Asian Journal of Water, Environment and Pollution, Vol. 17, No. 4 (2020), pp. 47-52.
DOI 10.3233/AJW200050

Column Study for Adsorption of Methylene Blue Dye using *Azadirachta indica* Adsorbent

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Received March 6, 2020; revised and accepted September 15, 2020

Abstract: In this study, synthesised *Azadirachta indica* adsorbent was used for the removal of methylene blue dye using a packed bed column. The effect of feed flow rate, feed methylene blue dye concentration, and bed height of column on percentage removal of dye was studied. It was observed that the column bed exhausted rapidly at a higher flow rate and therefore, a breakthrough occurred faster. However, it was observed that bed exhaustion time increases on increasing the bed height from 2 to 10 inch at 10 mg/L feed dye concentration and feed flow rate of 40 ml/min. It was also found that the breakthrough curve is more dispersed and the percentage removal of dye increases on decreasing the feed methylene dye concentration from 150 to 10 mg/L. The percentage removal was found to be 96.89% at 20 ml/min of feed flow rate under 10 inch of bed height and 10 mg/L of feed dye concentration. The atomic absorption spectrophotometer and scanning electron microscope were used for estimating the effluent dye concentration from the column and morphological study, respectively.

Key words: Methylene blue dye, adsorption, packed bed column, break through curve, *Azadirachta indica*.

Introduction

Numerous industries such as textile, paint, leather, paper, plastics, etc release various kinds of toxic dye and colour in the environment which are causing havoc to aquatic as well as human life (Rafatullah et al., 2010). Due to the continuous generation of toxic effluent, an enormous amount of water is getting polluted. Hence, these affluents require the separation of toxic impurities before being released into the water bodies and environment. Industries utilise various techniques for the treatment of toxic dyes as well as water purification (Pal et al., 2018, 2019; Upadhyaya et al., 2016b) from waste water such as advance oxidation (Jamal et al., 2015; Nidheesh et al., 2018), reverse osmosis (Abid et al., 2012), precipitation (Loekitowati Hariani et al., 2013; Zhu et al., 2007), vacuum membrane distillation (Baghel et al., 2017a, 2017b, 2018; Chaurasia et al., 2013; Singh et al., 2013; Singh et al., 2017; Upadhyaya et al., 2011, 2016a, 2018a, 2018b), coagulation (Moghaddam et al., 2010; SzyguÅ‚a et al., 2009), irradiation (Juang et al., 2010; Vaiano et al., 2015), ion exchange (Wu et al., 2008), photochemical degradation (Sohrabi and Ghavami, 2008) and adsorption (Agarwal et al., 2011; Gadekar and Ahammed, 2019; Goswami et al., 2018). Among them, the adsorption technique was found to be beneficial due to its cost-effectiveness and simple design. In the adsorption process, various types of adsorbents such as commercial activated carbon (Kannan and Sundaram, 2001), coal (McKay et al., 1999), agricultural (groundnut shell – Kannan and Sundaram, 2001; jute fibre – Senthilkumaar et al., 2005) and industrial derived activated carbon (activated tyres – Sainz-Diaz and Griffiths, 2000) and fly ash

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(Kumar et al., 2005) and sewage sludge from an urban waste water (Otero et al., 2003), natural adsorbents (clay – Bagane and Guiza, 2000), zeolite (DoÄŸan et al., 2000), and glass wool (Chakrabarti and Dutta, 2005), bio-adsorbents (algal waste – Vilar et al., 2007), green alga (El Sikaily et al., 2006), and dead fungus (Fu and Viraraghavan, 2000) are applicative for removal of toxic dyes from waste water. Adsorbent *Azadirachta indica* is used for the sorption of Methylene blue dye as reported by few authors using batch process. However, the removal from the continuous adsorption process is seen to be limited as per literatures. In the present study, Methylene blue dye is removed from the continuous adsorption column and the effect of various operating parameters such as feed flow rate, bed depth, MB dye concentration on the percentage removal is studied. Moreover, a scanning electron microscope is used to study the morphological changes that occur in the spent adsorbent.

Material and Methods

Methylene Blue

Methylene blue (MB) powder (molecular formula: $C_6H_{18}ClN_3S$; basic in nature) was purchased from Rankem Chemicals, India. Its molecular weight is MW: 319.851 g/gmole). The chemical structure (Rastogi et al., 2008) of MB is shown in Figure 1. In the present study, a stock solution of MB dye (concentration: 500 ppm) was prepared by dissolving MB powder using double distilled water; thereafter, various concentration range of MB from 10 to 150 ppm was prepared by dilution.

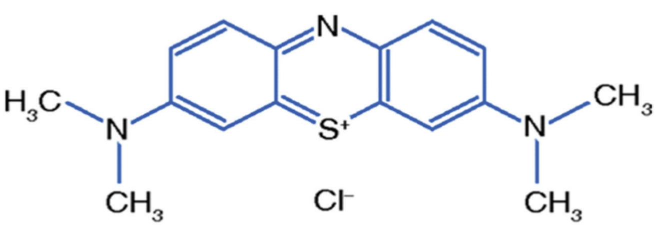


Figure 1: Chemical structure of methylene blue.

Preparation of Adsorbent

Initially, the quantified amount of raw *Azadirachta indica* leaves from the local area is taken and washed for few times with distilled water to remove adhering impurities, and then dried for 2 hours at 80°C in a dryer. The dried leaves were crushed, screened (100 mesh number), rewashed and again dried for 30 minutes. The sample was heated for 15 minutes in a furnace under a constant temperature of 220°C. The obtained heated sample was allowed to cool, continuously washed with water followed by drying for removal of moisture. The obtained *Azadirachta indica* powder was used as an adsorbent for column studies.

Experimental Procedure

Adsorption column studies were performed in a Pyrex glass tube of inner diameter and height of 3.7 cm and 90 cm, respectively, where a sieve of stainless steel was fixed along with glass wool at the bottom of the column. *Azadirachta indica* powder was packed in the column at various bed height varying from 2 to 10 inch. MB dye concentration ranging from 10 to 150 mg/L was pumped through a glass column using a peristaltic pump with various flow rates ranging from 20 to 60 ml/min. After a definite time, the effluent MB solution was collected and the concentration was measured using a double beam UV- spectrophotometer at 668 nm.

Results and Discussions

Effect of Flow Rate

The effect of flow rate on the removal of MB using prepared *Azadirachta indica* adsorbent is shown by the breakthrough curve (BTC) in Figure 2. It is observed that the breakthrough occurred speedily with a higher flow rate. This is because adsorption capacity decreased due to insufficient contact time for adsorption of MB on adsorbent, as a result diffusion of MB dye into the pores of adsorbent reduced and therefore solute exit from the column without sufficient adsorption before equilibrium. Further, it can be attributed that the performance of the continuous adsorption column was found to be more

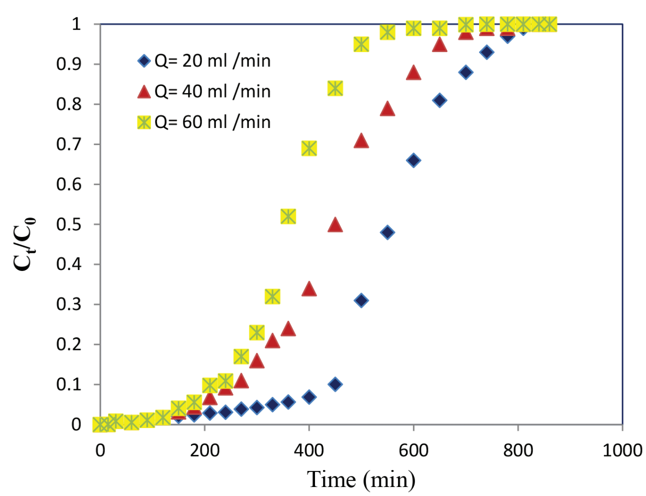


Figure 2: Effect of flow rate on BTC.

