Fixed-Bed Column Breakthrough Analysis for the Removal of Reactive Red 2 dye from Aqueous Solution using Zeolite-polyaniline Nanocomposite

Jacob Ochieng Kittinya, Maurice Stephen Onyango, and Aoyi Ochieng

***Abstract*—**This study investigated the performance of zeolite-polyaniline nanocomposite (ZPC) in the removal of Reactive Red 2 (RR2) dye from aqueous solution in a fixed-bed adsorption column. This work evaluated the effect of column aspect ratio, bed loading, flow velocity and initial concentration on the RR2 dye removal efficiency. The concentration-time profile of the treated effluent stream was expressed as breakthrough curves (BTC). The BTCs showed a steep slope with a short tail, characteristic of rapid surface reaction and dispersion effects, respectively. The adsorbent media had a dynamic adsorption capacity of 68 mg/g (at 5 mL/ min, 298 K and 100 mg/L RR2) that is quite competitive in comparison to other adsorbents.

***Keywords*—**Breakthrough, dye, wastewater, zeolite-polyaniline.

I. Introduction

TEXTILE industries consume large amounts of water, dyestuff and chemical additives within their fabric dyeing and finishing operations. In particular azo-group containing dyes are most popular in the textile fabric dyeing industries due to their resistance to light and oxygen [1]. However, most of these chemicals (dyestuff and additives such as starch, surfactants) are not wholly consumed and as such end up in the effluent streams. Moreover, the residual dyes found in these discharge streams are refractory, non-biodegradable and toxic in nature [2]. Discharge of such streams into natural water resources has a major environmental impact on the biota of the receiving water body. It is therefore imperative to treat these effluent streams prior to discharge into water bodies.

A number of remedial strategies have been explored in an attempt to mitigate the adverse environmental and human health effects resulting from the disposal of the textile dye wastewaters. These include treatment technologies such as adsorption, biological, chemical precipitation, ion exchange and membrane processes. Biological method is commonly used for treatment of organic wastewaters like textile dye and distillery effluent streams [3]. However some of the organic compounds found in these wastewater streams are hardly biodegradation or/and toxic effects on microbial processes. As a result, alternative physical and/or physical-chemical decolorization processes such as coagulation [4], membrane-filtration [5], ion exchange [6] and adsorption [7] have been explored. Among these techniques, adsorption is regarded as the most effective due to its simplicity, ease of operation and ability to remove pollutants to very low concentration levels in the effluent streams. In this regard, adsorbents such activated carbon [8]-[9], biosorbents, metal oxides, waste-derived sorbents such as fish scales [10], chitosan beads [11], clay [12], have been tested for the removal of RR2 dye from textile dye effluents. Most of the above-mentioned adsorbents are either expensive or have low removal capacity for RR2 dye. In an attempt to address these challenges, this study seeks to utilize natural zeolite, a material that is locally available in large deposits in South Africa and is also relatively cheap. However, natural zeolite exhibits low affinity for organics and anions [13] and has to be modified in order to enhance its removal capacity for organics. Recent studies have shown that surface modification of zeolite using certain organic surfactants improves their removal capacities for organic and anionic contaminants [14]. Armagan et al. [7] reported that the removal of reactive azo dyes was significantly improved by using zeolite treated with HDTMA-Br. Other researchers have investigated the application of polymers for the removal of dye from water and wastewater. Polypyrrole-polyaniline (PPy-PANI) nanofibers was used for the removal of Congo red dye from aqueous solution [15] and a polyaniline-clinoptilolite was used in the removal of methyl orange from aqueous solution [16].

The main objective of this study is to evaluate the performance of a conducting polymer modified zeolite as an adsorbent for the removal of RR2 in a fixed-bed mode. Even though, zeolite-polyaniline have been tested successfully for the removal of anionic dyes from aqueous solutions, their use as nanoadsorbents for the removal of RR2 dye in fixed-bed column has not been explored to date. Moreover, the data generated from such dynamic column studies can be as a benchmark to scale-up for industrial applications.

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II. MATERIALS AND METHODS

A. Materials

Natural clinoptilolite was purchased from Pratley Industries Ltd, Durban South Africa. Aniline (99.5% ACS reagent), ammonium persulfate (APS) were purchased from Sigma Aldrich, South Africa. Hydrochloric acid 32 % (w/v) was purchased from Merck, South Africa. All other chemical reagents used were of analytical grade.

