Journal of
Bioremediation & Biodegradation

ISSN: 2155-6199

Mahmoud and Fawzy, J Bioremed Biodeg 2015, 6:4
DOI: 10.4172/2155-6199.1000304

Research Article | Open Access

Statistical Methodology for Cadmium (Cd(II)) Removal from Wastewater by Different Plant Biomasses

Alaa El Din Mahmoud* **and Manal Fawzy**

Environmental Sciences Department, