Orbital: The Electronic Journal of Chemistry
journal homepage: www.orbital.ufms.br
ISSN 1984-6428

| Vol 6 | | No. 1 | | January-March 2014 |

Full Paper

Evaluation of Two Biosorbents in the Removal of Metal Ions in Aqueous Using a Pilot Scale Fixed-bed System

André G. Oliveira[a], Jefferson P. Ribeiro[b], Diego Q. Melo[a], Francisco W. Sousa[c], Vicente O. S. Neto[d], Giselle S. C. Raulino[b], Rivelino M. Cavalcante[e], Ronaldo F. Nascimento[a*]

[a]*Department of Analytical Chemistry and Physical Chemistry – Federal University of Ceará. Rua do Contorno, S/N Campus do Pici, Bl. 940 – CEP: 60451-970 – Fortaleza, CE – Brazil.*
[b]*Department of Hydraulic and Environmental Engineering – Federal University of Ceará. Rua do Contorno, S/N Campus do Pici, Bl. 713 – CEP: 60451-970 – Fortaleza – CE – Brazil.*
[c]*Federal Institute of Education, Science and Tecnology – Campus Crateús –Rua Lopes Vieira, s/n -CEP: 63700-000 – Crateús – CE – Brazil.*
[d]*Department of Chemistry – State University of Ceará. Rua Solon Medeiros, S/N – BR 020 – CEP: 63660-000 – Tauá – CE – Brazil.*
[e]*Institute of Marine Sciences, Federal University of Ceará. Av. Abolição,3207 – Meireles – CEP: 60165-081 – Fortaleza – CE – Brazil.*

Article history: Received: 25 April 2014; revised: 24 February 2014; accepted: 17 March 2014. Available online: 02 April 2014.

Abstract: The aim of the present work was to investigate the adsorption of toxic metal ions copper, nickel and zinc from aqueous solutions using low cost natural biomass (sugar cane bagasse and green coconut fiber) in pilot scale fixed-bed system. The Hydraulic retention time (HRT) was 229 minutes and the lowest adsorbent usage rate (AUR) found was 0.10 g.L^{-1} for copper using green coconut fibers. The highest values of adsorption capacities founded were 1.417 and 2.772 mg.g^{-1} of Cu(II) ions for sugarcane bagasse and green coconut fibers, respectively. The results showed that both sugarcane bagasse and green coconut fiber presented potential in the removal of metal ions copper, nickel and zinc ions from aqueous solution and the possible use in wastewater treatment station.

Keywords: multicolumn adsorption; toxic metal ions; wastewater

1. INTRODUCTION

Electroplating industries are considered one of the oldest, concentrating in areas of surface finishing and metal deposition [1]. However, these industries produce wastewater contaminated with toxic metals, becoming one of the most hazardous among chemical industries [2]. The contamination of water bodies by wastewater containing toxic metal ions is a worldwide environmental problem [3-5].

Toxic metal ions, known commonly as heavy metals, are classified as toxic materials due to their non-biodegradability and bioaccumulation tendency in living organisms. Its excessive amount cause health problem in animals, plants and humans [3]. In low concentration, these metal ions are essential to all living organisms [4]. However, these metals can cause various types of acute and chronic disease in humans like hemochromatosis, fever, lesions in the central nervous system, risk of lung cancer, etc., if ingested beyond the permissible levels [1-4, 6-7].

There are several technologies for removing toxic metal ions from wastewater: ion exchange, membrane separation, reverse osmosis, chemical precipitation, coagulation-flocculation, flotation and electrochemical treatment [2-3, 5-6, 8-9]. However, these methods have some disadvantages such as being costly, operation costs and high maintenance, ineffectiveness in removing traces of metal ions, and formation of polluted byproducts [3, 5-6].

In this context, adsorption is an attractive method because of its ease of operation and efficiency in removing toxic metal ions from wastewater [6]. Among the most used adsorbents the activated carbon stands, though in some cases their use becomes impractical due to its high cost [10]. With increasing

*Corresponding author. E-mail: ronaldo@ufc.br

environmental awareness and government policy rigidity, it became necessary to develop new ways to remove contaminants using low-cost methods [4]. Natural origin adsorbents have become an interesting alternative for removal of toxic metal ions using fixed-bed technology [3, 10-12].

The purpose of the study was to investigate the adsorption of toxic metal ions copper, nickel and zinc from aqueous solutions using sugar cane bagasse and green coconut fiber in fixed-bed system. The breakthrough curves were evaluated and Thomas and Yoon & Nelson models were applied to describe the dynamic performance of the adsorption process.