Zeolite-polyaniline (ZPC) nanocomposite was synthesized via an in situ chemical oxidative polymerization using the method described elsewhere [17]. In brief, 10 mL of aniline and 10 mL of 32% (v/w) HCL were added to 120 mL of deionized water contained in a 400 mL glass beaker. This mixture was stirred for 5 min to allow for dissolution of aniline after which 10.22 g of clinoptilolite (150 – 300 microns) was added to the glass beaker. An aqueous solution (80 mL) containing a given amount of ammonium persulfate (APS) was then added dropwise into the zeolite/aniline mixture while stirring for 24 h. The dark green precipitate obtained was filtered through a Whatman filter paper No. 42 using deionized water and acetone/methanol sequentially to remove the excess aniline monomer and oligomers. The residue on the filter was finally dried in vacuo at 60 °C for 3 h. The above method was used in synthesizing ZPC variants having weight ratios of zeolite to aniline of 1, 2, 5, and 10. The nanocomposite obtained were designated as ZPC-1, ZPC 2, ZPC-5 and ZPC-10, respectively. In each of the synthesis method, a molar ratio of APS to aniline was maintained at 1.25 with a fixed amount of zeolite at 10.22 g. As a control, a sample of pure polyaniline (PANI) was prepared using the above method without the addition of zeolite.

B. Methods

The prepared adsorbent was used in performing batch and fixed-bed column studies. The process conditions used in the fixed-bed column experiments are summarized in Table 1. In brief, zeolite-polyaniline composite was packed between glass wool with inert glass beads placed at the bottom and top ends of the column. The dye (RR2) aqueous solution was introduced into the column in upflow mode using a Cole Palmer MasterFlex L/S Digital Economy peristaltic pump. This was to ensure complete wetting of the particles. The flow velocity was measured periodically by collecting 50 mL of the treated effluent and recording the time taken for the given volume. The effects of bed loading, initial concentration, volumetric flow-rate and column diameter on the breakthrough of the dye solution were studied. The solution exiting from the column top was collected at pre-determined time intervals then analysed to determine its dye concentration using a WTW PhotoLab 6100 VIS spectrophotometer at a wavelength of 538 nm. The data obtained was then used to generate the breakthrough curves (BTC). The bed capacity at breakthrough point q_b was determined from the expression:

$$q_b = \frac{C_o}{m}\int_0^{V_b}(1-\frac{C_t}{C_o})dV \quad (1)$$

Where q_b is bed capacity at breakthrough point (mg·g^{-1}), m is the bed loading (g), C_o is the initial concentration (mg·L^{-1}), C_t is the concentration in the exit stream at any time (mg·L^{-1}), and V_b is the volume processed at breakthrough point (L). The number of bed volumes (BV) was calculated from the correlation: $BV=V_b/V_{adsorbent}$ where V_b is the same as above and $V_{adsorbent}$ is the volume of the adsorbent (m^3)

TABLE I
FIXED-BED COLUMN STUDIES OPERATING CONDITIONS

Process variable			
Column internal diameter[a] (mm)	15	20	30
Bed loading[b] (g)	5	10	15
Flowrate[c] (mL·min)	2.5	5.0	10
Initial concentration[d] (mg·L)	50	100	200

[a]Run = 10 g ZPC-10, 5 mL·min^{-1}, 100 mg·L^{-1}; [b]Run = 5 mL·min^{-1}, 15 mm diameter column, 100 mg·L^{-1}; [c]Run = 10 g ZPC-10, 15 mm diameter column, 100 mg·L^{-1}; [d]Run = 5 mL·min^{-1}, 15 mm diameter column, 100 mg·L^{-1}

III. RESULTS AND DISCUSSION

Optimization studies carried out using the different variants of ZPC (data not shown) revealed that ZPC-10 had the highest removal capacity for RR2 dye. Subsequently batch equilibrium and kinetic studies was carried out using ZPC-10. The equilibrium data was best described by the Langmuir isotherm with the following corresponding isotherm parameters: Langmuir adsorption constant (K_L) = 0.196 L.mg^{-1} and maximum adsorption capacity (q_m) = 68.8 mg·g^{-1}. Under the batch kinetic studies, the fractional dye uptake data was used in estimating the effective diffusivity (D_e). The values for D_e were in the range of 2.9-16 x 10^{-9} cm^2·s^{-1} indicating an internal diffusion-controlled process.

