Column Adsorption Studies of Textile Wastewater using Iron Oxide Nanoparticles doped Zeolite A

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ABSTRACT

In this work, iron oxide nanoparticles were doped on zeolite A (MZA) for treatment of textile wastewater via column adsorption studies. The physicochemical parameters of the wastewater were conducted using standard methods. The effects of bed heights, flow rates and inlet concentrations on the breakthrough curves were studied to examine the performance of the adsorbent. The column studies revealed that the exhaustion and breakthrough time increased with increase in bed height while they decreased with increase in flow rates and inlet concentrations. The maximum adsorption of the chemical parameters was 45.83 %, 53.09 %, 45.50 %, 54.23 %, 49.48 %, 34.63 % for chloride, cyanide, chemical oxygen demand (COD), biological oxygen demand (BOD), nitrite and total organic carbon (TOC) respectively at 5 cm bed height, 4 ml/min flow rate and 10 % inlet concentrations. The Thomas model was found to predict the breakthrough of the pollutants better than Adams-Bohart with high R^2 values of 0.882-0.978, 0.899-0.984 and 0.876-0.981 for bed height, flow rate and inlet concentrations accordingly. The presented results show that FeONP-ZA developed is suitable for textile wastewater.

Keywords: *chemical parameters, column studies, MZA, textile wastewater.*

1 INTRODUCTION

Textile industry is an important manufacturing process which involves various stages of dry and wet processes for the production of fabrics. The wet processes such as desizing, scouring, bleaching, mercerizing, dyeing and finishing are of great concern as they pose potential risk to the ecosystem (Tafesse et al., 2015). As a result of these aforementioned processes, large amount of wastewater is generated from textile industries which are not treated prior to its discharge into the surface water (Elango et al., 2017) despite the strict legislations by the governments of most countries. Textile waste waters are highly coloured, salty and contain non-biodegradable compounds; they are also high in BOD and COD, which make their treatments difficult (Tafesse et al., 2015). However, the high cost of the conventional adsorbent has been identified as one of the factors responsible for non-compliance to this legislation, adversely resulting to degradation of water quality. Thus, developing a low cost adsorbent from local material will be economical and sustainable alternative for textile wastewater treatment. This will treat or at least reduce the pollutants to permissible limits to obtain cleaner water, thereby; protecting the environment as well as ensuring healthy lives of human beings and the aquatic lives.

Adsorption has been recognized as a technology in wastewater treatment and has been successfully employed by many researchers (Bankole et al., 2017; Yusuf-Alaya, 2014; Dada et al., 2012; Piccin et al., 2011) in that regards. Similarly, nanotechnology has recently revealed high impacts on society and environment due to their various industrial applications, especially in water remediation and treatments (Balamurugan et al., 2014). Iron nanoparticles just like any other nanoparticles have much larger surface areas than bulk particles which make them applicable in water treatments. They can be synthesised and functionalized using various chemical functional group in order to increase their affinity towards target compound (Dhermendra et al., 2008). They have unique properties to develop high capacity and selective sorbents for metal ions and anions. Different nanomaterials can help to purify water through different mechanisms such as adsorption of pollutants, removal and inactivation of pathogens and transformation of toxic materials into less toxic materials (Gholamreza et al., 2014).

However, applying nanoparticles directly might result to aggregation in aqueous solution which consequently reduces their efficiencies (Girilal et al., 2015). Thus, loading nanoparticles within the pores of substrates such as mesoporous silica, zeolite, ceramics, activated carbon and chitosan have been reported to be efficient in wastewater/water treatments (Thamilselvi and Radha, 2017). Zeolites have been identified to be a potential support for nanoparticles due to their well-defined structures and microporous cavities (Kaya et al., 2013; Alfadul, 2007; Yamaura and Fungaro, 2013). Thus, doping iron oxide nanoparticles synthesized from biosynthesis route using mango leaf extract on the surface of synthesised zeolite A for treatment of textile waste water will eliminate the problem of nanoparticles agglomeration and environmental problem posed by bye-product of conventional treatment methods.

Even though several works have been conducted on wastewater treatments using batch adsorption mode (Bankole et al., 2017; Yusuf-Alaya, 2014; Dada et al., 2012; Piccin et al., 2011), however batch mode can only be used on laboratory scale. Thus, it is paramount to ascertain the applicability of the adsorbents using column/continuous adsorption mode (Tamilselvi and Asaithambi, 2015). More so, continuous studies can be used in treatment of large volume of wastewater, which has been useful and reliable in removal of pollutants from industrial wastewater (Biswas and Mishra, 2015).

This study therefore focuses on the green synthesis of iron oxide nanoparticles with mango leaves extract as the reducing agent. The synthesized nanoparticles was doped on the surface of zeolite A, developed from Ahoko kaolin for the treatment of textile wastewater using continuous process.

2 METHODOLOGY

The materials used, the synthesis of the iron oxide nanoparticles doped zeolite A (MZA) and the characterizations have been discussed in our conference paper (Alaya-Ibrahim *et al.*, 2018).

2.1 Collection and Characterization of the Textile Wastewater (TWW)

The textile wastewater used in this study was collected from Unique Tie and Dye textile Industry in Ilorin, Kwara State, Nigeria. The wastewater was analysed based on recommendations of standard methods of water and wastewater analysis at Regional Water Quality Laboratory, Federal Ministry of Water Resources, Minna, Niger State, Nigeria. The chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solid (TDS), alkalinity, the total amount of nitrate, nitrite, sulphate, phosphate, ammonium, chloride, cyanide and fluoride were determined by HACH instruments, USA using American Public Health Association (APHA, 2017) method. Other parameters investigated are Turbidity (Turbidity meter); pH (a multi-parameter analyser C3010); electrical conductivity (a multi-parameter analyser 2510B) and dissolved oxygen (dissolved oxygen meter).

