Biosorption of Metal Ions from Sarcheshmeh Acid Mine Drainage by Immobilized *Bacillus thuringiensis* in a Fixed-Bed Column

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Abstract—Heavy metals have a damaging impact for the environment, animals and humans due to their extreme toxicity and removing them from wastewaters is a very important and interesting task in the field of water pollution control. Biosorption is a relatively new method for treatment of wastewaters and recovery of heavy metals. In this study, a continuous fixed bed study was carried out by using *Bacillus thuringiensis* as a biosorbent for the removal of Cu and Mn ions from Sarcheshmeh Acid Mine Drainage (AMD). The effect of operating parameters such as flow rate and bed height on the sorption characteristics of *B. thuringiensis* was investigated at pH 6.0 for each metal ion. The experimental results showed that the breakthrough time decreased with increasing flow rate and decreasing bed height. The data also indicated that the equilibrium uptake of both metals increased with decreasing flow rate and increasing bed height. BDST, Thomas, and Yoon–Nelson models were applied to experimental data to predict the breakthrough curves. All models were found suitable for describing the whole dynamic behavior of the column with respect to flow rate and bed height. In order to regenerate the adsorbent, an elution step was carried out with 1 M HCl and five adsorption-desorption cycles were carried out in continuous manner.

Keywords—Acid Mine Drainage, *Bacillus thuringiensis*, Biosorption, Cu and Mn ions, Fixed bed.

I. INTRODUCTION

HEAVY metal ions in wastewater cause serious problems on environment and human health. The main sources of these ions are mining and electroplating. Cu, Mn, Pb, Cr, Zn, Ni and Cd are some metals that these industries discharge into the environment [1]. Various techniques have been employed to treat these heavy metals including ion exchange, membrane technologies and electrolysis [2], reduction and precipitation [3], adsorption [3] and coagulation and flotation [4]. Most of these methods are expensive, ineffective with low selectivity and some generate secondary wastes and toxic sludge which need other treatments [5].

Biosorption is the capability of active sites on the surface of biomaterials to bind and concentrate heavy metals from even the most dilute solutions. The process of metal ion binding is comprised of many physiochemical processes like ion exchange, complexation, micro precipitation, and electrostatic interaction [6].

Several studies showed that non-living microorganisms including bacteria [7]-[9], fungi [10], [11], yeast [12], [13] and algae [14], [15] are effective for heavy metal removal because of their small size, their ubiquity, their ability to grow under controlled conditions, and their resilience to a wide range of environmental situations [16]. Bacterial species such as *Bacillus*, *Pseudomonas*, *Streptomyces*, *Escherichia*, *Micrococcus*, etc., have been tested for uptake metals or organics [17]. In literature, there are several reports showing that *Bacillus* sp. is an appropriate sorbent of heavy metal ions [7]-[8].

Biosorption process can be performed either in a batch or continuous mode but most of research on biosorption is based on batch kinetic and batch equilibrium studies that is useful in providing fundamental information about the effectiveness of metal biosorbent systems. However, the data of batch studies may not be applicable to most treatment systems such as continuous operations where contact time is not sufficient for the attainment of the equilibrium [18].

In the practical operation of full-scale biosorption process, column experiments are preferred for continuous wastewater treatment, as it makes the best use of the concentration difference known to be a driving force for heavy metal biosorption and allows more efficient utilization of biosorbent capacity and results in a better quality of the effluent [19]. Hence there is a need to perform biosorption studies in column mode.

For a continuous process, the effectiveness of a biomass can be evaluated from the breakthrough curve of the effluent concentration. A typical S-shaped breakthrough curve is usually observed [20]. Breakthrough is the point on the S-shaped curve at which the effluent solute concentration reaches its maximum allowable value. The point where the effluent solute concentration reaches 95% of the influent concentration is usually called the point of column exhaustion [21]. In order to predict the breakthrough of an adsorption process in a fixed bed, the Bohart – Adams, Thomas, Yoon – Nelson and Yan models have been often used [22]-[24]. Moreover, the required bed height that is an important parameter in designing an adsorption column can be determined from the breakthrough curve and the Bed Height

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service Time (BDST) model.

