

Research Article

Removal of Multi-active-blue Dye from Aqueous Phase using Magnetic Poly-pyrrole Nanocomposites: Fixed-bed Adsorption Studies

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Abstract: The aim of this study was to explore the use of adsorption in the removal of synthetic dyes in water bodies. These dyes pose a serious threat to both aquatic and human lives because of their toxicity and persistence in the environment. There is therefore an urgent need to remove them from water before discharge to the environment. Many of the current dye treatment methods are generally inefficient and expensive; however, adsorption is the most preferred method due to its inherent benefits such as simplicity, ease of operation, low cost and insensitivity to toxic environments. The study evaluated the removal of Multi-Active-Blue (MAB) dye from aqueous solution using poly-pyrrole-magnetitenano-composite (PPy/Fe₃O₄) adsorbent in a fixed-bed adsorption column. The influences of initial MAB dye concentration, bed mass and flow rate at the influent stream on the adsorption performance were investigated in an up-flow fashion. Results showed that early breakthrough time (t_b) was attained at high solution flow rates and dye concentrations and low bed mass. Increasing concentration from 50 to 150mg/L resulted in a decrease in t_b from 610 to 110 min. Furthermore, at the studied conditions, the highest breakthrough time obtained was 690 min at which 228 bed volumes were processed at 1.45g/L Adsorbent Exhaustion Rate (AER). The adsorber design parameters were calculated by fitting the experimental data to the column adsorption models and based on analysis of linear regression coefficients (R^2), it was established that the MAB dye adsorption was described best by Yoon-Nelson model throughout the entire breakthrough profile, while Bohart-Adams model fitted only the initial portion of the profiles. Accordingly, it was concluded that PPy-Fe₃O₄ nano-composite material is a promising adsorbent for cleaning textile dye polluted water.

Keywords: Adsorption, breakthrough, fixed-bed, Multi-Active-Blue (MAB) dye

INTRODUCTION

Rapid growth of textile, paper, plastics, cosmetics and rubber and printing industries in developing countries has resulted in increased discharge of wastewater polluted with different types of synthetic dyes (Yagub *et al.*, 2014). The presence of such dyes in water mainly occurs as a result of insufficient treatment processes thus creating a negative impact on human and aquatic lives and the environment in general (Vieira *et al.*, 2014). Synthetic dyes are non-biodegradable, toxic in nature and their presence in the aquatic ecosystem obstructs the growth of biota and affects the food network (Chinoune *et al.*, 2016, Dutta *et al.*, 2009). In addition, long term human exposure to dye pollutants increases the risk of tumours, cancers, cerebrovascular and lung diseases (Gupta and Suhas, 2009; Verma *et al.*, 2012). Due to such adverse effects coupled with strict environmental regulation

requirements, it is imperative for textile industries to seek alternative and efficient methods to reduce or completely remove dyes from wastewater.

Coloured effluents are usually treated using physical or chemical processes (Robinson *et al.*, 2001). However, those technologies are costly, less effective and lack adaptability to a wide range of dyes present in the wastewaters. Therefore, adsorption process is the most preferred method for removal of synthetic dyes from aqueous phase because it yields high quality water at low cost and the absence of secondary sludge (Olivares-Marín *et al.*, 2009; Kyzas and Lazaridis, 2009). Through adsorption, dyes are transferred from liquid phase to solid materials while at the same time minimising their presence in the effluent. Adsorption has been shown to be a low cost and efficient approach which allows the adsorbent to be regenerated and reused or even isolated from contact with the environment (Taleb *et al.*, 2012; Ho and McKay, 2003;

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Liu *et al.*, 2013). Moreover, it is an environmentally friendly technique capable of removing a wide range of contaminants even at very low concentrations (Hashem, 2012).