effective at a low flow rate of 20 ml/minute at constant bed height, initial MB dye concentration of 10 inch and 10 mg/L of MB dye concentration, respectively. This may be due to the reason that at a low feed flow rate of influent, MB had more contact time with the adsorbent. The maximum percentage removal of MB dye was found to be 96.89% at a feed flow rate 20 ml/min. The trend of experimental BTC is found to be in good agreement with the reported studies (Dawood et al., 2018; Tan et al., 2008).

Effect of Bed Height

The BTC at various bed height is illustrated in Figure 3. It is found that on increasing the bed height from 2 to 10 inch, the breakthrough and exhaustion time increases from 400 to 740 minutes at a constant flow rate of 40 ml/min and feed MB dye concentration of 10 mg/L. This increment may be due to an increase in surface area of *Azadirachta indica* adsorbent, which creates more sites for the adsorption of MB dye as a result effluent concentration of MB dye decreases at higher bed height under the same contact time. It is also attributed from Figure 3 that the slope of BTC decreases on increasing the bed height which is indicated by the widening of the solute transfer (MB dye) spectrum and hence the percentage removal gets increased under higher bed height. The same observations towards BTC have been reported by other authors (Al-Husseiny, 2014; Hayati et al., 2018)

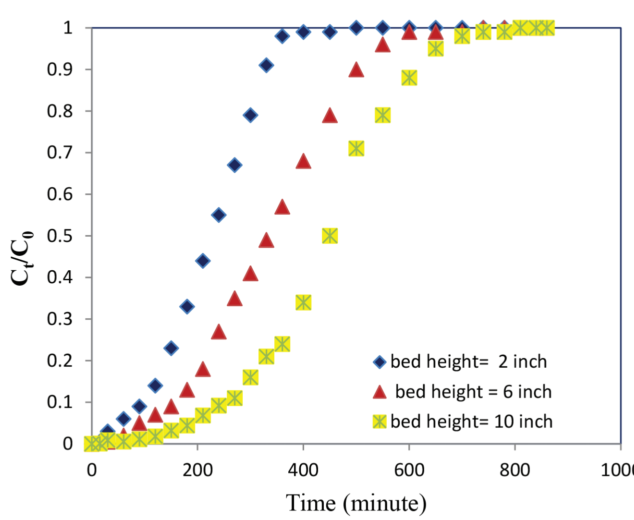


Figure 3: Effect of bed height on BTC.

Effect of Feed Dye Concentration

The effect of MB dye concentration on BTC is represented in Figure 4 by varying the MB concentration in the feed from 10 to 150 mg/L under constant bed height and flow rate of 10 inch and 20 ml/minute, respectively. It is observed that BTC dispersed more at lower feed concentration as the breakthrough time gets increased.

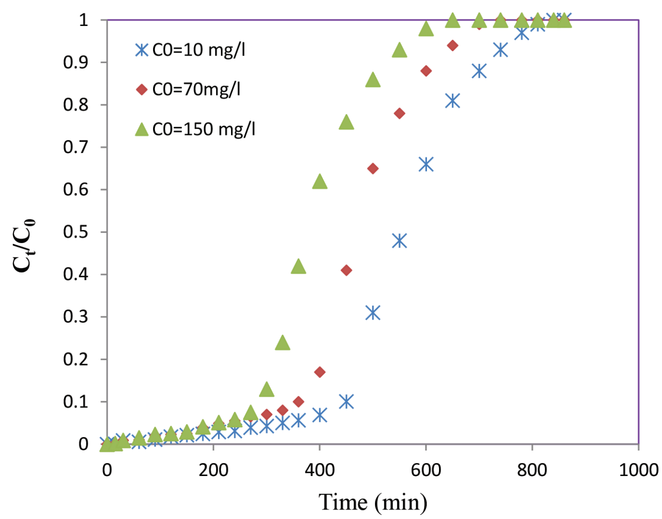


Figure 4: Effect of MB dye concentration on BTC.