2.2 Column Adsorption Studies

The column adsorption studies were carried out based on the work of Patel and Vashi, 2015 with little modifications. The study was carried out with the aid of a glass column of 3 cm internal diameter and a height of about 30 cm. The iron oxide nanoparticles doped zeolite A (MZA) was packed on the glass wool in the column which serves as a support to prevent it from flowing through the outlet while an improvised device was used in controlling the flow rate of the effluent from the tank into the glass column. Various parameters such as bed height, flow rate and inlet concentrations were studied at a predetermined interval. The effects of bed height were studied from 3 cm- 5 cm, the flow rate from 3 ml/min-5 ml/min while that of inlet concentration were in the range of 10 %-20 %. All the experiments were performed with 10 % inletl concentrations of the wastewater, 4 cm bed height of the MZA at a flow rate of 4 ml/min except those studies where bed heights, inlet concentrations and flow rates were studied accordingly. The initial and final concentrations of the parameters studied were obtained using HACH instruments in all cases. The schematic diagram of the experimental setup is given in the Figure 1

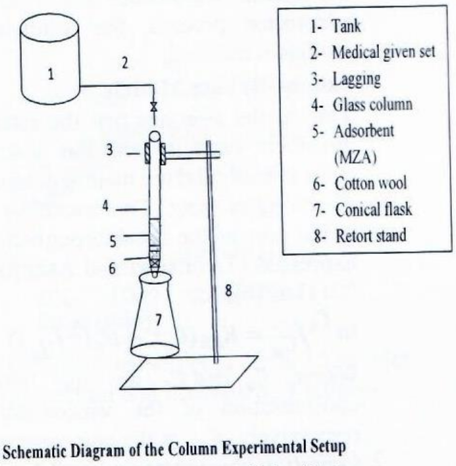

Figure 3.2 Schematic Diagram of the Column Experimental Setup

Figure 1: Schematic Diagram of the Column Experimental Setup

2.3 Mathematical Modeling of Column Studies

The various parameters associated with column adsorption studies were adopted from the work of Shadeera Rouf (2015) and were calculated as described thus;

Effluent volume $V = Qt_T$ (1)

Where the effluent volume in ml is V, Q is the flowrate in ml/min and t_T is the total flow time in min.

The maximum column bed capacity, q for the textile wastewater concentration and the influent flow rate was calculated using (2)

$$q_{max} = \frac{Q}{1000}\int_{t=0}^{t=t_T} C_{ad}dt \quad (2)$$

q_{max} is the maximum bed capacity in mg; C_{ad}, the adsorbed pollutants concentration in mg/L. The integral values were obtained from the area under the plot of C_{ad} versus time.

The maximum adsorption capacity at the exhaustion time was calculated using (3);

$$q_{exp} = {q_{max}}/{m} \quad (3)$$

The amount of the MZA in the column in (g) is m.
The total amount of pollutant concentration sent to the column M_T (mg) was obtained from (4);

$$M_T = \frac{C_o Q t_T}{1000} \quad (4)$$

C_o = The initial concentration of pollutants in mg/L
The percentage removals of the pollutants were calculated via (5);

$$\% \, removal = {q_{max}}/{M_T} \, x \, 100 \quad (5)$$

2.4 BREAKTHROUGH CURVE MODELLING

The breakthrough curves and times are very important in column adsorption studies as they are used in defining the operation and dynamic response of the study (Biswas and Mishra, 2015). In order to predict the breakthrough data for the textile wastewater for a successful design of the adsorption process, the following breakthrough curve models were used;

Adams-Bohart Models

This model assumes that the rate of adsorption, residual adsorbent capacity and the adsorbate concentration are proportional; and are mainly determined by the surface site of the adsorbents. This model is used in describing the initial part of the breakthrough curve and can be linearly expressed (Tamilselvi and Asaithambi, 2015: Trgo *et al.*, 2011) as (6);

$$ln \, {C_t}/{C_o} = K_{AB}(C_o t - N_o({Z}/{U_o})) \quad (6)$$

Where C_o *and* C_t are the initial concentration and concentration of the wastewater at time t in mg/L respectively, K_{AB} is the rate constant (L/mg.min), N_o is the saturation concentration (mg/L), t is flow time (min), Z is the bed height of the column (cm) and U_o is the superficial velocity.

Thomas Model

This is the most commonly used breakthrough model and it is used in calculating the maximum adsorption of the adsorbates by the adsorbents and the adsorption rate constant of the adsorption column. This is linearly expressed (Trgo *et al.*, 2011) as (7);

$$\ln \left[{C_o}/{C_t} - 1\right] = K_{TH} \frac{q_o}{Q}(m - V_o) \quad (7)$$

$K_{TH}$is the rate constant (ml/min.mg), q_o is the amount of pollutants adsorbed per gram of adsorbent (mg/g) and m is the amount of adsorbent used for the column adsorption (g). K_{TH} and q_o are obtained from the plot of $\ln \left[{C_o}/{C_t} - 1\right]$ versus V_o.