Numerous adsorbents such as peat (Sepúlveda *et al.*, 2004), wood (Poots *et al.*, 1978), maize cob (Suteu *et al.*, 2011), clay minerals (Rahmana *et al.*, 2013) and bagasse pith (Sharma and Kaur, 2011) have been reported as viable prospects to remove dyes from aqueous solutions. However, low sorption capacity, slow kinetics, high cost and limited active surface sites are some of the disadvantages which limit their practical application. Consequently, nano-materials and their composites have received a great deal of attention as alternative adsorbents for dye removal from aqueous solution due to their exceptionally large surface area, unique chemical selectivity properties and short diffusion length resulting in high adsorption performance (Yi and Zhang, 2008). In order to achieve dual benefits in both adsorption and adsorbent separation with external magnetic field, the current practice is to tailor conducting polymer-based nano-composites with magnetic nanoparticles dispersed in their matrices (Muliwa *et al.*, 2016).

The decolourization of dye containing wastewater has mainly been studied by performing batch equilibrium and kinetic studies. Although valuable information regarding the adsorption capacity and rates is obtained in such studies, it is important to further explore the applicability of those experiments in a real wastewater treatment system. To achieve this, adsorption studies using fixed-bed column configuration is the most desirable experimental set up which may demonstrate the application of adsorption in continuous wastewater treatment processes (Chelliapan *et al.*, 2011). Besides, fixed-bed operation offers enhanced adsorption performance due to maximal utilization of the capacity and minimal attrition of the adsorbent. Moreover, column adsorption configuration boosts the interfacial area while decreasing the mass transfer resistance (Jahangiri-Rad *et al.*, 2014).

The aim of this study was to prepare and evaluate the adsorption performance of PPy/Fe₃O₄ nano-composite on removing MAB dye as a model synthetic dye from aqueous solution in a fixed-bed set up. In order to quantify and understand the influence of parameters such as flow rate, bed mass and concentration on breakthrough profiles, continuous experiments were conducted. The breakthrough time and capacity, empty bed residence time and adsorbent exhaustion rate were all computed from the experimental column data at various conditions. Thereafter, column adsorption design parameters were predicted by subjecting the experimental data on Yoon-Nelson and Adams-Bohart models.

MATERIALS AND METHODS

Materials: Magnetite (Fe₃O₄) nanoparticles (average particle size <50 nm) were purchased from Sigma-Aldrich (Germany). Anhydrous ferric chloride (FeCl₃) for use as an oxidant during polymerisation and Pyrrole (Py) liquid monomer (C₄H₅N) were purchased from by Merck Schuchardt (Pty) Ltd, South Africa. Multi-active blue dye powder was obtained from Hirst (Pty) Ltd, South Africa. A stock solution containing 1000 mg/L of MAB dye was prepared in 1 L round-bottomed glass flask and to obtain different desired concentrations, dilution were made with double-distilled water. Throughout this study, Analytical Reagents (AR) grade chemicals were used as received.

Preparation of adsorbent: Poly-Pyrrole-magnetite (PPy-Fe₃O₄) nano-composite material was prepared by chemical oxidative polymerization method as reported in the literature (Bhaumik *et al.*, 2013). A mass of 0.4 g of Fe₃O₄ nanoparticles was carefully weighed using a weighing balance (PS 750/C/2, Radwag, Poland) and was dispersed in 80 mL of deionized water in a 250 mL conical flask. This mixture was placed in an ultrasonicator (UD 9300SH-10L, Labotech-South Africa) for 20 minutes to ensure dispersion of the Fe₃O₄ nanoparticles in the aqueous. To this mixture, 0.8 mL of Pyrrole (Py) monomer was syringed and the resulting mixture was hand-shaken thoroughly for about 5 minutes to achieve homogeneity. In order to initiate polymerization, 5 g FeCl₃ was added slowly while swirling the mixture resulting to the formation of a black mixture (PPy-Fe₃O₄ nano-composite). The mixture was left for at least 4 h at room temperature to allow for polymerization to proceed into completion. Thereafter, acetone was added to stop polymerization and the mixture was washed repeated with deionized water in a vacuum filter to remove color and adhering oligomers as well as to neutralize the material. The black solid filter cake was dried at 60°C for at least 6 hours using vacuum drier (Townson and Mercer Ltd-England). Prior to use in adsorption studies, the dried material lumps were crush-broken to loosen the particles.