In this study, removal of copper and manganese in AMD water of Sarcheshmeh copper mine by one of its own organisms, *B. thuringiensis*, has been studied in a fixed bed column. Being resistant and compatible with solute toxic metal ions was the main advantage of using this native microorganism. Important design parameters such as column bed height and flow rate of AMD water into the column have been identified. The breakthrough profile for the sorption of Cu and Mn was analyzed using 3 well known models.

II. MATHEMATICAL DESCRIPTION OF CONTINUOUS BIOSORPTION

The evaluation of the column performance was conducted by plotting Cu and Mn relative concentration, defined as the ratio of Cu and Mn ions concentration in effluent to Cu and Mn ions concentration in influent (C_e/C_0), as a function of flow time (t, min). The total adsorbed metal ions q_{total} (mg) in the column for a given solute concentration and flow rate is calculated from (1) [25]:

$$q_{total} = \frac{FA}{1000} = \frac{F}{1000} \int_{t=0}^{t=t_e} C_{ad} dt \tag{1}$$

where F (mL.min^{-1}) is the volumetric flow rate, t_e is the exhaustion time (min) and C_{ad} (mg.L^{-1}) is the adsorbed concentration. The total amount of metal ions sent to the column can be calculated from (2) [26]:

$$M_{total} = \frac{C_0.F.t_{total}}{1000} \tag{2}$$

where C_0 is the inlet metal ion concentration (mg.L^{-1}). The equilibrium uptake (q_{eq}, mg/g) (or column capacity) in the column is defined by (3) [27]:

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

where X (g) is the weight of immobilized bacterial biomass in the alginate beads. The material removal (%) with respect to flow volume can be calculated from the ratio of metal mass adsorbed (M_{ad}) to the total amount of metal ions sent to the column (M_{total}) as (4) [27]:

$$\text{Total metal removal (\%)} = \frac{M_{ad}}{M_{total}} \times 100 \tag{4}$$

Successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve and adsorption capacity for the effluent under given specific operating conditions. The use of simpler and more tractable models that avoid the need for numerical solution appears more suitable and logical and could have immediate practical benefits. Several such models have been applied to biosorption columns in the literatures [28]-[30]. BDST [31], Thomas [32] and Yoon–Nelson [33] which have been used as the most important models characterizing the fixed bed performance for the removal of ions are presented here.

A. BDST

BDST is a simple model for predicting the relationship between the bed height (z), and service time (t), in terms of process concentrations and adsorption parameters. The bed-height service time model can be used to estimate the required bed height for a given service-time. The BDST model can be expressed as (5):

$$t = \frac{N_0 Z}{C_0 v} - \frac{1}{K_a C_0} \ln\left[\frac{C_0}{C_b} - 1\right] \tag{5}$$

where C_b is ion concentration in the effluent of the column at breakthrough, C0 is the ion concentration in the influent of the column. The adsorption capacity, N_0 (mg.L^{-1}), can be determined from slope of the plot service time t_b versus the bed height Z. The rate constant, K (L.mg^{-1}.min^{-1}), can be obtained from the intercept of the plot, which represents the rate of solute transfer from the liquid phase to the solid phase.

B. Thomas

The Thomas model is widely used to evaluate the column performance. It can be used to predict the breakthrough curve and the maximum solute uptake by the adsorbent. These parameters are essential for a successful design of an adsorption column [34]. Thomas model was applied to the experimental data with respect to flow rate. A non-linear regression analysis was used on each set of data to determine the Thomas model parameters of q_t and k_{Th}. Equation (6) presents the linearized form of the Thomas model as:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{K_{Th} q_{0Th} M}{F} - K_{Th} C_0 \tag{6}$$

where k_{Th} (mL.min^{-1}.mg) is the Thomas rate constant, q_{0Th} (mg.g^{-1}) the maximum solid phase concentration of the solute (column capacity), F (mL.min^{-1}) the flow rate and M (g) is the amount of sorbent in the column. The kinetic coefficient k_{Th} and the adsorption capacity of the bed q_{0Th} can be determined from a plot of $\ln((C_0/C)-1)$ against t at a given flow rate.