2. MATERIAL AND METHODS

Chemical and reagents

Standard solutions of metal ions composed of $Zn(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.6H_2O$ were purchased from Merck (São Paulo, Brazil). The concentrations of ions were determined by atomic absorption spectrophotometry (AAS, GBC 933 plus model) in an air-acetylene flame.

Adsorbent preparation

Sugar cane bagasse and green coconut fibers were used as adsorbents, which were initially crushed, and the fractions corresponding to 20-150 mesh were used in the work. The mass of each adsorbent used was 1000 g.

Column studies

The column system, Figure 1, consist of 5 PVC columns (160 cm length and 5.4 cm I.D each) connected in series and a pump that provided a continue solution circulation through the columns system. Firstly, the columns were conditionated with deionized water and the flow rate of 80 mL.min^{-1} was achieved. A volume of 50 L of multielement synthetic solution (pH = 5.0) was percolated and aliquots of 50 mL were collected at every 15 min at the exit of the column. The adsorption capacity was determined from breakthrough curves of multielement synthetic solutions of metal ions Cu(II), Ni(II) and Zn(II). The experiments with the adsorbent sugar cane bagasse were performed with the concentration of solution of 216 mg.L^{-1} Cu(II), 60 mg.L^{-1} Zn(II) and 7 mg.L^{-1} Ni(II), whereas, the experiments with green coconut fiber were performed with the concentration of solution of 126 mg.L^{-1} Cu(II), 42 mg.L^{-1} Zn(II) and 6 mg.L^{-1} Ni(II).

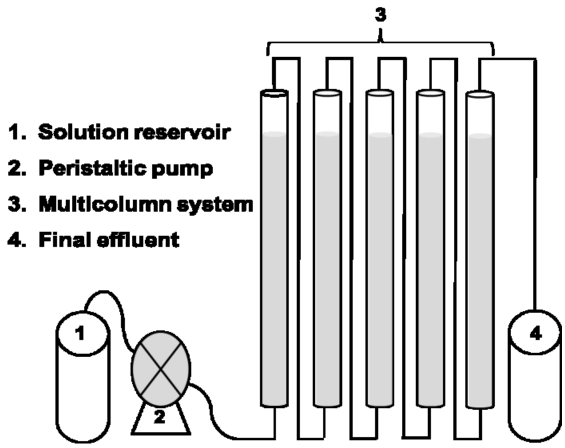

Figure 1. Schematic diagram of the experimental set up for a continuous process.

Designing of fixed bed biosorbent

A conventional fixed bed system is compound of a column where particles of biosorbent are placed in contact with the solution to be treated. The dynamic behavior and efficiency of a fixed-bed column are described in terms of effluent/influent (C/C_0) concentration versus time or volume of treated liquid, called breakthrough curve [10, 13].

In an ideal breakthrough curve it is assumed that removal of adsorbate is complete in the early stages of operation. Usually the breakthrough point (C_b) is the point at that the concentration of adsorbate effluent the column is 5% of the initial concentration (C_0) and the exhaustion point (C_x), around 90% of C_0 [14]. The primary adsorption zone (PAZ) or mass transfer zone (MTZ) in the fixed bed adsorber develops between the section of the column that is saturated with adsorbate and section that still contains no saturated biosorbent. It is represented by the portion of the curve between C_x and C_b which is assumed to have a constant length or depth, δ. This zone moves through the column in the flow direction at a certain speed, and when reaches the end of column, the concentration of adsorbate in the effluent begins to increase gradually. The column is operational until the MTZ reaches the end of the column and effluent is practically free adsorbate [14-17].

Some parameters that characterize the PAZ are described by [14, 17, 18] and were determinate in this work according to them. These parameters are listed below: Total time to establish the PAZ (t_x), Time necessary to move the PAZ along the column (t_δ), Length of PAZ (δ), Time necessary for the formation of PAZ (t_f), Fractional capacity of biosorbent (F), Percentage of saturation in the column (%S).

The maximum adsorption capacity of biosorbent is given by equation 1 [15]:

$$q_{exp} = \frac{C_0 * F_m}{m_s} \int_{t=0}^{t=x} \left(1 - \frac{C}{C_0}\right) dt \qquad \text{eq. 1}$$

where q is the maximum adsorption capacity (mg g^{-1}); Co is the initial concentration of solution; C is the concentration of adsorbate at certain volume; m_s the mass of biosorbent (g); F_m is the volumetric flow (L min^{-1}) and t the time (min.).