Column adsorption dynamic studies:

Experimental set up: The fixed-bed column experimental setup that was used in this study is shown in Fig. 1. Briefly, the set up consisted of an acrylic plastic column with an internal diameter of 1.6 cm and a height of 30 cm. The adsorbent material was placed in the middle of the column supported by glass wool and glass beads on each end. Two beakers placed at both ends of the set up acted as MAB dye solution feed (influent) tank and treated (effluent) water storage tanks, respectively. A peristaltic pump (Masterflex,

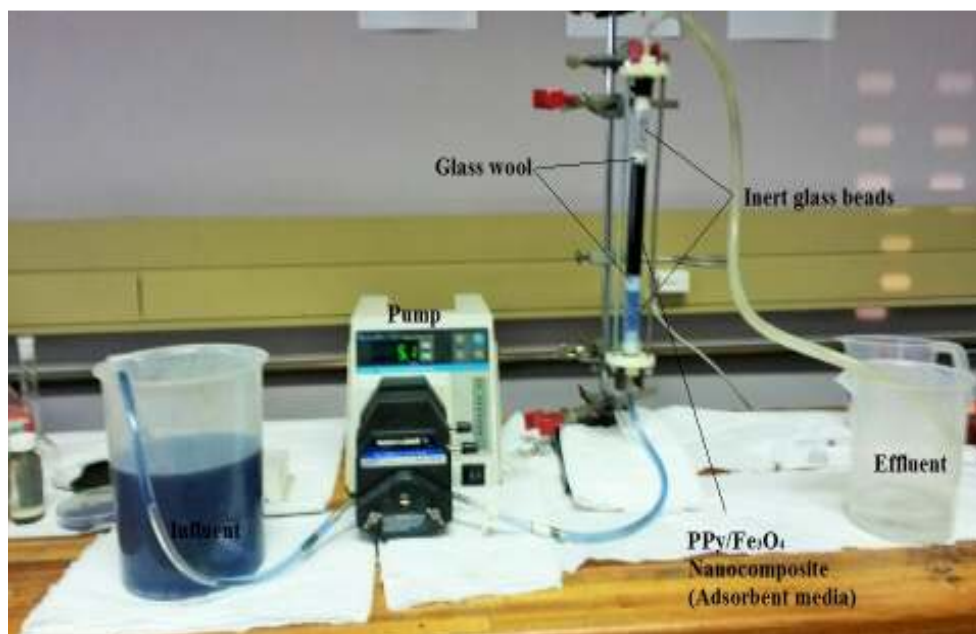


Fig. 1: A photographic caption of fixed-bed adsorption experimental set up

Cole-Parmer, model-77202-50-easy load-USA) was used to pump the prepared MAB dye solution through the column at controlled flow rates. The flow of the dye solution from one part to the other was facilitated by plastic tubing with internal diameter of 3 mm.

Adsorption experiments: Adsorption experiments were conducted in a fixed bed set-up (Fig. 1) by varying bed mass (column height), initial MAB dye concentration in the influent and flow rates. Before running experiments with the dye solution, deionised water was passed through the column in an up-flow fashion in order to rinse the adsorbent and equilibrate the particles. The initial pH of the MAB dye solution ranged from 6.85-7.33. To ascertain the actual flow rate (mL/min) during each experimental run the effluent solution was collected periodically in a measuring cylinder. The effect of various process variables like initial concentration (50, 100 and 150 mg/L), flow rate (2, 3 and 4 mL/min) and adsorbent bed mass (1, 2 and 3 g) on breakthrough time were studied to aid in designing a continuous adsorption system. Effluent samples were collected at certain time intervals, until the effluent dye concentration was nearly equal to the initial concentration. The concentration of dye in the collected samples was analysed by measuring absorbance in a Photolab (6100 VIS, Labotech-South Africa) at maximum wavelength of 611 nm. In this study, breakthrough time was determined based on maximum permissible colour of 5 units based on platinum-cobalt scale by World Health Organization (WHO, 2011). Finally, the breakthrough data was fitted to Yoon-Nelson and Bohart-Adams models to determine the adsorption column design parameters.