A. Effect of process variables on breakthrough curve profile

Fig. 1 shows the effect of bed loading on the breakthrough curve. It can be seen that a higher bed loading leads to more uptake of the RR2 dye. It can be seen (Table III) that as the bed loading capacity increases, the difference between dynamic bed capacity and batch (Langmuir) maximum adsorbent capacity decreases. The possible explanation for this observation is that at higher adsorbent loading, local (Langmuir) equilibrium is attained within the column.

Fig. 2 shows the plot of breakthrough curves at three different flow rates at a fixed bed loading of 10 g and initial RR2 dye concentration of 100 mg·L^{-1}

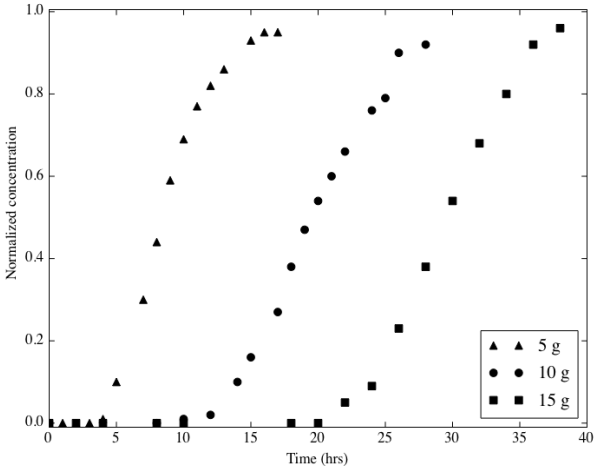

Fig. 1 Effect of bed loading on breakthrough curve for the adsorption of RR2 dye from aqueous solution onto ZPC-10

It is observed that at higher flow rates, breakthrough is reached faster with the curves having a steep slope, suggestive of a higher internal mass transfer effect [18].

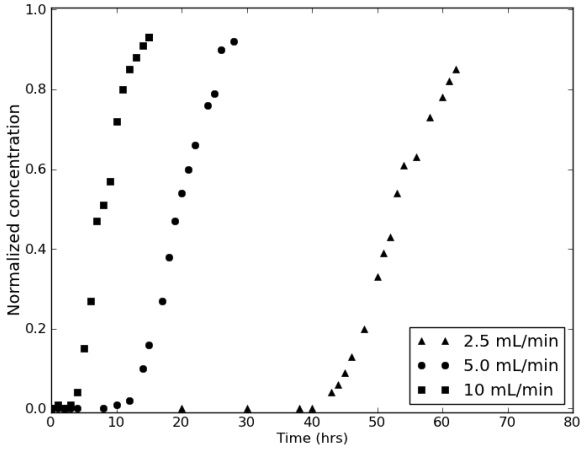

Fig. 2 Effect of flowrate on breakthrough curve for the adsorption of RR2 dye from aqueous solution onto ZPC-10

At low flow rates, breakthrough is reached later since the solute has more contact time with the adsorbent within the column. This affords more time for adsorption and thereby permits the attainment of near-local equilibrium conditions.

Fig. 3 illustrate the effect of initial concentration on the breakthrough curve. The change in inlet solute concentration has a remarkable effect on the shape and point of the break-through curve. As such, higher solute concentration, leads to faster attainment of breakthrough.

Fig. 4 depict the effect of column aspect ratio on the breakthrough curve at a fixed bed loading of 10 g ZPC-10, initial concentration of 100 $mg \cdot L^{-1}$ and volumetric flowrate of $5mL \cdot min^{-1}$.