Column adsorption models

Several models can be used to calculate kinetic constants and maximum adsorption capacities of a column. In this work, are used the Thomas and Yoon-Nelson models.

Thomas model

This model assumes a fixed bed behavior with continuous flow and uses the Langmuir isotherm for equilibrium and reaction kinetics second order reversible [19, 20]. It is applicable for conditions of favorable and unfavorable adsorption. The Thomas model can be expressed as a function of volume of effluent and in function of time [21, 22], equations 2 and 3.

$$\frac{C_e}{C_o} = \frac{1}{1 + e^{\left[\frac{k_{TH} q_o m}{F} - k_{TH} C_o t\right]}} \qquad \text{eq. 2}$$

The linearized form is described as

$$\ln\left(\frac{C_o}{C_e} - 1\right) = \frac{k_{TH} q_o m}{F} - k_{TH} C_o t \qquad \text{eq. 3}$$

where C_e is the effluent concentration (mg.L^{-1}), C_0 the influent concentration (mg.L^{-1}), F the flow rate (mL.min^{-1}), V the effluent volume (mL), m the mass of the adsorbent (g) and t the time (min), k_{TH} (L.mg^{-1}.min^{-1}) and q_{TH} (mg.g^{-1}) are the adsorption kinetic rate constant and the maximum adsorption capacity of the column, respectively. The constants (k_{TH}, q_{TH}) can be determined from the plot of ln(C_e/C_0) against t.

Yoon & Nelson Model

Yoon & Nelson [23] developed a relatively simple model, related to adsorption of gases with respect to activated carbon. This model not only is simpler than other designs and does not require detailed data relating to the characteristics of the solute, the type of adsorbent and physical properties of the bed. The nonlinear equation for this model is expressed as:

$$\frac{C_e}{C_o} = \frac{1}{1 + \exp[k_{YN}(\tau - t)]} \qquad \text{eq. 4}$$

The linearized equation of Yoon-Nelson is described as following:

$$t = \tau + \frac{1}{k_{YN}} \ln\left(\frac{C_e}{C_o - C_e}\right) \qquad \text{eq. 5}$$

where Ce and Co are the effluent and influent concentrations (mg.L^{-1}) at a given time *t* and *t*=0, K_{YN}(L.min^{-1}) is the Yoon-Nelson constant, τ (min) is the time required for 50% adsorbate breakthrough. From a linear plot of ln(C_0/Ce–C_0) against time t, values of K_{YN} and τ were determined from the intercept and slope of the plot.

3. RESULTS AND DISCUSSION

Characterization of adsorbent bed

Physical properties of the column bed containing the adsorbent are shown in Table.

Table 1. Physical parameters of the column bed containing the adsorbent.

Properties	Fixed Bed
Column diameter (d_L) (cm)	5.4
Total Bed height (cm)	800
Total area of the column (cm^2)	13610.58
Volume of the empty column (V_L) (cm^3)	18312.48
Mass of adsorbent in the column (g)	1000

Breakthrough curves

The breakthrough curves for studied ions using sugarcane bagasse and green coconut fibers are shown in Figure 2(a) and (b), respectively. It can be seen that breakthrough occurred rapidly for the three metal ions studied. At Figure 2(b) can be seen that copper didn't reach saturation, indicating a great affinity by green coconut fibers and this metal ions. The concentration of metal ions in synthetic solutions were with the intent of simulate an effluent of an electroplating industry. The higher concentration of copper than nickel and zinc ions may have led to this greater uptake efficiency of copper, instead of nickel and zinc. This concentration gradient favors a higher adsorption of the higher concentration adsorbates in relation to other presents in solution. Sousa et al. [10] studying metal ions uptake using green coconut shell powder in a column system founded the same results.