The time at which breakthrough is reached and the shape of the breakthrough profile are two very important factors which determine the performance of fixed-bed column adsorption (Mohammed *et al.*, 2016). The dye loading behaviour onto the adsorbent is depicted by breakthrough curves and is usually expressed as the ratio of outlet MAB dye concentration to inlet concentration C_t/C_o as a function of volume or time of the effluent for a given bed height. The volume of effluent (V_{eff}) in mL at any time t (min) is calculated as follows:

$$V_{eff} = Qt_{tot} \quad (1)$$

where,

Q (mL/min): The MAB dye influent flow rate

t_{tot} : The exhaustion time (min). Similarly, the maximum column capacity

yq_{tot} : Given by the area under the curve of adsorbed dye concentration versus time (Yaghmaeian *et al.*, 2014). It can be obtained by integrating the following equation:

$$q_{tot} = \frac{Q}{1000} \int_{t=0}^{t=t_{tot}} (C_o - C_t) dt \quad (2)$$

where, C_o and C_t are the influent and effluent dye concentration, Q is the volumetric flow rate (L/min) and t_{tot} (min) is the total flow time.

Subsequently, the maximum bed adsorption capacity q_{max} (mg/g) is calculated by dividing q_{tot} by the mass, m of the adsorbent (g) in the column as:

$$q_{max} = \frac{q_{tot}}{m} \quad (3)$$

Finally, the total amount, M_{tot} of dye (g) sent through the column is calculated from the following equation:

$$M_{tot} = Q \frac{C_0 t_{tot}}{1000} \quad (4)$$

RESULTS AND DISCUSSION

Effect of bed mass: The study of the effect of bed mass on breakthrough is an important undertaking because it relates to the number of available adsorption sites and at the same time controls the rate of mass transfer zone movement. Figure 2 shows the breakthrough profiles when bed mass was 1, 2 and 3 g. The breakthrough times (t_b) obtained were 75, 270 and 600 min when the bed mass was 1, 2 and 3 g respectively. These results revealed that increasing bed mass increased the bed service time. Increasing bed mass increases the number of available sorption sites hence early breakthrough is achieved with lower bed mass and vice versa. For all the three profiles, there was a sharp rise in breakthrough profile immediately after the breakthrough point due to the exit of the Mass Transfer Zone (MTZ). Furthermore, the total volumes treated at breakthrough were 1.8 L, 0.81 L and 0.225 L and the bed was completely exhausted after 200, 450 and 700 min when the bed masses were 1, 2 and 3 g, in that order.

Meanwhile, a summary of parameters such as Adsorbent Exhaustion Rate (AER), Empty Bed Residence Time (EBRT) and bed capacity at breakthrough were calculated from breakthrough curves and are presented in Table 1. With longer treatment times, it follows logically that larger volumes of wastewater can be treated before the effluent concentrations become unacceptable. Notably, for all parameters varied, the AER decreased as each parameter was increased indicating favourable adsorption performance. These findings agreed well with results reported by other researchers (Bhaumik *et al.*, 2013; Karunarathe and Amarasingha, 2013).

