed column resulted in a decrease in the solute concentration in the effluent at the same time. The slope of breakthrough curve decreased with increasing bed height, which resulted in a broadened mass transfer zone. Higher uptake was observed at the highest bed height due to an increase in the surface area of the adsorbent, which provided more binding sites for the adsorption (Vijayaraghavan et al., 2004).

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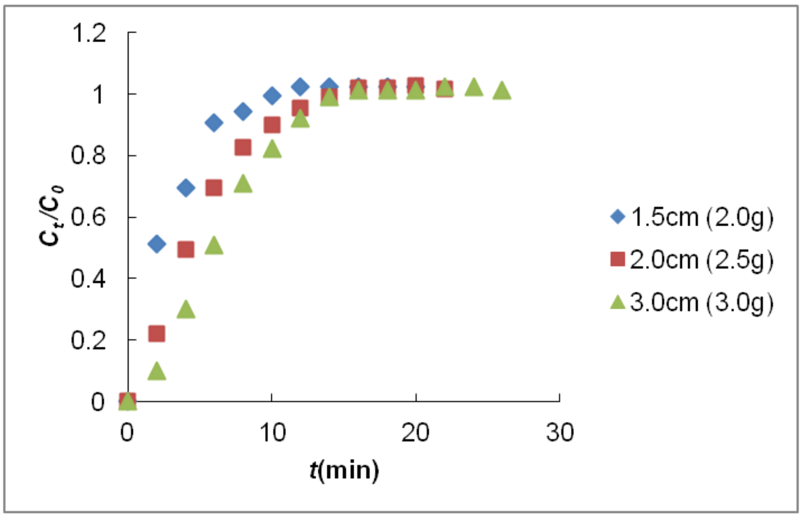

Figure 7: Effect of various bed height of CR on the breakthrough curve of CR adsorption onto NPS.

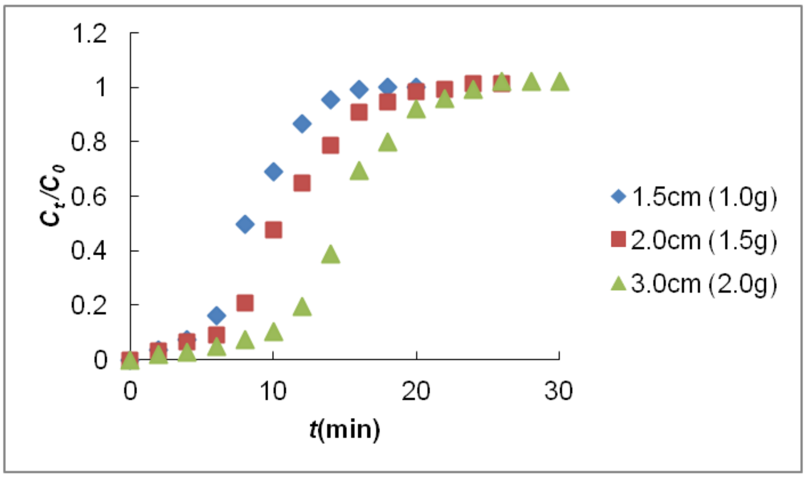

Figure 8: Effect of various bed height of CR on the breakthrough curve of CR adsorption onto MPS.

3.3 Effect Of Flow Rate

The effect of flow rate on MB adsorption onto NPS and MPS was measured by the same variation of flow rate from 15, 25 and 35 mL/min and keeping the initial MB concentration (25 mg/L) and bed height (2.0cm) constant. Figures 9 and 10 shows the effect of the various flow rates on adsorption of MB onto NPS and MPS respectively using a plot of dimensionless concentration (C_t/C_0) versus time (t). It was observed from both that the breakthrough curves became steeper as the flow rate increased. Breakthrough time reaching saturation was increased at lower flow rates. Although MB adsorption was a fast process, diffusion effects were lower due to insufficient residence time of dyes in the column at higher flow rates. Hence, lower flow rates were desirable for the effective removal of MB in column or fixed-bed system.

According to Han, Zhang, Zou, Xiao, Shi, & Liu, (2006), breakthrough generally occurred faster with a higher flow rate as could be seen in the breakthrough curves at the various flow rates. Breakthrough time reaching saturation was increased with a decrease in the flow rate.