3 RESULTS AND DISCUSSION

3.1 PHYSICOCHEMICAL ANALYSIS OF TEXTILE WASTEWATER

The physicochemical parameters, heavy metals and methylene blue analyses (before and after treatment) were conducted on the local textile wastewater and the results with their various permissible limits based on WHO/EPA and NIS are presented in Table 1;

According to the presented results in Table 1, the colour, and turbidity concentration of the textile wastewater was 124620 TCU and 7638 NTU respectively. This is due to the different types of dyes used in imparting colour to the fabrics during production (Elango *et al.*, 2017). Colour is easily noticed to human eyes even in small amount, which is not desirable. Moreover, they alter the photosynthesis in plants and affect the growth of bacteria (Sanni *et al.*, 2016). However, after treatment with MZA, the colour reduced to 120 TCU while the turbidity reduced to 75 NTU respectively. The values of turbidity and colour obtained after treatment are higher than those sets by WHO/EPA/NIS (see Table 1) for drinking water. This might be due to the very high concentrated wastewater treated and as it is known that the rate of removal of pollutant also depends on its initial concentrations (Margata *et al.*, 2013). Nonetheless, the developed adsorbent removed 99.02 % and 99.9 % % for turbidity and colour accordingly.

The total dissolved solid of the raw water was 36723 mg/L which reduced to 500 mg/L; while the electrical conductivity was 54810 mg/L and reduced to 860 mg/L after treatment. These values conformed well to the standard set by WHO/EPA /NIS (see Table 1).

TABLE 1:PHYSICOCHEMICAL PARAMETERS OF WATER AT 5 CM BEDHEIGTS, 10 % INLET CONCENTRATIONS AND 4 ML/MIN FLOWRATE

Physicochemical Parameters	Raw Value	Treatment with MZA	Standard limits (WHO/ EPA)	Standard limit (NIS)
Colour (TCU)	124620	120	20/100	15
pH	11.4	8.5	6.5-8.5/6.5-9.5	6.5-8.5
TDS (mg/L)	36723	500	1000/-	500
Conductivity ($\mu S/cm$)	54810	860	-/1000	1000
Dissolved oxygen (mg/L)	2.65	4.25	-	-
Turbidity (NTU)	7638	75	5.0	5.0
Total alkalinity (mg/L)	16443	380	-/400	-
Nitrate (mg/L)	1804	20.0	50/50	50
Ammonium (mg/L)	276	3.5	1.3-3.5/ 0.2-4.0	-
Chloride (mg/L)	9711	31.0	250/250	250
Phosphate (mg/L)	113	0.5	-/0.5-0.7	-
Cyanide (mg/L)	22.2	0.01	-/0.05	0.01
Fluoride (mg/L)	226	1.48	1.5/1.7	1.5
Sulphate (mg/L)	7111	25	500/250	100
COD (mg/L)	31044	36.7	-/40	-
BOD (mg/L)	6287	2.35	-/5.0-7.0	-
TOC (mg/L)	2990	20	-	5.0
Carbonate (mg/L)	780	20	-	-
Nitrite (mg/L)	21.9	0.04	3.0/5.0	0.2
Iron (mg/L)	3.6477	0.0549	-/0.3	0.2
Chromium (mg/L)	0.1240	0	0.05/0.05	0.05
Nickel (mg/L)	0.0045	0	0.07/0.02	0.02
Zinc (mg/L)	1.1476	0	-/3	-
Lead (mg/L)	0.0748	0	0.01/0.01	0.01
Cadmium (mg/L)	0.5431	0	0.003	0.005
Copper (mg/L)	2.1347	0.0057	2/1	2
Manganese (mg/L)	0.0128	0	-/0.2	0.05

Key: World Health Organization (WHO, 2011), Environmental Protection Agency (EPA, 2001) , Nigerian Industrial Standards (NIS, 2007)

The chemical inorganic parameters studied are nitrate, nitrite, ammonium, phosphate, cyanide, chloride, fluoride and sulphate. The values of nitrite, nitrate and ammonium were 21.9 mg/L, 1804 mg/L and 276 mg/L , which were reduced to 0.04 mg/L, 20 mg/L and 3.5 mg/L accordingly. Whilst that of sulphate, fluoride, chloride, cyanide, and phosphate were 7111 mg/L, 225 mg/L, 9711 mg/L, 22.2 mg/L, 113 mg/L, which were reduced to 25 mg/L, 1.48 mg/L, 31 mg/L, 0.01 mg/L, 0.5 mg/L and 25 mg/L accordingly, after having contact with the developed adsorbent in the column. This is evident that the pollutants were able to diffuse into the pores of the MZA and did not clog it (Zainal Abadin *et al*., 2017). These values correlated well with all the standards, suggesting that the treated water can be used for drinking and other purposes (WHO, 2011; EPA, 2001; NIS, 2007).

The organic contents of the textile wastewater were also examined before and after passing through the columns and the results are presented in Table 1. As presented in the table, the dissolved oxygen, COD, BOD and TOC were 2.65 mg/L, 31044 mg/L, 6287 mg/L and 2990 mg/L which were brought to 4.25 mg/L, 36.7 mg/L, 2.35 mg/L and 20 mg/L accordingly. They all conformed to all the standards except for the TOC which is slightly above the standard set by NIS for drinking water as WHO/EPA did not see it as a factor of concern in drinking water. This might be due to the fact that TOC is the measure of total carbon in organic compounds in aqueous system and carbon has the ability to form complex molecules with the structural iron present in the MZA, thereby making its binding onto the surface of MZA not as fast as others (Pouran *et al*., 2014).