C. Yoon–Nelson

Yoon and Nelson have developed a relatively simple model that based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The Yoon and Nelson model not only is less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of adsorption bed [33]. The linear form of Yoon and Nelson equation regarding to a single-component system is expressed as Yoon–Nelson model can be described as (7):

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN} t - \tau k_{YN} \tag{7}$$

where k_{YN} the Yoon–Nelson model rate constant (1.min^{-1}); τ the time required for 50% sorbate breakthrough (min); C_0 the influent ion concentration (mg.L^{-1}), C_t the effluent ion

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concentration at time (t). The parameters k_{YN} and τ may be determined from a plot of $\ln(C/(C_0 - C))$ versus sampling time (t).

III. METHODS

A. Preparation of Biomass

B. thuringiensis was obtained from Sarcheshmeh copper mine AMD and maintained on nutrient agar slants. In order to prepare biomass, bacterial strain was inoculated from slants to 200 ml nutrient broth growth medium. Afterwards, flasks were shaken at 310°K and 100 rpm for 24 hours. In order to kill bacteria, flasks were autoclaved at 393 °K, then centrifuged and supernatant (growth medium) was discarded. Remaining biomass was dried at 333°K oven for 24 hours and then crushed and sieved to obtain homogeneous powder.

B. Acid Mine Drainage Characterization

A sample of acid mine drainage was analyzed and some solute metal ions were detected. Table I shows concentration of these metals in the sample. As seen in the table, concentration of Cu and Mn ions were higher than the other metal ions. Hence removal of Cu and Mn ions was investigated in this study.

TABLE I
ACID MINE DRAINAGE ANALYSIS RESULTS

Metal ion	Mo	Al	Mn	Ag	Ni	Pb	Cu	Fe
Concentration (ppm)	0.29	0.24	8	0.06	0.003	0.65	5.5	0.1

C. Preparation of Alginate Beads

Sodium alginate (2.5 g) was dissolved in hot distilled water (500 ml) with constant stirring to avoid lumps formation. On cooling to room temperature, 2.5g of bacterial biomass was added under stirring condition to form a uniform mixture. The solution was left 12 h and then added drop wise into 500 ml of 0.2 M CaCl$_2$ solution with gentle stirring by means of magnetic stirrer. Ca – alginate gel beads were formed upon contacts with the cross linker solution and were left overnight to stabilize. The remaining CaCl$_2$ solution was removed by filtration and the resulting beads (diameter 2 ± 0.2 mm) were washed with distilled water several times. The beads were dried at room temperature for three days. Blank alginate beads without biosorbent were also prepared.

D. Column Experiments

Column studies (down flow mode) were conducted in Ca-alginate immobilized *B. thuringiensis* glass column with an internal diameter of 2 cm and column length varying from 20 to 50 cm. Influent Cu and Mn ion concentrations were 4.5 and 8 ppm respectively. AMD water with pH equal to 6 was passed through the columns at desired flow rates of 2, 4 and 6 mL.min^{-1}. Samples were collected at the exit at different time intervals and analyzed for Cu and Mn concentrations. The columns were run till exhaustion of the biosorbent capacity. A blank column was designed to investigate whether blank alginate beads can remove metal ions or not.

E. Regeneration Studies

The primary objective of regeneration is to retain the sorption capacity of exhausted biomass; a secondary objective is to recover bound ions [35]. In order to regenerate the biosorbent, an elution step was carried out (with 1 M HCl) when the column reached saturation. In the column, 5 consecutive cycles were performed and adsorption-desorption efficiencies for each cycle were investigated

IV. RESULTS AND DISCUSSION

Blank alginate beads removed very few amounts of metal ions; hence, their influence on biosorption process was ignored.