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At a low rate of influent, MB had more time to be in contact with adsorbent, which resulted in a greater removal of MB molecules in the column (Han et al., 2006). The variation in the slope of the breakthrough curve and adsorption capacity may be explained on the basis of mass transfer fundamentals. The reason is that at higher flow rate the rate of mass transfer gets increased, for example the amount of dye absorbed onto unit bed height (mass transfer zone) get increased with increasing flow rate leading to faster saturation at higher flow rate (Ko, Porter, & McKay, 2000).

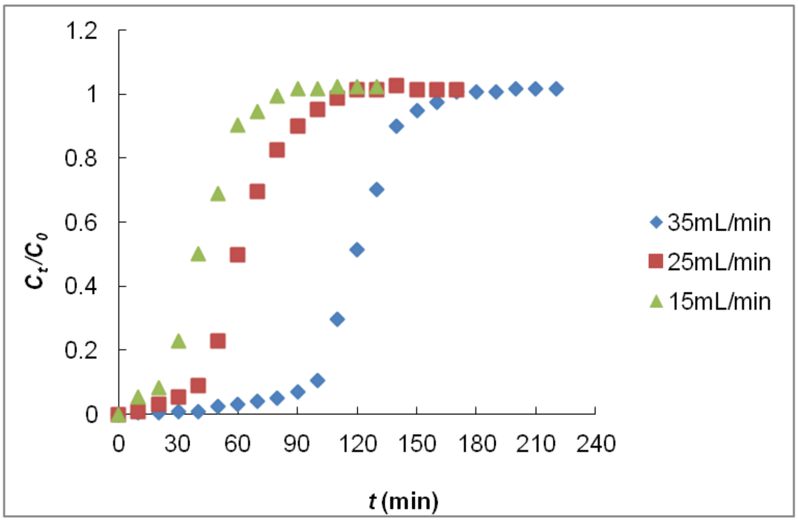

Figure 9: Effect of various initial flow rate of MB on the breakthrough curve of MB adsorption onto NPS.

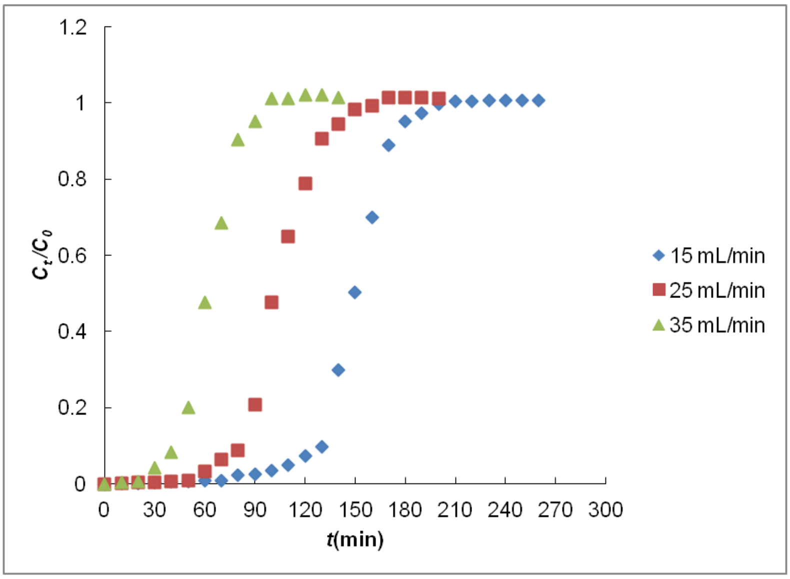

Figure 10: Effect of various initial flow rate of MB on the breakthrough curve of MB adsorption onto MPS.

It could be seen from Figures 11 and 12 that breakthrough curves generally occurred faster with a higher flow rate. Breakthrough time for reaching saturation was increased with a decrease in the flow rate. When at a lower rate of influent, CR had more time to contact with papaya seed and resulted in higher removal of CR in the column.