Effect of initial concentration: The effect of initial concentration (50, 100 and 150 mg/L) on breakthrough point was investigated and results are shown in Fig. 3. The shape of the curve for the concentration of 50 mg/L deviated from the expected s-shape. Increasing concentration from 50 to 150 mg/L resulted in a decrease in t_b from 610 to 110 min, which corresponded to an increase in V_b of 1.83 to 0.33 L. The observed behaviour is attributed to the fact that high influent concentrations represent high driving forces in adsorption which means dye molecules interacted fast with active sites of the adsorbent resulting in early bed

Table 1: Summary of fixed-bed column parameters at breakthrough point for MAB dye adsorption onto PPy/Fe₃O₄ nano-composite

Parameter	EBRT(min)	Service time, t_b (min)	Uptake q_0 (mg/g)	Bed volumes processed	AER(g/L)
Adsorbent mass (g)					
1	1.01	75	21.4	75	4.44
2	2.01	270	38.5	134	2.47
3	9.05	600	57.0	66	1.67
Initial dye conc. (mg/L)					
50	2.01	560	40.0	278	1.20
100	2.01	270	38.5	134	2.47
150	2.01	110	23.5	55	6.10
Flow rate (mL/min)					
2	3.01	690	65.6	228	1.45
3	2.01	270	38.5	134	2.47
4	1.51	132	25.1	87	3.79

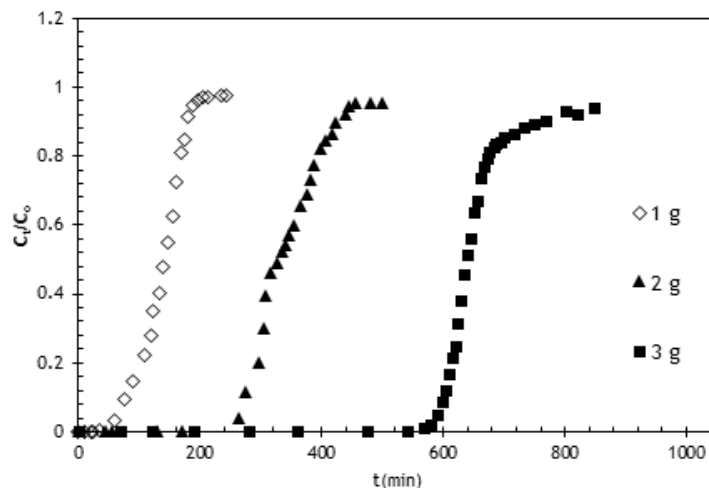


Fig. 2: Effect of mass (g) of adsorbent in column (flow rate 3 mL/min, initial concentration 100mg/L)

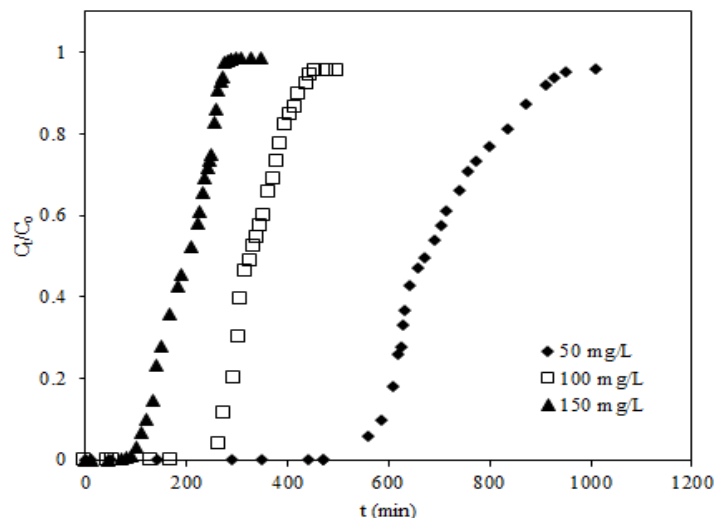


Fig. 3: Effect of concentration on breakthrough profiles (flow rate 3 mL/min, adsorbent mass 2 g)