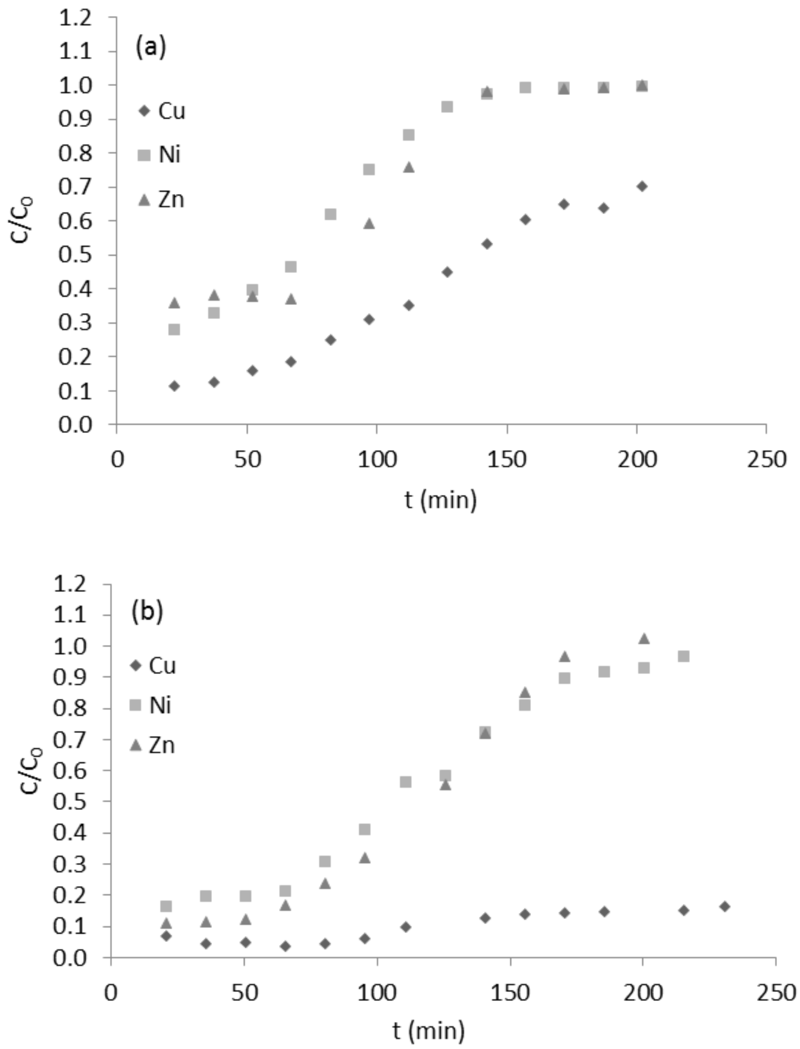

Figure 2. Breakthrough curves for (a) sugarcane bagasse and (b) green coconut fiber. Conditions: pH = 5, mass of adsorbent = 1 kg, flow rate=80 $mL.min^{-1}$.

Hydraulic retention time (HRT) is a typical parameter of design and operation for columns. Large residence times can lead to a decrease in the contaminant removal while shorter times do not allow an effective contact interaction to occur between the sorbent and sorbate [15, 24]. HRT is given by the ratio between the volume of the column and the flow rate. HRT for studied system was 229 min. Another important parameter is the adsorbent usage rate (AUR) that is the ratio between the weight of biosorbent in the column and the amount of liquid passed into the column at the time breakthrough occurs [15]. AUR gives information about the amount of adsorbent needed to treat a fixed volume of solution. Table 2 shows the breakthrough and exhaustion times, HRT, adsorbent usage rate and adsorption capacity obtained according equation 1.

As can be seen on Table 2, AUR was the same for the three metal ions studies as breakthrough time was the same either. That results means that only 0.57 g of adsorbent are needed to treat 1 L of contaminated solution for sugarcane bagasse and 0.62 $g.L^{-1}$ for green coconut fibers, exception for copper where AUR was 0.1 $g.L^{-1}$. The low values of AUR are due to the high bed height of the column, leading to a high HRT and high removal of metal ions. This parameter is an important concept in case of industry applies.

Table 2. Breakthrough times (t_b), exhaustion times (t_x), adsorbent usage rate and adsorption capacities (when C/C_0 = 0.5) obtained from breakthrough curves of sugarcane bagasse and green coconut fibers (Figure 1).

Adsorbent	Metal ion	t_b(min.)	t_x(min.)	AUR($g.L^{-1}$)	$q_{exp.}$ ($mg.g^{-1}$)
Sugarcane Bagasse	Cu (II)	22	202	0.57	1.417
	Ni (II)	22	127	0.57	0.029
	Zn (II)	22	142	0.57	0.286
Green Coconut Fibers	Cu (II)	140	>250	0.10	2.772
	Ni (II)	20	185	0.62	0.032
	Zn (II)	20	170	0.62	0.248