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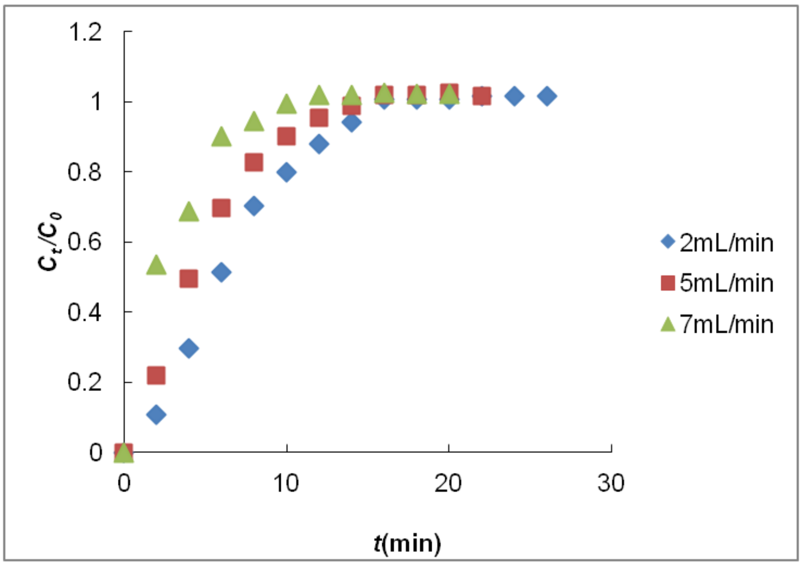

Figure 11: Effect of various initial flow rate of CR on the breakthrough curve of CR adsorption onto NPS.

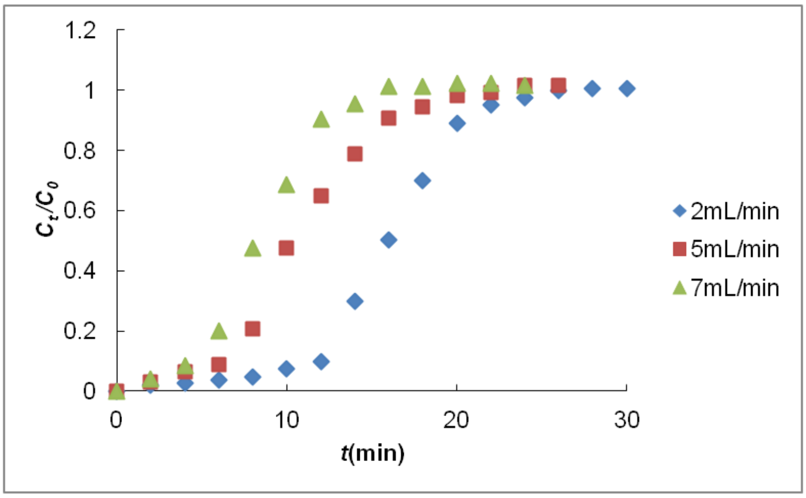

Figure 12: Effect of various initial flow rate of CR on the breakthrough curve of CR adsorption onto MPS.

4. CONCLUSION

This study identified that NPS and MPS have an effective and promising adsorbent property that can be utilized for the removal of MB from aqueous solutions. The experimental breakthrough curves confirmed that lower flow rates were desirable and effective in the removal of MB and CR in the column or fixed-bed system. The MB adsorption was a fast process compared to CR adsorption. This is due to the agro based adsorbent containing bonded OH groups, C=O stretching, aromatic nitro compound and C=C group which indicate involvement of nucleuphile towards cationic dye (MB) (Nasuha, Hameed, & Mohd, 2010). However breakthrough time reaching saturation of MB and CR increased at lower flow rates. Thus, high removal of MB and CR resulted at low feed flow rate because the contact time was longer. Furthermore, as the initial influent concentration increased, the breakthrough curves became much sharper and decreased in breakthrough time. The saturation was faster and the breakthrough time decreased with increasing initial influent concentration of MB onto NPS

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and MPS. Therefore, it demonstrates that the change of concentration gradient affects the saturation rate and breakthrough time. With a decrease in MB and CR concentration, the treated volume was the greatest at the lowest initial concentration. The slope of breakthrough curve decreased with increasing bed height. The higher bed column resulted in a decrease in the solute concentration in the effluent. So, as the bed height increased, MB ad CR had more time to contact with the adsorbents resulting in higher removal efficiency. This study confirmed that NPS and MPS can be one of the effective adsorbent used for the removal of MB and CR in a fixed-bed column in a continuous system. Variables such as feed flow rate, initial influent concentration and adsorbent bed height can affect the breakthrough curve which means that these variables must be taken into account when building fixed-bed column in a continuous system in industrial applications in future in the removal of dye wastewaters.

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