A. Effect of Bed Height

Breakthrough curves at 25, 35 and 50 cm bed heights were obtained at 2 mL.min^{-1} flow rate. The breakthrough curves followed the typical S-shaped curves at all bed heights. The shape and the gradient of the breakthrough curves changed significantly with the bed height, as can be seen in Fig. 1. The slope of the breakthrough curve of a 50-cm height bed is lower than that of a shorter bed. For a taller bed, a larger volume of the metal solution could be treated, and a higher percentage metal removal was obtained (Table II). It is self-evident that a taller bed has more adsorbent available for metal binding; hence, more liquid could be treated and the breakthrough time is longer.
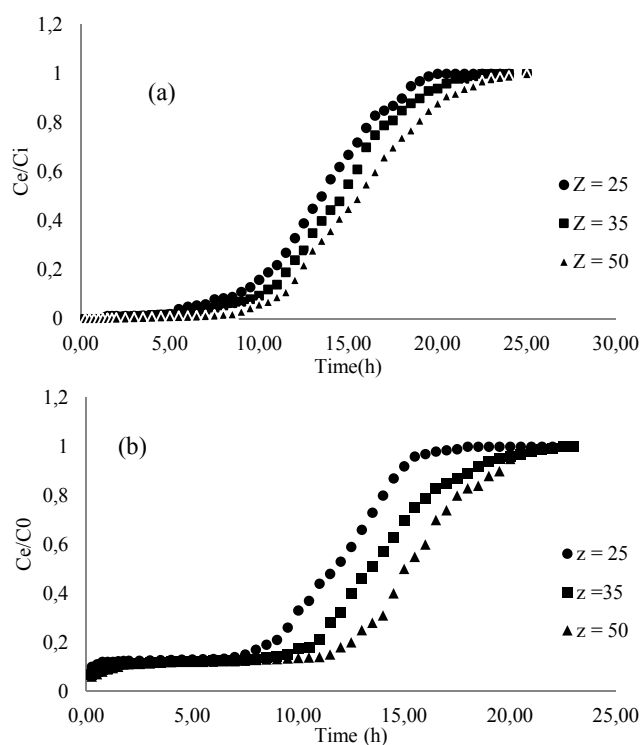

Fig. 1 Breakthrough curves for biosorption of Cu (A) and Mn (B) ions at different bed depths

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TABLE II
COLUMN DATA AND PARAMETERS OBTAINED AT DIFFERENT BED HEIGHTS
(FLOW RATE: 2ML.MIN^{-1})

Metal ion	Z (cm)	m_{total} (mg)	q_{total}	q_{eq} (mg/g)	Removal (%)
Cu	25	13.2	12.5	8.3	94.71
	35	13.2	12.8	8.53	96.97
	50	13.2	13.1	8.73	99.24
Mn	25	15.36	15.1	10.06	98.31
	35	15.36	15.12	10.08	98.44
	50	15.36	15.31	10.21	99.67

B. Effect of Flow Rate

It is very important to optimize the flow rate for maximum removal of metal at fixed bed height in laboratory conditions. In present study, performance of Ca-alginate immobilized *B. thuringiensis* was investigated as a function of flow rate. The plots of dimensionless concentration (C/C_0) of Cu and Mn ions versus time at different flow rates are shown in Fig. 2. Breakthrough curves at 2, 4 and 6 mL.min^{-1} flow rates were obtained at 25 cm bed height. The breakthrough curves followed the typical S-shaped curves at all flow rates. An earlier breakthrough and exhaustion time were observed in the profile when the flow rate increased from 2 to 6 mL.min^{-1}.

As seen in Table III maximum adsorption for Cu and Mn ions was obtained at a flow rate of 2 ml.min^{-1}. The higher percentage of metal removal obtained at lower flow rates can be explained by the fact that at higher flow rates the residence time of the solute in the column is too short and the solute does not have enough time to interact with the surface sorbent and diffuse into the pores [26]. However, the metal uptake per unit mass of *B. thuringiensis* remained relatively constant for different flow rates. This indicates that the metal uptake amount was directly proportional to the amount of adsorbent available in the bed.

At all flow rates studied, *B. thuringiensis* loaded Ca-alginate beads initially adsorbed Cu and Mn ions rapidly and then gradually equilibrium was reached.

TABLE III
COLUMN DATA AND PARAMETERS OBTAINED AT DIFFERENT FLOW RATES
(BED HEIGHT: 25 CM)

Metal ion	F (mL/min)	m_{total} (mg)	q_{total} (mg)	q_{eq} (m/g)	Removal (%)
Cu	2	13.2	12.5	8.3	94.71
	4	21.12	12.3	8.2	58.24
	6	28.71	12.2	8.13	42.5
Mn	2	15.36	15.1	10.1	98.31
	4	25.92	14.3	9.53	55.16
	6	34.56	13.7	9.13	39.64