Table 3 presents the parameters t_x, t_δ, t_f, F, δ and percentage saturation (%S) of the column obtained from the breakthrough curves of Figure 2(a) – (b). The results show that the total time to establish the primary adsorption zone (t_x) was maximum for copper for both adsorbents used. The time required to move adsorption zone through the column (t_δ) was between 105 – 360 min. The time to form the primary adsorption zone (t_f) was between 18 – 42 min for sugarcane bagasse and 14 – 170 min for green coconut fibers. The length of PAZ was between 782 - 993 cm for sugarcane bagasse and 769 – 873 cm for green coconut fiber. This parameter is related to the region in the breakthrough curve situated between breakthrough and exhaustion time. The values obtained for the three metal ions for both adsorbents studied were near or higher than the column length (800 cm) probably due to the breakthrough occurred most of the time at the first point collected.

Table 3. Parameters t_x, t_f, t_δ, F, δ and percentage saturation of column for sugarcane bagasse and green coconut fibers.

Adsorbent	Metal ion	Parameters					
		t_x (min)	t_δ (min)	f	t_f (min)	δ (cm)	%
Sugarcane Bagasse	Cu (II)	202.50	180.40	0.90	18.00	782.24	90.24
	Ni (II)	127.10	105.00	0.59	42.53	993.27	49.71
	Zn (II)	142.10	120.00	0.65	41.61	955.29	58.60
Green Coconut Fibers	Cu (II)	500.00	360.00	0.53	170.46	873.93	48.28
	Ni (II)	215.50	195.00	0.85	30.00	840.98	83.83
	Zn (II)	173.75	153.25	0.91	14.41	769.45	90.95

Fixed bed column modeling

The experimental data obtained were fitted to the most commonly used kinetic models for adsorption in a fixed bed, Thomas and Yan & Nelson models. Nonlinear regression analysis was performed. The sum of the squares of the errors (SSE) was examined for every experimental data set, and the parameters of K_{TH} and q_{TH}as well as k_{YN} and T were determined for the lowest error values in each case by adjusting and optimizing the functions themselves using the *solver* add-in for Microsoft Excel®.

The Figures 3 and 4 show a comparison of the curves obtained from experimental data and theoretical models predicted by Thomas and Yoon & Nelson. These figures show that the Thomas model can be considered as a more suitable kinetic model to describe Cu(II), Zn(II) and Ni(II) adsorption in a fixed bed column of sugarcane bagasse and green coconut fibers. However, at the initial stage of adsorption, a small deviation between the model prediction and the experimental data was observed, mainly for zinc by sugarcane bagasse. 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 [25]. Yoon & Nelson model just fitted well the data obtained for nickel by sugarcane bagasse and for copper by green coconut shell fibers.