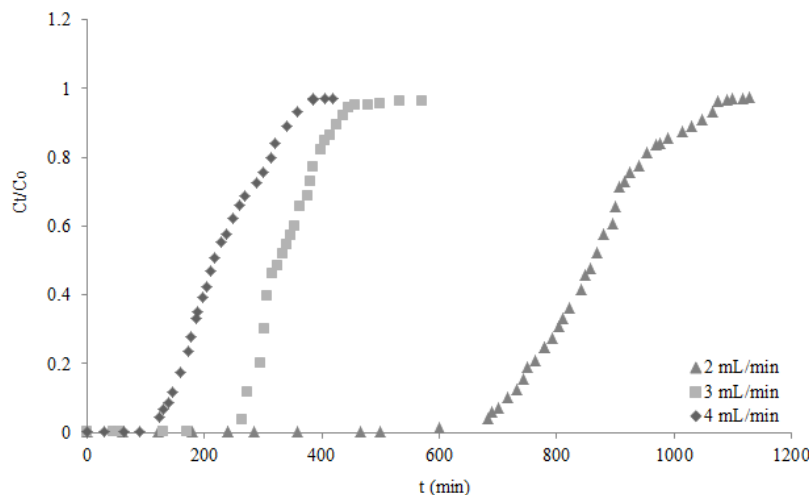


Fig. 4: Effect of flow rate on breakthrough time (MAB dye concentration: 100 mg/L, adsorbent mass 2 g)

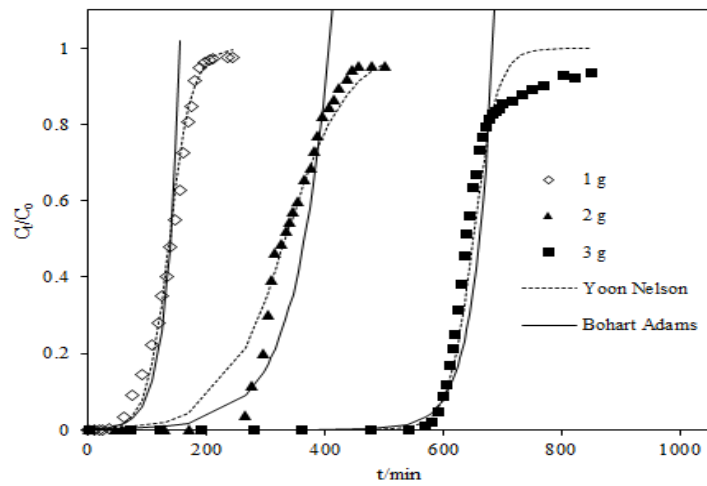
saturation (Hu *et al.*, 2016). Thus large volumes of MAB dye solution could be treated using lower initial concentrations before the adsorbent could be regenerated. Increased dye solution concentrations enhanced diffusion process in the column leading to shorter breakthrough time as also reported in a previous study (Simsek *et al.*, 2014).

Effect of flow rates: The adsorption performance of a fixed-bed column is significantly affected by the influent flow rate. Hence it is very important to evaluate the effect of solution flow rate on the efficiency of the adsorbent. In this study, the effect of MAB dye influent solution flow rates on breakthrough time was investigated and results are plotted in Fig. 4. Results indicate early breakthrough time at higher flow rate compared to lower flow rates. Low flow rates indicated longer residence times thus dye molecules had sufficient time to interact with the adsorbent active sites via diffusion process. These observations are supported