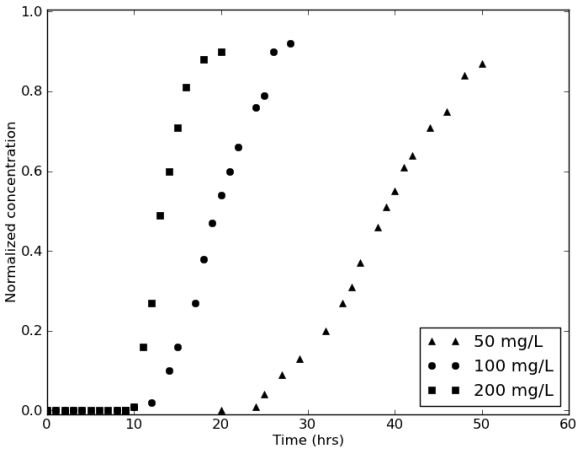

Fig. 3 Effect of initial concentration on breakthrough curve for the adsorption of RR2 dye from aqueous solution onto ZPC-10

It can be observed that column aspect ratio has little effect on the shape of the breakthrough curve. The calculated column performance indicators are summarized in Table II.

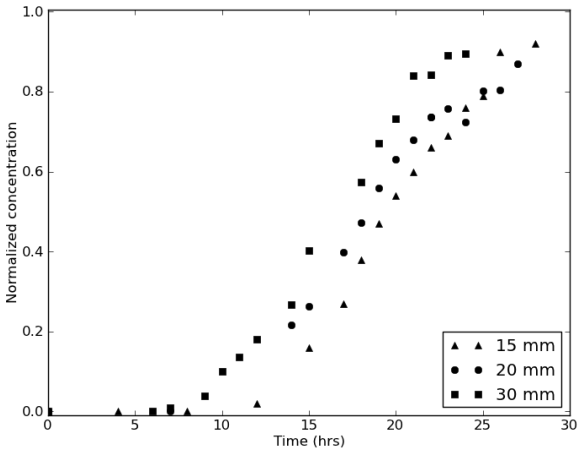

Fig. 4 Effect of column diameter on breakthrough curve for the adsorption of RR2 dye from aqueous solution onto ZPC-10

B. Breakthrough curve analysis

The experimental breakthrough curves were analyzed using an empirical model: 3-parameter logistics model) and surface reaction model: Thomas model. The three parameter logistic (3PL) also known as the Hill function (2) generates an S-shaped curve with the parameter *t* being the column residence time, *a* is the influent concentration, *k* is the value of time *t* when the effluent concentration is half the influent concentration, and *n* the Hill coefficient, determines how steep the slope of the breakthrough curve is at *k*.

TABLE II
SUMMARY OF BED PERFORMANCE PARAMETERS AT BREAKTHROUGH POINT

Parameter	Breakthrough time t_b (h)	Bed capacity q_b (mg·g^{-1})	Bed Volume (BV)
Bed loading (g)			
5.0	4	24	272
10.0	12	36	308
15.0	20	40	389
Initial concentration (mg·L^{-1})			
50	4.30	36	680
100	3.10	36	308
200	2.20	60	284
Flowrate (mL·min^{-1})			
2.5	2.40	60	514
5.0	3.10	36	308
10.0	6.03	18	154

Hill function is based on a Langmuir kind of isotherm as shown (2) [19]

$$C_t = \frac{bt^n}{k^n + t^n} \tag{2}$$

Fig. 5 shows the experimental data with the breakthrough curve fitted using 3PL model. It can be seen that 3PL satisfactorily describes the experimental data. However, the information derived from this model is abstract and cannot be used in designing a fixed-bed adsorber. Table III presents the parameters derived from the logistic model. The values of *b* representing the inlet dimensionless concentration is near unity for all the cases, while *k* indicates the time taken to reach 50 % inlet concentration. The equivalent experimental values of k are shown in parentheses.

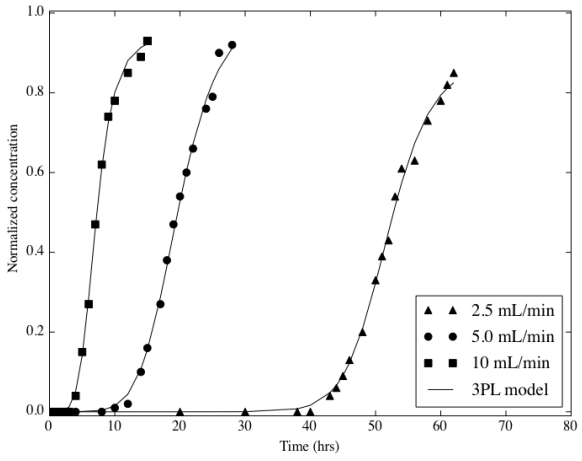

Fig. 5 Comparison of experimental and theoretical breakthrough curve derived logistic parameter model for the effect of flowrate