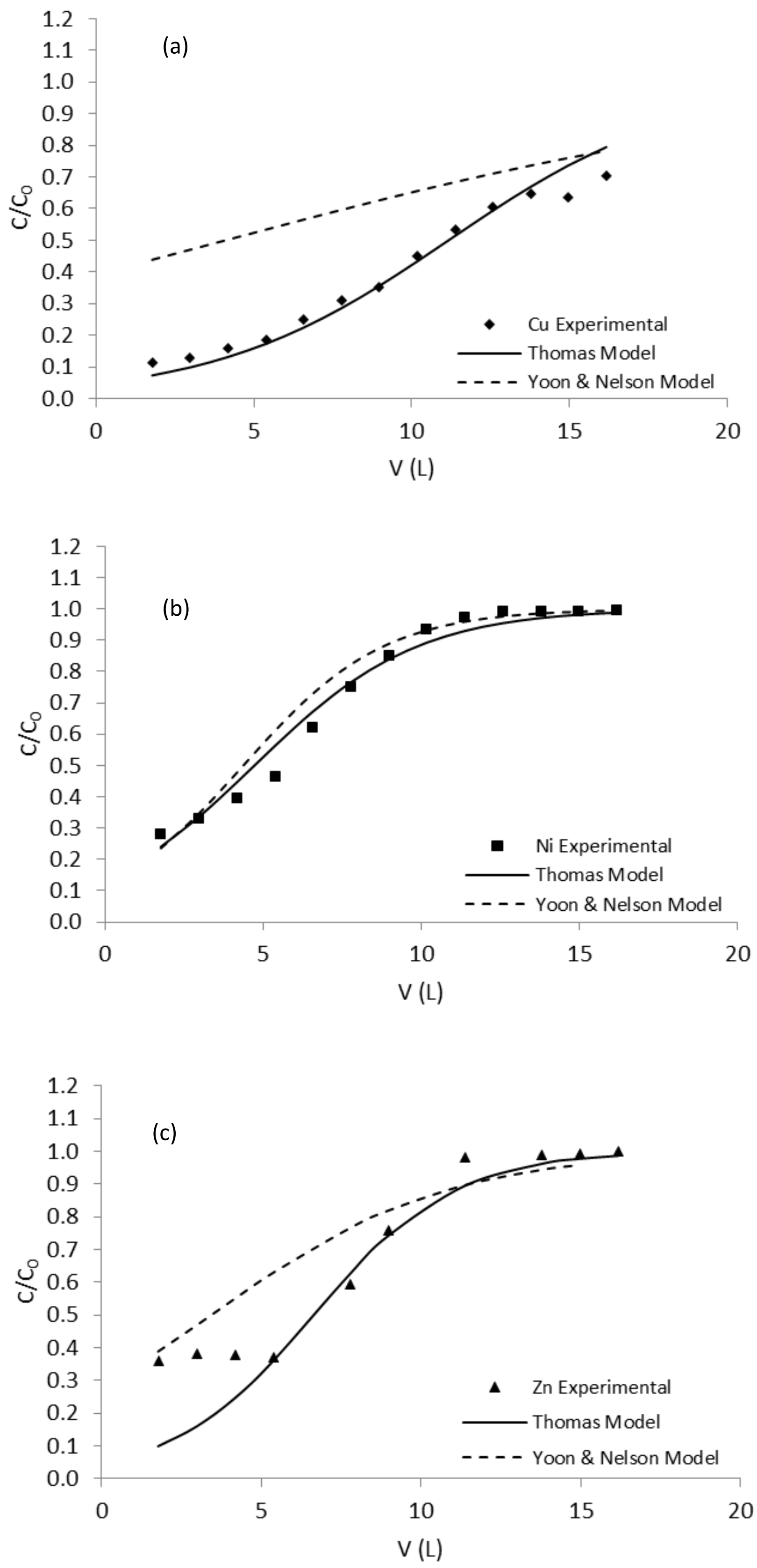

Figure 3. Comparison of the experimental and theoretical breakthrough curves obtained for (a) Cu(II), (b)Ni(II) and (c) Zn(II) by sugar cane bagasse