C. Regeneration Studies

Sorption – desorption efficiencies are shown in Table IV. As seen in the table, the removal efficiency and the metal uptake capacity were found to decrease in the successive cycles. This behavior is primarily due to gradual deterioration of biosorbent because of continuous usage. It is noted that the elution efficiency remained relatively the same in all desorption cycles.
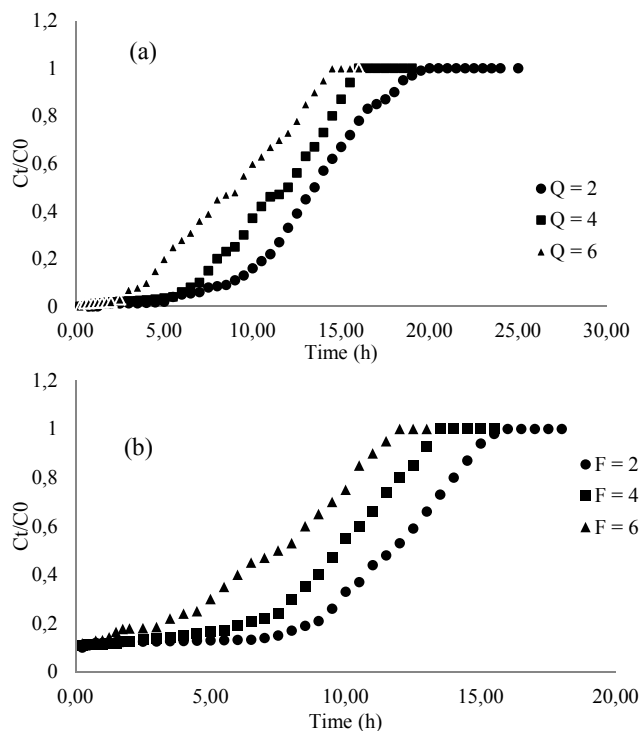

Fig. 2 Breakthrough curves for biosorption of Cu (A) and Mn (B) ions at different flow rates

TABLE IV
SORPTION – DESORPTION CYCLE OF Cu AND Mn IONS IN THE FIXED-BED
COLUMN (BED HEIGHT: 25CM; FLOW RATE: 2ML.MIN-1)

		Cycle number				
		1	2	3	4	5
Cu	Removal efficiency	94.71	88.54	79.34	70.82	66.86
	Desorption efficiency	97.31	95.46	96.39	95.23	94.58
Mn	Removal efficiency	98.31	92.43	85.33	78.45	72.54
	Desorption efficiency	98.84	96.18	96.31	95.22	94.52

D. BDST Model

Fig. 3 shows the plots of the service-time (t_b) at the 10% breakthrough point (i.e. t_b at C_{out} =0.55 mg.L^{-1} for Cu and t_b at C_{out} =0.8 mg.L^{-1} for Mn) versus the bed height at different flow rates. The linear relationship between t_b and the bed height was obtained with the R^2 values mostly close to unity, indicating the suitability of the BDST model to represent the adsorption of Mn^{2+} and Cu^{2+} in a fixed bed of *B. thuringiensis*. The sorption capacity of the bed per unit bed volume, N_0, was calculated from the slope of BDST plot, assuming initial concentration, C_0, and linear velocity, υ, as constant during the column operation. The rate constant, K_a, calculated from the intercept of BDST plot, characterizes the rate of solute transfer from the fluid phase to the solid phase [36]. The computed N_0 and K_a values were 4188 mg.L^{-1} and 0.072 L.mg.h^{-1} for Cu and 3164 mg.L^{-1} and 0.246 L.mg.h^{-1} for Mn respectively (Table V). If K_a is large, even a short bed will avoid breakthrough, but as K_a decreases a progressively longer bed is required to avoid breakthrough [36]. The BDST model parameters can be useful to scale up the process for other flow rates without further experimental run.

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The adsorption capacity, N_0, only slightly decreased with the flow rate while the rate constant K increased significantly with the flow rate, as can be seen in Table V.