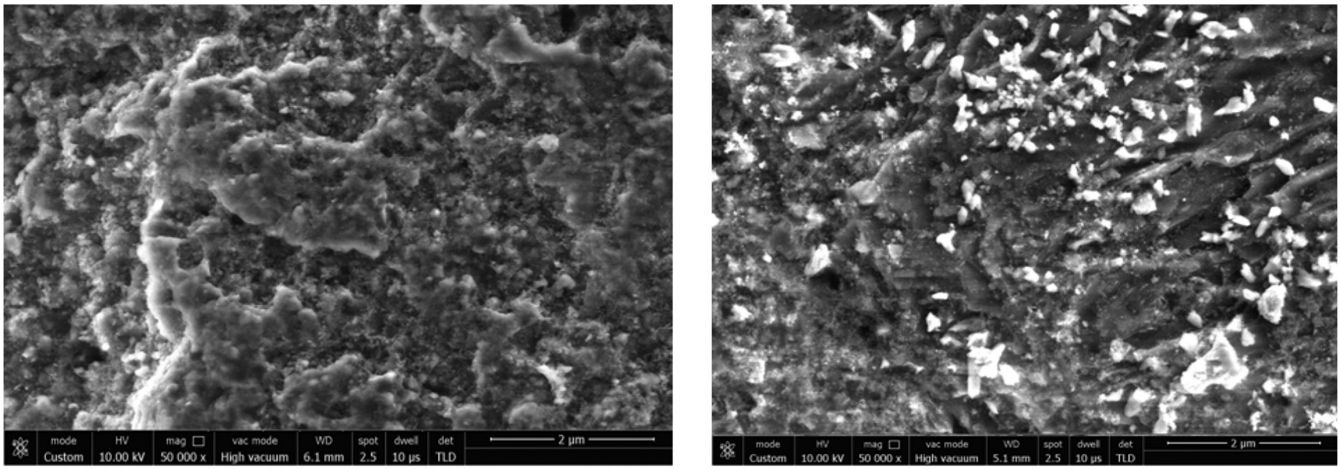
However, under higher influent concentration, the BTC appears sharper which may be due to the higher concentration gradient as a result of which saturation rate commences faster. It is also attributed that at higher MB dye concentration, the adsorbent gets exhausted sooner because the active sites become saturated by the MB dye in the column. Therefore, the percentage of removal decreases.

Morphology Study

Figure 5 a,b shows the scanning electronic microscope (SEM) images for the morphological study of freshly prepared *Azadirachta indica* powder before using them in continuous column and spent adsorbent after continuous usage in the column for 740 minutes, respectively. Large and developed pores can be clearly seen on the surface of fresh adsorbent of Figure 5 a before adsorption. However, from Figure 5 b, it can be seen that the MB dye gets deposited on the pores of the adsorbent, which results in the reduction of the adsorption sites.

Conclusion

The *Azadirachta indica* adsorbent was prepared for removal of MB dye using a packed bed column. The effect of various parameters involved in the experimental study such as feed flow rate, the concentration of MB dye, and bed height was investigated. It was found that the percentage removal of MB dye decreases on



(a) **(b)**

Figure 5: SEM micrographs: (a) Fresh Azadirachta indica adsorbent (50000X); (b) spent *Azadirachta indica* adsorbent (50000X).

increasing the feed flow rate. However, the removal increases on increasing the bed height. Further, it was also observed that the percentage removal decreased on increasing the feed MB dye concentration. The breakthrough time was depicted to be 810, 740 and 550 minutes for 20 ml/minute, 40 ml/minute, and 60 ml/minute, respectively, at bed height of 10 inch and feed MB dye concentration of 10 mg/L. The surface morphological study was also conducted after bed exhaustion at 740 minutes which attributes the reduction in percentage removal of MB dye.

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