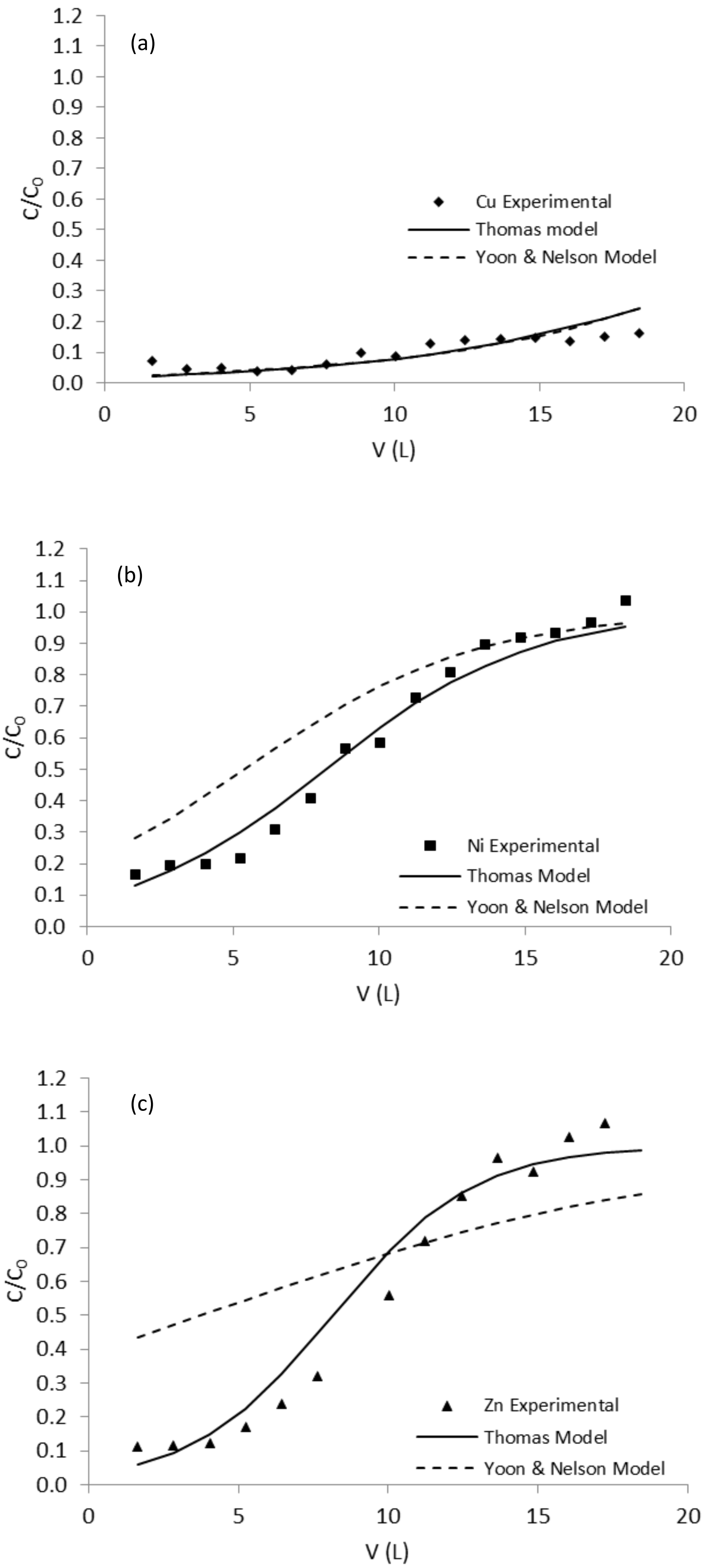

Figure 4. Comparison of the experimental and theoretical breakthrough curves obtained for (a) Cu(II), (b)Ni(II) and (c) Zn(II) by green coconut fiber.

Tables 4 and 5 shows the values of the parameters of each model for each metal ion studied, where it is found that the experimental data fitted well to the Thomas model, with low values of SSE, while the model of Yoon & Nelson showed high values of SSE reaching 8.87. The Thomas constant, k_{TH}, which characterizes the rate of transfer of metal ions from solution to the adsorbent, is related to the slope of the curve. The larger the slope is, the smaller the constant. The steeper the curve, the greater the constant is. In case of sugarcane bagasse, the constant value was lower for copper ion, as well as for green coconut fibers.

Comparing the adsorption capacities obtained by Thomas Model (Table 4 and 5) and the experimental results (Table 2), it can be seen that the values were close, especially for green coconut fibers. The q_{TH} for copper ions about 34 times larger than the zinc and nickel ions on sugarcane bagasse while for green coconut fibers it was 64 times than nickel and 9 times than zinc. In fact, the higher concentration of copper ions in solution favors adsorption. Obviously, other factors such as electronegativity, ionic radius, etc., may be involved. Therefore, the Thomas model can be considered as a suitable kinetic model to describe adsorption in a fixed bed. On the other hand, as Yoon & Nelson model didn't fitted well the data it was observed that the 50% breakthrough time (T) obtained from the model was different from the experimental.

Table 4. Calculated Parameters for Thomas and Yoon & Nelson Model from sugarcane bagasse.

Metal ions	Thomas Model			Yoon& Nelson Model			
	k_{TH}	q_{TH}	SSE	k_{YN}	T	T_{exp}	SSE
Cu(II)	9.9×10^{-2}	2.42	2.2×10^{-20}	8.4×10^{-3}	51.2	142.1	8.87
Ni(II)	2	0.07	4.0×10^{-18}	3.6×10^{-2}	54.6	72.1	1.3×10^{-1}
Zn(II)	2	0.07	5.7×10^{-1}	2.2×10^{-2}	42.9	97.1	3.36×10^{-1}

Table 5. Calculated Parameters for Thomas and Yoon & Nelson Model from green coconut fiber.

Metal Ions	Thomas Model			Yoon& Nelson Model			
	k_{TH}	q_{TH}	SSE	k_{YN}	T	T_{exp}	SSE
Cu (II)	1.0×10^{-1}	3.23	3.0×10^{-33}	1.0×10^{-2}	426.0	320.5	2.2×10^{-29}
Ni (II)	3.78	0.05	7.29×10^{-15}	2.0×10^{-2}	67.3	110.5	2.58
Zn (II)	8×10^{-1}	0.35	3.6×10^{-20}	9.8×10^{-3}	47.0	125.5	9.1×10^{-1}

4. CONCLUSION

The results indicated that the use of sugar cane bagasse and green coconut fibers as adsorbents of toxic metal ions in a fixed bed system is a feasible technology in wastewater treatment. The adsorbent usage rate was low for both materials studied, indicating a possible application in industry. Among the models applied, Thomas model fitted better the data than Yoon & Nelson model.