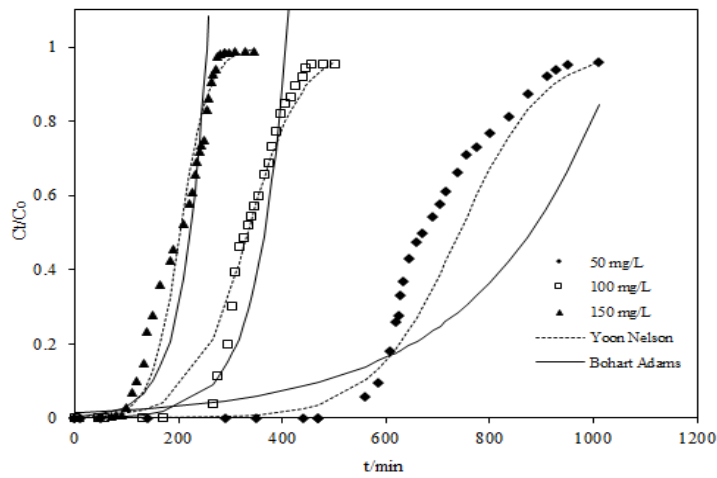
by computed column parameters presented in Table 1. For instance, the EBRT decreased from 3.01 to 1.52 min, the AER increased from 1.45 to 3.79 g/L, the bed service time decreased from 690 to 132 min and the bed volumes processed decreased from 228 to 3 when MAB dye influent flow rate was increased from 2 to 4 mL/min. Moreover, at high flow rates the breakthrough profile seemed to be less steep, an indication that probably convective flow may be the governing mechanism at higher flows (Acheampong *et al.*, 2013).

Application of column dynamic models to breakthrough profiles: In order to be able to predict the fixed-bed adsorption performance for application in an industrial scale, the breakthrough data was subjected to Yoon-Nelson and Bohart-Adams models (Fadzil *et al.*, 2016).

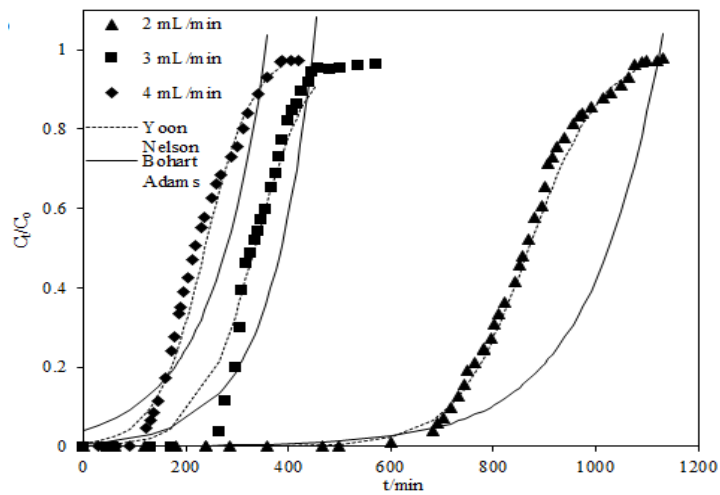
The Yoon-Nelson model assumes that the rate of decrease in the probability of adsorption for each adsorbent molecule is proportional to the probability of



(a)



(b)



(c)

Fig. 5: Breakthrough profiles for adsorption of MAB dye onto PPy/Fe₃O₄ nano-composite fitted with Yoon-Nelson and Adams-Bohart models at different experimental conditions (a-bed mass, b-concentration and c-flowrate)

Table 2: Yoon-Nelson and Bohart-Adams model parameters under different experimental conditions

Parameter	Yoon-Nelson model			Bohart-Adams model		
	$k_{YN}(\text{min}^{-1})$	τ (min)	R^2	$k_{BA} 10^{-4}$ (L/mg min)	N_0 (mg/L)	R^2
Bed mass (g)						
1	0.052	137.76	0.972	4.3	12375.22	0.894
2	0.019	333.37	0.988	1.7	16186.99	0.910
3	0.048	650.00	0.955	3.0	18134.82	0.832
Initial conc. (mg/L)						
50	0.012	741.08	0.94	0.8	11421.17	0.850
100	0.023	340.70	0.988	1.7	16186.99	0.910
150	0.036	203.11	0.942	1.5	15183.92	0.834
Flow rate (mL/min)						
2	0.014	870.00	0.985	0.7	27962.24	0.845
3	0.023	340.70	0.988	1.7	16186.99	0.910
4	0.021	236.85	0.966	0.9	17700.46	0.764

adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent (Sharma and Singh, 2013). This model, further assumes that the amount of dye adsorbed in a fixed-bed is half of the total dye entering the adsorbent bed within time period 2τ , where τ (min) is the time required for 50% adsorbate breakthrough. In its linearized form, this model is described as follows:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}t - k_{YN}\tau \quad (5)$$

where,

k_{YN} : The rate constant in (min^{-1})

t : The processing time (min)

A linear plot of $T \ln(C_t/(C_0 - C_t))$ versus t helps in calculating its parameters (k_{YN} and τ) from the slope and intercept at different bed depth, concentration and flow rate.