TABLE V
PARAMETERS PREDICTED FROM THE BDST MODEL FOR BIOSORPTION OF CU AND MN ON *B. THURINGIENSIS*

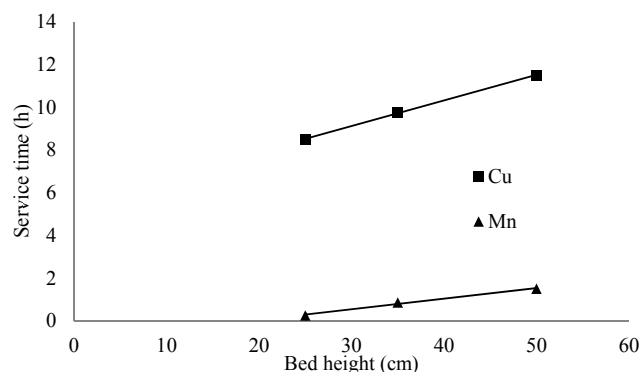| Flow rate (L.min⁻¹)	Cu		Mn	
	N_0 (mg.L⁻¹)	K (L.mg⁻¹.min⁻¹)	N_0 (mg.L⁻¹)	K (L.mg⁻¹.min⁻¹)
2	4188	0.072	3164	0.246

Fig. 3 Effect of bed height by the bed depth service time model for sorption of Cu and Mn ions

E. Thomas Model

The Thomas rate constant (K_{TH}) and the maximum adsorption capacity (q_0) were determined, respectively, from the slope and intercept of the plots of $\ln[(C_0/C_t)-1]$ versus time as shown in Fig. 4 (a), (b). The values obtained are given in Table VI for Cu and Mn ions. As seen from the table, the values of K_{Th} and q_0 were influenced significantly by flow rate. The maximum adsorption capacity (q_0) of *B. thuringiensis* for both metals was found to decrease, but the Thomas rate constant (K_{Th}) increased by increasing flow rate.

TABLE VI
PARAMETERS PREDICTED FROM THE THOMAS MODEL FOR BIOSORPTION OF CU AND MN ON *B. THURINGIENSIS*

Ion	Flow rate	$q_{0 (exp)}$	K_{Th}	$q_{0 (cal)}$	R^2
Cu	2	8.3	0.0423	8.38	0.9358
	4	8.2	0.0521	8.24	0.9622
	6	8.13	0.0561	8.11	0.8639
Mn	2	10.1	0.1702	10.23	0.8978
	4	9.53	0.3344	9.74	0.9245
	6	9.13	0.6424	8.95	0.9054

The breakthrough curves predicted with the Thomas model at different flow rates were shown in Fig. 4. Obviously, the breakthrough curves calculated from this model were in good agreement with experimental data for all flow rates. This model was able to give a good prediction of the maximum adsorption capacity for *B. thuringiensis* biosorption in the fixed-bed.
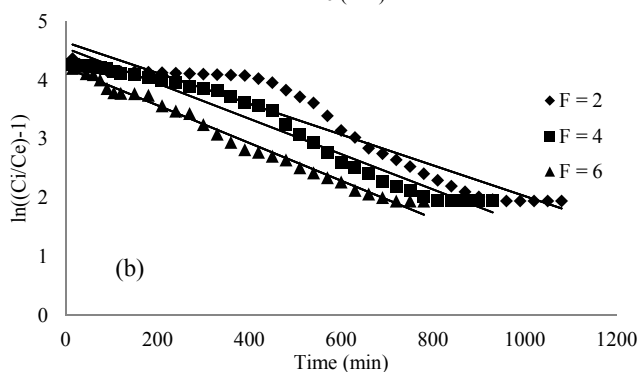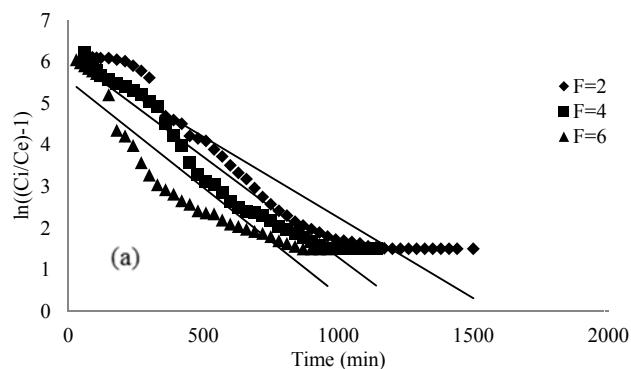

Fig. 4 Thomas model for biosorption of Cu (A) and Mn (B) ions at different flow rates

F. Yoon-Nelson Model

Yoon and Nelson model was also applied to investigate the breakthrough behavior of Cu and Mn ions on *B. thuringiensis* column. A linear regression was then performed on each set of transformed data to determine the coefficients from slope and intercept of plot $Ln(C_t/(C_0-C_t))$ vs. time (Fig. 5). The values of parameters k_{YN} (rate constant) and τ (the time required for 50% adsorbate breakthrough) in this model were determined at three different flow rates for each metal ions (Table VI). As the flow rate increased, the values of k_{YN} increased and the values of τ decreased.