The heavy metals investigated on the raw textile wastewater include; Fe, Cr, Ni, Zn, Pb, Cd, Cu and Mn. These were treated with MZA and the obtained results are presented in Table 1. The Fe concentration in the effluent was 3.6477 mg/L, which was above all the permissible limit by WHO/EPA/NIS of the range of 0.2-0.3 mg/L According to Cadmus *et al*., (2018), the concentration of iron above 1 mg/L can damage the gills of fishes and the toxicity depends on the species and size of the fish (Cadmus *et al*., 2018). Thus, consuming these fishes has detrimental effects on the consumers. However, this was reduced to 0.0549 mg/L which conformed well to all the standards (WHO, 2011; EPA, 2001; NIS, 2007). The Chromium was 0.1240 mg/L which was reduced to a value below detectable limits (see Table 1). Exposure to chromium can cause allergic reactions, nose irritation, kidney and liver damage and long term effects can lead to death (Oliveira, 2012).

The copper content of the effluent was 2.1347 mg/L and this was reduced to 0.0057 mg/L after treatment. Whilst the concentration of lead and cadmium were 0.0748 mg/L and 0.5431 mg/L respectively which were found to be undetected after treatment with MZA. This is an indication that these metals were completely removed and as such compared well with the standards. Acute exposure to both lead and cadmium causes pulmonary and gastrointestinal disease, brain and kidney damages (Mahino *et al*., 2014; Oliveira, 2012).

All the heavy metals treated conformed to all the standards (see Table 1), the efficient removal of these pollutants by MZA is attributed to the isomorphical substitution of Fe in the magnetite by these metals. More so, this adsorbent has octahedral sites at the surface of the crystal structure, which made binding easier (Uddin, 2017). Therefore, the treated water can be used for drinking and other domestic purposes.

3.1.1 EFFECTS OF BEDHEIGHTS ON BREAKTHROUGH CURVE

The results of effects of bed height on the breakthrough curves of the chemical parameters are presented in Figure 2;

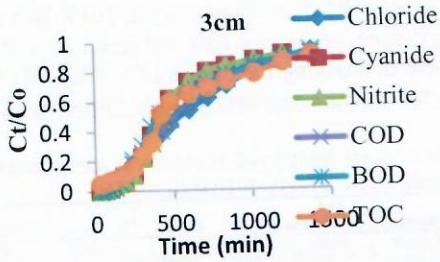

Figure 2a: Effect of Bedheight at 3 cm, 10 % inlet concentration and flowrate of 4 ml/min

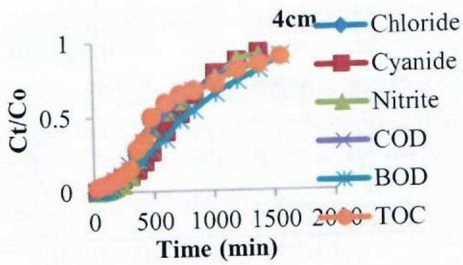

Figure 2b: Effect of Bedheight at 4 cm, 10 % inlet concentration and flowrate of 4ml/min

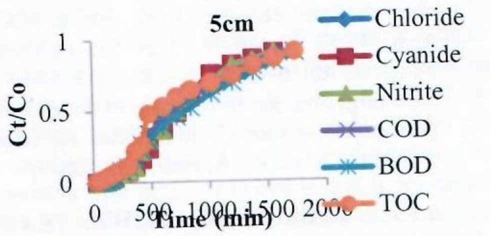

Figure 2c: Effect of Bedheight at 3 cm, 10 % inlet concentration and flowrate of 4 ml/min

From the presented results, it is evident that increase in bed height resulted to increase in breakthrough time as well as exhaustion time. For instance, the breakthrough time and exhaustion time of chloride, COD, BOD and TOC increased from 180-300 minutes and 1380-1740 minutes with increase in bed height from 3 cm to 5 cm respectively. Whilst that of cyanide and nitrite increased from 240-360 minutes and 1200-1560 min respectively for breakthrough and exhaustion time respectively. It can also be observed that the chloride, COD, BOD and TOC with higher concentration reached the breakthrough time earlier than cyanide and nitrite with lower concentration; this might be due to the fact that increase in concentration affects the saturation rate which consequently reduced the breakthrough time of these pollutants (Rouf and Nagapadma, 2015). This observation can be attributed to the fact that increase in bed height gave rise to more contact between the MZA and the contaminants due to higher dosage of MZA in the bed, thus, increasing the adsorption efficiency (Rouf and Nagapadma, 2015; Han *et al.*, 2009). The column adsorption data and parameters obtained in the course of studying the effects of bed height on removal of chemical parameters and MB are shown in Table 2

TABLE 2:EXPERIMENTAL DATA OF COLUMN STUDIES WITH RESPECT TO DIFFERENT BED HEIGHTS

Parameters	Chloride	CN	COD	BOD	Nitrite	TOC
	3cm					
$V\,(mg)$	5520	4800	5520	5520	4800	5520
$q_{max}(mg)$	23376.75	43.36	72003.18	13196.08	42.53	5137.8
$q_{exp}(\frac{mg}{g})$	1948.06	3.61	6000.27	1099.67	3.54	428.15
$M_T\,(mg)$	53604.72	106.56	171362.9	34704.41	105.12	16504.8
$\%\ removal$	43.61	40.69	42.02	38.02	40.56	31.13
	4cm					
$V\,(mg)$	6240	5520	6240	6240	5520	6240
$q_{max}(mg)$	26775.53	62.023	84575.39	20187.81	57.06	6047.40
$q_{exp}(\frac{mg}{g})$	1673.47	3.88	5285.96	1261.74	3.57	377.96
$M_T\,(mg)$	60596.64	122.54	193714.60	39230.88	120.89	18657.6
$\%\ removal$	44.19	50.61	43.66	51.46	47.20	32.41
	5cm					
$V\,(mg)$	6240	5520	6240	6240	5520	6240
$q_{max}(mg)$	30973.42	73.54	98316.35	23730.01	67.62	7206.6
$q_{exp}(\frac{mg}{g})$	1548.67	3.68	4915.82	1186.50	3.38	360.33
$M_T\,(mg)$	67588.56	138.53	216066.20	43757.52	136.66	20810.40
$\%\ removal$	45.83	53.09	45.50	54.23	49.48	34.63