On the other hand, Adams-Bohart model stands on the premise that the adsorption equilibrium is not reached instantaneously and the rate of adsorption is proportional to both the residual capacity of the adsorbent and the concentration of the sorbate species. In addition, this model is based on the surface reaction theory describing the relationship between C_t/C_0 and t in a continuous flow system. Mathematically it is expressed in linear form as:

$$\ln\left(\frac{C_t}{C_0}\right) = k_{BA}C_0t - N_0k_{BA}\left(\frac{z}{U_0}\right) \quad (6)$$

where, k_{BA} (L/mg.min) is the Adams-Bohart kinetic constant, C_0 (mg/L) is the saturation concentration, C_t (mg/L) is the concentration of effluent at time t , z (cm) is the bed depth, N_0 (mg/L) is the maximum dye uptake per unit volume of the adsorbent column and U_0 (cm/min) is the linear velocity defined as the ratio of volumetric flow rate, Q (mL/min) to the cross sectional area, A (cm^2) of the bed. The values of k_{BA} and N_0 are determined from the slope and intercept of $\ln(C_t/C_0)$ versus t .

Figure 5a to 5c illustrates the plotted models fitted to experimental breakthrough data (linear plots not shown). It is clearly seen that for all variables (flow rate, concentrations and bed mass), Yoon-Nelson model describes the experimental breakthrough data appropriately. This is because Yoon-Nelson model follows experimental data closely from the beginning to the bed saturation. This is further supported by high linear regression coefficients obtained for Yoon-Nelson model compared to those of Bohart-Adams model (Table 2) at all variables studied. On its part, Bohart-Adams models appears to fit only the initial portion of the breakthrough profiles but deviates considerably as the adsorption proceeds towards saturation. This behaviour exposes its unsuitability in describing the entire column adsorption process. A summary of computed parameters from both models are listed in Table 2. Specifically, k_{YN} increased while τ decreased when the influent dye concentration was increased. The values of k_{BA} and N_0 in Adams-Bohart models were calculated and together with their correlation coefficients are given in Table 2. These values did not show any trend and they depended on individual variable. Validation of Adams-Bohart model has been found to be limited to the range of conditions used despite its simplicity and comprehensive approach in conducting and evaluating fixed-bed column tests.

CONCLUSION

This study evaluated the removal of Multi-Active-Blue (MAB) from aqueous solution in a fixed-bed set up packed with PPy/Fe₃O₄ adsorbent. The effect of different variables such as bed mass, influent flow rate and concentration on breakthrough time were investigated. Thereafter, the experimental data was used to calculate the fixed-bed adsorption performance while Yoon-Nelson and Adams-Bohart models were applied in predicting adsorber design parameters. Results showed that breakthrough time, t_b decreased at both high influent flow rates and initial dye concentration and increased with bed mass. At the studied conditions, the highest breakthrough time obtained was 690 min at

which 228 bed volumes were processed at 1.45 g/L AER. The correlation coefficients (R^2) suggested that Yoon-Nelson equation sufficiently described the MAB dye adsorption onto PPy/Fe₃O₄ in a fixed-bed configuration. According to the findings it was concluded that PPy/Fe₃O₄ nano-composite can effectively be applied as an adsorbent in a fixed-bed set up to continuously treat dye containing wastewater.

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Conflict of interest statement: The authors would like to state that there are no conflicts of interest in this manuscript.

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