TABLE VII
PARAMETERS PREDICTED FROM THE YOON-NELSON MODEL FOR BIOSORPTION OF CU AND MN ON *B. THURINGIENSIS*

Ion	Flow rate (mL.min⁻¹)	K_{YN} (L/min)	τ (min)	τ_{exp} (min)	q_{0YN} (mg/g)	R^2
Cu	2	0.0039	967.38	810	14.23	0.9764
	4	0.0048	845.93	720	11.24	0.9446
	6	0.0051	670.41	555	6.92	0.9574
Mn	2	0.0026	768.61	705	25.27	0.9742
	4	0.003	543.93	585	19.39	0.9656
	6	0.0032	467.59	450	11.43	0.9985

The time required for 50% sorbate breakthrough (τ) obtained from the Yoon and Nelson model agreed well with the experimental data at all conditions examined. In general, good fits were obtained in all cases with correlation coefficients ranging from 0.9446 to 0.9985. The bed capacity values (q_{0YN}) are also presented in Table VII. The bed capacity q_{0YN} decreased with increasing flow rate similar to change of Thomas sorption capacity with these parameters. It can be said

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that both the models were able to describe the column data well with high correlation coefficients.
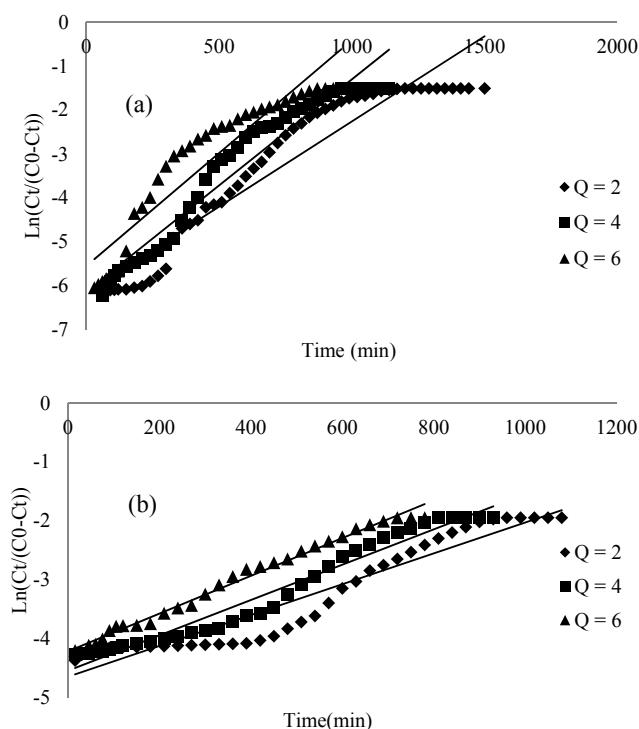

Fig. 5 Yoon-Nelson model for biosorption of Cu (A) and Mn (B) ions at different flow rates

V. CONCLUSION

The biosorption of Cu and Mn ions from AMD water on a fixed bed of dried *B. thuringiensis* was investigated in a continuous mode. It was found that the sorption of each metal ion is influenced by the flow rate as well as by the bed height. It was observed that the higher flow rate and lower bed height could result in poor effluent quality and steeper breakthrough curves, probably due to an insufficient residence time of the AMD water in the column. Thomas, Yoon–Nelson and BDST models were used successfully for the evaluation of the column performance. The sorbed Cu and Mn ions can be effectively eluted. After acid elution, the biomass can be regenerated and reused effectively. It may be concluded *B. thuringiensis* can be used as potential and promising biosorbent for the removal of Cu and Mn ions from Acid Mine Drainage.

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