According to Table 2, increase in bed height resulted to increase in amount of contaminants adsorbed as well as the percentage removal in all cases; the percentage removal of chloride, cyanide, COD, BOD, nitrite, TOC increased from 43.61-45.83 %, 40.69-53.09 %, 42.02-45.50 %, 38.02-54.23 %, 40.56-49.48 % and 31.13-34.63 % respectively. This might be due to increase in the quantity of the MZA, giving rise to more binding sites for adsorption (Lopez-Cervantes *et al.*, 2018; Han *et al.*, 2009)

3.1.2 EFFECTS OF FLOWRATE ON BREAKTHROUGH CURVE

The results of effects of flow rate on the breakthrough curves of the chemical parameters and MB are presented in Figure 3;

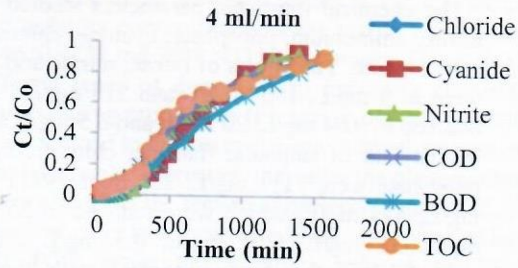

Figure 3a: Effect of Flow rate at 4 ml/min, 10 % concentration and bed height of 4cm

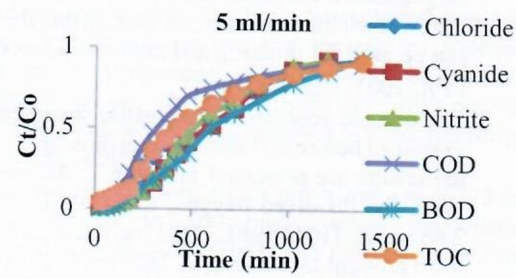

Figure 3b: Effect of Flow rate at 5 ml/min, 10 % concentration and bed height of 4cm

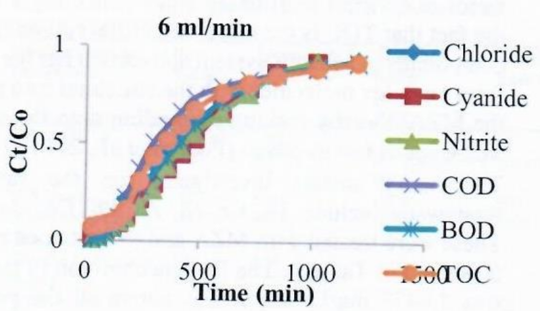

Figure 3c: Effect of Flow rate at 6 ml/min, 10 % concentration and bed height of 4cm

The results as presented in Figure 3 show that increase in flow rate consequently brought about decrease in breakthrough and exhaustion time. The breakthrough time and exhaustion time of chloride, COD, BOD and TOC reduced from 240-150 minutes and 1560-1200 min respectively, when the flow rate was increased from 4 ml/min to 6 ml/min. whilst that of cyanide and nitrite are 300 -150 min and 1380-1020 min. This observation is attributed to the MZA getting saturated faster as the flow rate increased (Lopez-Cervantes *et al.*, 2018; Patel and Vashi, 2015).
The column adsorption data and parameters obtained in the course of studying the effects of flow rate on removal of chemical parameters as shown in Table 3;

TABLE 3: EXPERIMENTAL DATA OF COLUMN STUDIES WITH RESPECT TO FLOW RATE

Parameters	Chloride	CN	COD	BOD	Nitrite	TOC
	4 ml/min					
V (ml)	6240	5520	6240	6240	5520	6240
q_{max} (mg)	26775.53	62.0	84575.39	20187.81	57.06	6047.40
$q_{exp}(\frac{mg}{g})$	1673.47	3.88	5285.96	1261.74	3.57	377.96
M_T (mg)	60596.64	122.54	193714.60	39230.88	120.89	18657.6
% removal	44.19	50.61	43.66	51.46	47.20	32.41
	5 ml/min					
V (ml)	6900	6000	6900	6900	6000	6900
q_{max} (mg)	25348.63	61.76	68285.73	18950.24	56.64	5955
$q_{exp}(\frac{mg}{g})$	1584.29	3.86	4267.86	1164.39	3.54	372.19
M_T (mg)	67005.9	127.42	214203.6	40157.32	121.78	20631
% removal	37.83	48.47	31.88	47.19	46.51	28.86
	6 ml/min					
V (mg)	7200	6120	7200	7200	6120	7200
q_{max} (mg)	24923.04	61.58	67868.23	17080.39	56.32	5796
$q_{exp}(\frac{mg}{g})$	1557.69	3.84	4241.77	1067.52	3.52	362.25
M_T (mg)	67487.25	135.86	223516.8	45266.4	122.89	21528
% removal	36.93	45.83	30.36	37.73	45.83	26.92

With respect to Table 3, it is evident that increase in flow rate led to subsequent reduction in maximum adsorption of contaminants(q_{max}), the uptake capacity of the contaminants by MZA(q_{exp}) and percentage removal in all cases. The percentage removal of chloride, cyanide, COD, BOD, nitrite and TOC reduced from 44.16 %, 50,61 %, 43.66 %, 51.46 %, 47.20 %, 32.41 %, 49.40 % to 36.93 %, 45.83 %, 30.36 %, 37.73 %, 45.83 % and 26.92 % respectively with increase in flow rate from 4 ml/min to 6 ml/min. This is because as the flow rate increase, the mass transfer rates also increase which consequently lead to faster saturation of the MZA. Similar effect was observed in literature (Lopez-Cervantes *et al.*, 2018; Han *et al.*, 2009).