5. REFERENCES AND NOTES

[1] Ajmal, M.; Rao, R. A. K.; Ahmad, R.; Ahmad, J.; Rao, L. A. K. *J. Hazard. Mater.* **2001**, *B87*, 127. [CrossRef]

[2] Kurniawan, T. A.; Chan, G. Y. S.; Lo, W-H.; Babel, S. *Chem. Eng. J.* **2006**, *118*, 83. [CrossRef]

[3] Hasfalina, C. M.; Maryam, R. Z.; Luqman, C. A.; Rashid M. *APCBEE Procedia* **2012**, *3*, 255. [CrossRef]

[4] Kumara, R.; Bhatia, D.; Singh, R.; Rani, S.; Bishnoi, N. R. *Int. Biodeter. Biodegr.* **2011**, *65*, 1133. [CrossRef]

[5] Kumara, R.; Bhatia, D.; Singh, R.; Rani, S.; Bishnoi, N. R. *Int. Biodeter. Biodegr.* **2012**, *66*, 82. [CrossRef]

[6] Futalan, C. M.; Kan, C-C.; Dalida, M. L., Pascua, C.; Wan, M-W. *Carbohyd. Polym.* **2011**, *83*, 697. [CrossRef]

[7] Priya, P. G.; Basha, C. A.; Ramamurthi, V.; Begum, S. N.

J. Hazard. Mater. **2009**, *163*, 899. [CrossRef]

[8] Low, K. S.; Lee, C. K.; Leo, A. C. *Bioresource Technol.* **1995**, *51*, 227. [CrossRef]

[9] Sousa, F. W.; Sousa, M. J.; Oliveira, I. R. N.; Oliveira, A. G.; Cavalcante, R.M.; Fechine, P. B. A.; Neto, V. O. S.; Keukeleire, D.; Nascimento, R. F. *J. Environ. Manage.* **2009**, *90*, 3340. [CrossRef]

[10] Sousa, F. W.; Oliveira, A. G.; Ribeiro, J. P.; Rosa, M. F.; Keukeleire, D.; Nascimento, R. F. *J. Environ. Manage.* **2010**, *91*, 1634. [CrossRef]

[11] Malkoc, E.; Nuhoglu, Y. *J. Hazard. Mater.* **2006**, *B135*, 328. [CrossRef]

[12] Suksabye, P.; Thiravetyan, P.; Nakbanpote, W. *J. Hazard. Mater.* **2008**, *160*, 56. [CrossRef]

[13] Aksu, Z.; Gönen, F. *Sep. Purif. Technol.* **2006**, *49*, 205. [CrossRef]

[14] Gupta, V. K.; Srivastava, S. K; mohan, D.; sharma, S. *Waste manage.* **1997**, *17*, 517. [CrossRef]

[15] Cooney, D.O.; Adsorption Design for Wastewater Treatment. Boca Raton, Florida: CRC Press, 1999.

[16] Naja, G.; Volesky, B. *Environ. Sci. Technol.* **2006**, *40*, 3996. [CrossRef]

[17] Gupta, V. K.; Srivastava, S. K.; Tyagi, R. *Water res.* **2000**, *34*, 1543. [CrossRef]

[18] Kundu, S.; Gupta, A. K. *J. Colloid Interf. Sci.* **2005**, 290, 52. [CrossRef]

[19] Zhang, W.; Simanek, E.E. *Org. Lett.* **2000**, *2*, 843. [CrossRef]

[20] Markovska, L.; Meshko, V.; Noveski, V. *Korean J. Chem. Eng*. **2001**, *18*, 190. [CrossRef]

[21] Muhamad, H.; Doan, H.; Lohi, H. *Chem. Eng. J.* **2010**, *158*, 369. [CrossRef]

[22] Aksu, Z.; Gonen, F. *Process Biochem.* **2003**, *39*, 599. [CrossRef]

[23] Ipek, I. Y.; Kabay, N.; Yuksel, M.; *Desalination* **2013**, *310*, 151. [CrossRef]

[24] Ayoob, S.; Gupta, A. K.; Bhakat, P. B. *Sep. Purif. Technol.* **2007**, *52*, 430. [CrossRef]

[25] Shahbazia, A.; Younesi, H.; Badiei, A. *Chem. Eng. J.* **2011**, *168*, 505. [CrossRef]