Thomas model assumes a plug-flow behavior and neglects mass transfer resistances in a fixed-bed column. This model assumes that the adsorbate is adsorbed directly onto the particle surface through Langmuir kinetics. This means that the rate of adsorption is a function of surface reaction between the adsorbate and the unused active sites on the adsorbent [20]. Thomas model can be is expressed as (3):

$$\frac{C_o}{C_t} = \frac{1}{1 + \exp\left[\left(k_{Th}/Q\right)\left(Q_o M - C_o V_t\right)\right]} \tag{3}$$

where Q is the flow rate (mg L^{-1}), M is the mass of adsorbent (g), V_t is the volume of effluent treated (mL), Q_0 is the maximum solid phase concentration of adsorbate per gram of sorbent (mg g^{-1}), and k_{Th} is the Thomas rate constant (mL·mg^{-1} ·min^{-1}). A plot of ln [(C_t /C_0) − 1] versus t gives the dynamic bed capacity (Q_0) as intercept and Thomas rate constant (k_{Th}) as the gradient. The breakthrough curves generated using Thomas model (Fig. 6) satisfactorily matches the experimental data. A summary of the Thomas model parameters is presented in Table IV.

TABLE III
LOGISTIC MODEL PARAMETERS AT ZERO EFFLUENT CONCENTRATION BREAKTHROUGH POINT

Parameter	b	k	n
Bed loading (g)			
5.0	0.980	8.3 [8]	4.654
10.0	1.016	19.75 [20]	6.206
15.0			
Initial concentration (mg·L^{-1})			
50	0.952	38.27 [40]	7.601
100	1.016	19.75 [20]	6.206
200	0.902	12.99 [13]	10.314
Flowrate (mL·min^{-1})			
2.5	1.192	51.96 [53]	14.398
5.0	1.016	19.75 [20]	6.206
10.0	0.940	7.10 [7]	4.975

The dynamic bed capacity (Q_o) obtained from the Thomas model is very close to the Langmuir bed capacity calculated from batch studies. This may be attributed to the attainment of local equilibrium conditions within the column, a fingerprint of a fast surface reaction between the sorbate and the adsorbent.

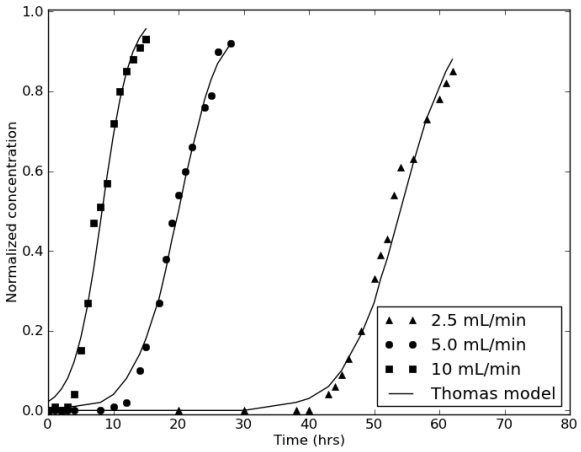

Fig. 6 Comparison of experimental and theoretical breakthrough curve derived Thomas model for the effect of flowrate

TABLE IV
THOMAS MODEL PARAMETERS AT ZERO EFFLUENT CONCENTRATION BREAKTHROUGH POINT

Parameter	Thomas rate constant (k_{Th})	Dynamic bed capacity Q_o ($mg \cdot g^{-1}$)	Correlation Coefficient (R^2)
Bed loading (g)			
5.0	3.78	50.14	0.977
10.0	3.10	59.92	0.982
15.0	3.76	63.40	0.995
Initial concentration ($mg \cdot L^{-1}$)			
50	4.30	59.30	0.951
100	3.10	59.92	0.995
200	2.20	86.48	0.920
Flowrate ($mL \cdot min^{-1}$)			
2.5	2.40	52.34	0.971
5.0	3.10	59.92	0.995
10.0	6.03	59.00	0.909

IV. CONCLUSION

The bed performance indicators showed that more bed volumes are processed at lower flow rate, lower initial concentration and higher bed loading. In this adsorption system, where intraparticle diffusion is the rate-limiting step, the use of low flow rates can significantly improve the efficiency of the column performance.

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