3.1.3 EFFECTS OF INLET CONCENTRATIONS ON THE BREAKTHROUGH CURVE

According to the presented results, the breakthrough time and exhaustion time of the pollutants reduced with increase in the inlet concentrations of the textile wastewater. The breakthrough time and exhaustion time of chloride, COD, BOD, TOC reduced from 240-150 min and 1560-1200 min accordingly when the inlet concentration was increased from 10 % to 20 %. Whilst that of cyanide and nitrite decrease from 300 min to 180 min, in order to attain the breakthrough; and 1380-1200 min to get exhausted. These results demonstrated that the breakthrough time and saturation rate are greatly influenced by change in concentration (Chowdhurry *et al.*, 2013). This is because of more active sites coverage as the concentration increased which consequently increase the rate of exhaustion. More so, more volume of effluent can be treated with decrease in inlet concentration as a result of slower transport of mass transfer reduction (Lopez-Cervantes *et al.*, 2018). The column adsorption parameters are presented in Table 4;

TABLE 4: EXPERIMENTAL DATA OF COLUMN STUDIES WITH RESPECT TO INLET CONCENTRATION

Parameters	Chloride	CN	COD	BOD	Nitrite	TOC
	10 %					
V (ml)	6240	5520	6240	6240	5520	6240
q_{max}(m	26775	62.0	84575.	20187.81	57.0	6047
$q_{exp}(\frac{mg}{g}$	1673.47	3.88	5285.96	1261.74	3.57	377.96
M_T (mg)	60596.64	122.54	193714.60	39230.88	120.89	18657.6
% remo	44.19	50.61	43.66	51.46	47.20	32.41
	15 %					
V (ml)	5520	4800	5520	5520	4800	5520
q_{max}(m	27463.05	62.42	86243.46	20708.88	58.18	6115.2
$q_{exp}(\frac{mg}{g}$	1716.44	3.91	5390.22	1294.31	3.64	382.2
M_T (mg)	61645.15	122.54	185928.7	39882.55	120.91	13137.6
% remo	44.55	50.93	46.39	51.92	48.11	46.55
	20 %					
V (ml)	4800	4080	4800	4800	4080	4800
q_{max}(m	27964.22	64.22	90843.19	21143.95	58.60	6221.4
$q_{exp}(\frac{mg}{g}$	1747.76	4.01	5677.70	1321.50	3.66	388.84
M_T (mg)	55935.35	116.85	178813.4	37920	111.30	12384
% remo	49.99	54.96	50.80	55.76	52.65	50.24

With respect to Table 4.29, it can be deduced values of q_{max} and q_{exp} increased as the initial concentration increased in all cases. However, the volume of effluent reduced with increase in concentration. This is due to the faster transport of molecules as the concentration increased resulting to treatment of less effluent (Han *et al.*, 2009).

3.2 MODELING OF COLUMN ADSORPTION STUDIES

Three models (Adams-Bohart, Thomas and Yoon-Nelson) were used in studying the column adsorption behaviour through the estimation of the kinetic model of the column as well as the breakthrough curve.

3.2.1 ADAMS-BOHART MODEL

The initial part of breakthrough curve was investigated through the application of Adams-Bohart model to experimental data. Using linear regression analysis on the breakthrough curves, the values of kinetic constants K_{AB} and maximum adsorption capacity N_o were estimated and presented in Tables 5-7. According to Table 5, there was no substantial changes in the values of K_{AB} when the bed depth was increased from 3-5 cm, however the values of N_o decreased with increase in bed height in all cases. The N_o values of chloride, cyanide, COD, BOD, nitrite and TOC from 3-5 cm are 1902.32-1454.47 mg/L, 3.66-2.97 mg/L, 5960.55-4551.53 mg/L, 1172.41-1016.02 mg/L, 3.61-2.93 mg/L and 600.09-467.23 mg/L respectively. In addition, the K_{AB} (see Table 6) for chloride, cyanide, COD increased with increase in flow rate while that of BOD, TOC, decreased and no significant change in the value of

K_{AB} for nitrite. Nonetheless, the N_o values increased in all cases with increase in flow rate as presented in Table 6. Furthermore, the values of K_{AB} reduced with increase in concentration while that of N_o increased when the concentration was increased from 10 % to 20 % as shown in Table 7. It can be observed from these results that the N_o increased with increase in flow rates and concentrations, while it decreased with bed height. This is because N_o is also related to saturation concentration (Biswas and Mishra, 2015) and as such observation is expected.

Although, Adams-Bohart model is based on assumption that the equilibrium is instantaneous and the adsorption rate is proportional to adsorption capacity remaining on the adsorbents (Tamilselvi and Asaithambi, 2015: Trgo et al., 2011). However, this model cannot be used to describe the experimental data in the present study due to the low R2 (0.550-0.878) values obtained in all cases.

TABLE 5: ADAMS BOHART PARAMETERS AT BEDHEIGHTS OF 3-5 CM, 10 % INITIAL CONCENTRATION AND FLOWRATE 0F 4 ML/MIN

Contaminants	$K_{AB}(\frac{L}{mg}/min)$	$N_o\,(mg/L)$	R^2
3 cm			
Chloride	$3.4x10^{-4}$	1902.32	0.649
Cyanide	$1.85x10^{-1}$	3.66	0.689
COD	$1.13x10^{-4}$	5960.55	0.622
BOD	$5.73x10^{-4}$	1172.41	0.572
Nitrite	$1.87x10^{-1}$	3.61	0.691
TOC	$7.69x10^{-4}$	600.09	0.764
4 cm			
Chloride	$3.3x10^{-4}$	1593.28	0.674
Cyanide	$1.71x10^{-1}$	3.32	0.754
COD	$1.03x10^{-4}$	5120.55	0.623
BOD	$5.25x10^{-4}$	1077.13	0.641
Nitrite	$1.83x10^{-1}$	3.24	0.729
TOC	$7.69x10^{-4}$	507.50	0.755
5 cm			
Chloride	$2.99x10^{-4}$	1454.47	0.692
Cyanide	$1.71x10^{-1}$	2.97	0.693
COD	$1.00x10^{-4}$	4561.53	0.632
BOD	$5.09x10^{-4}$	1016.02	0.616
Nitrite	$1.69x10^{-1}$	2.93	0.724
TOC	$7.79x10^{-4}$	457.23	0.705

TABLE 6: : ADAMS-BOHART PARAMETERS AT FLOW RATES OF 4-6 ML/MIN, 10 % INITIAL CONCENTRATION AND BED HEIGHT OF 4 CM

Contaminants	$K_{AB}(\frac{L}{mg}/min)$	$N_o\,(mg/L)$	R^2
4 ml/min			
Chloride	$3.3x10^{-4}$	1593.28	0.679
Cyanide	$1.71x10^{-1}$	3.32	0.754
COD	$1.03x10^{-4}$	5120.55	0.623
BOD	$5.25x10^{-4}$	1077.13	0.641
Nitrite	$1.83x10^{-1}$	3.24	0.729
TOC	$7.69x10^{-4}$	507.50	0.755
5 ml/min			
Chloride	$3.09x10^{-4}$	1709.15	0.568
Cyanide	$1.40x10^{-1}$	3.79	0.844
COD	$8.05x10^{-5}$	5434.79	0.550
BOD	$5.40x10^{-4}$	1168.39	0.681
Nitrite	$1.69x10^{-1}$	3.54	0.801
TOC	$7.36x10^{-4}$	559.11	0.720
6 ml/min			
Chloride	$3.09x10^{-4}$	1826.30	0.624
Cyanide	$1.58x10^{-1}$	3.81	0.825
COD	$9.34x10^{-5}$	5630.67	0.605
BOD	$5.56x10^{-4}$	1150.17	0.614
Nitrite	$1.83x10^{-1}$	3.66	0.755
TOC	$8.03x10^{-4}$	571.63	0.734

TABLE 7: ADAMS-BOHART PARAMETERS AT INITIAL CONCENTRATION OF 10-20 %, FLOW RATE OF 4 ML/MIN AND BED HEIGHT OF 4 CM

Contaminants	$K_{AB}(\frac{L}{mg}/min)$	$N_o\,(mg/L)$	R^2
10 %			
Chloride	$3.3x10^{-4}$	1593.28	0.679
Cyanide	$1.71x10^{-1}$	3.32	0.754
COD	$1.03x10^{-4}$	5120.55	0.623
BOD	$5.25x10^{-4}$	1077.13	0.641
Nitrite	$1.83x10^{-1}$	3.24	0.729
TOC	$7.69x10^{-4}$	507.50	0.755
15 %			
Chloride	$3.0x10^{-4}$	1647.75	0.65
Cyanide	$1.57x10^{-1}$	3.40	0.77
COD	$9.5x10^{-5}$	5422.29	0.636
BOD	$4.98x10^{-4}$	1079.46	0.622
Nitrite	$1.59x10^{-1}$	3.50	0.719
TOC	$1.05x10^{-4}$	520.46	0.79
20 %			
Chloride	$2.83x10^{-4}$	1663.07	0.649
Cyanide	$1.47x10^{-1}$	3.44	0.814
COD	$8.32x10^{-5}$	5865.56	0.60
BOD	$4.68x10^{-4}$	1084.16	0.653
Nitrite	$1.47x10^{-1}$	3.63	0.756
TOC	$1.0x10^{-4}$	536.91	0.798

3.2.2 THOMAS MODEL

The column adsorption data was also fitted with the Thomas model to establish the behaviour of the contaminants breakthrough with respect to MZA. The Thomas rate constant K_{TH} and q_o were evaluated from the slope and intercept of plots of $\ln(\frac{C_t}{C_o} - 1)$ against volume as presented in Table 8-10.

With respect to Table 8, increase in bed height from 3 cm to 5 cm, brought a corresponding decrease in the values of K_{TH} as well as the q_o. This result is in agreement with that obtained by Nwabanne and Igbokwe, (2012). On the other hand, the K_{TH} increased while the q_o decreased with increasing flow rates (see Table 9). The K_{TH} reduced, while the q_o increased with increase in inlet concentrations. These results are in line with literature (Lopez-Cervantes *et al.*, 2018; Nwabanne and Igbokwe, 2012). The high R^2 values (0.882-0.978), (0.899-0.994), (0.876-0.981) for bed heights, flow rate and inlet concentrations accordingly shows the provision of good correlation between the experimental and calculated data. Hence, this model can be used to predict the breakthrough curve of the pollutants.

TABLE 8: THOMAS PARAMETERS AT DIFFERENT BED HEIGHTS OF 3-5 CM, 10 % INITIAL CONCENTRATION AND FLOW RATE OF 4 ML/MIN

Contaminants	$K_{TH}(\frac{ml}{min}.mg)$	$q_o(mg/g)$	R^2
3 cm			
Chloride	1.03x10^{-3}	1352.68	0.933
Cyanide	0.5063	2.79	0.933
COD	3.33x10^{-4}	4306.01	0.913
BOD	1.73x10^{-3}	831.95	0.882
Nitrite	0.5151	2,74	0.935
TOC	2.52x10^{-3}	385.81	0.967
4 cm			
Chloride	9.1x10^{-4}	1277.34	0.950
Cyanide	0.4450	2.77	0.974
COD	2.90x10^{-4}	4045.29	0.920
BOD	1.39x10^{-3}	886.26	0.910
Nitrite	0.4749	2.69	0.962
TOC	2.31x10^{-3}	370.88	0.978
5 cm			
Chloride	8.90x10^{-4}	1102.78	0.959
Cyanide	0.4180	2.70	0.941
COD	2.85x10^{-4}	3449.04	0.930
BOD	1.37x10^{-3}	784.09	0.916
Nitrite	0.4475	2.44	0.965
TOC	2.27x10^{-3}	350.36	0.966

TABLE 9: THOMAS PARAMETERS AT DIFFERENT FLOW RATES OF 4-6 ML/MIN, 10 % INLET CONCENTRATION AND BED HEIGHT OF 4 CM

Contaminants	$K_{TH}(\frac{ml}{min}.mg)$	$q_o(mg/g)$	R^2
4 ml/min			
Chloride	9.1x10^{-4}	1277.34	0.950
Cyanide	0.4450	2.77	0.974
COD	2.90x10^{-4}	4045.29	0.920
BOD	1.39x10^{-3}	886.26	0.910
Nitrite	0.4749	2,69	0.962
TOC	2.31x10^{-3}	370.88	0.978
5 ml/min			
Chloride	1.35x10^{-3}	1126.91	0.912
Cyanide	0.5495	2.67	0.991
COD	3.56x10^{-4}	3177.76	0.899
BOD	2.18x10^{-3}	820.38	0.960
Nitrite	0.6370	2.62	0.991
TOC	3.53x10^{-3}	331.92	0.973
6 ml/min			
Chloride	1.34x10^{-3}	976.78	0.934
Cyanide	0.5865	2.29	0.994
COD	4.09x10^{-4}	2943.51	0.910
BOD	2.20x10^{-3}	569.86	0.934
Nitrite	0.6493	2.30	0.974
TOC	3.73x10^{-3}	282.65	0.969

TABLE 10: THOMAS PARAMETERS AT DIFFERENT INLET CONCENTRATIONS OF 10 %-20 %, FLOW RATE OF 4 ML/MIN AND BED HEIGHT OF 4 CM

Contaminants	$K_{TH}(\frac{ml}{min}.mg)$	$q_o(mg/g)$	R^2
10 %			
Chloride	9.1x10^{-4}	1277.34	0.950
Cyanide	0.4450	2.77	0.974
COD	2.90x10^{-4}	4045.29	0.920
BOD	1.39x10^{-3}	886.26	0.910
Nitrite	0.4749	2,69	0.962
TOC	2.31x10^{-3}	370.88	0.978
15 %			
Chloride	7.99x10^{-4}	1363	0.929
Cyanide	0.367	3.08	0.965
COD	2.68x10^{-4}	4166.89	0.917
BOD	1.21x10^{-3}	950.05	0.886
Nitrite	0.3970	2.96	0.950
TOC	2.85x10^{-3}	393.25	0.981
20 %			
Chloride	7.1x10^{-4}	1374.12	0.916
Cyanide	0.316	3.27	0.965
COD	2.3x10^{-4}	4430.82	0.878
BOD	1.06x10^{-3}	996.97	0.879
Nitrite	0.362	3.02	0.961
TOC	2.63x10^{-3}	412.17	0.981

4 CONCLUSION

In the studies, iron oxide nanoparticles synthesized using mango leaf extract as a reducing agent was doped on zeolite A and used for treatment of textile wastewater, the following were deduced;

- Biosynthesis of iron nanoparticles was carried out with mango leaf extract as a reducing agent and the synthesized FeONPs was doped onto the surface of zeolite A to produce Nano adsorbents (MZA) for textile wastewater treatment via column studies.
- The column studies showed that the exhaustion and breakthrough time were influenced by increase in bed height, flow rates and inlet concentrations; and the breakthrough time and exhaustion time increased with increase in bed height while they decreased with increase in flow rates and inlet concentrations. The percentage removal of chemical parameters increased with increase in bed heights and inlet concentrations and decreased with increase in flow rates. The maximum adsorptions of the chemical parameters by MZA are 45.83%, 53.09 %, 45.50 %. 54.23 %, 49.48 % and 34.63 % for chloride, cyanide, COD, BOD, Nitrite and TOC accordingly, at 5 cm bed heights, 4ml/min flow rates and 10 % in let concentrations. The Thomas model was found to predict the breakthrough of the pollutants better than Adams-Bohart with R^2 values (0.882-0.978), (0.899-0.994), (0.876-0.981) for bed heights, flow rate and inlet concentrations respectively. This shows the provision of good correlation between the experimental and calculated data.

Thus, It can be informed from various analysis conducted that the developed adsorbent is suitable for textile wastewater treatments

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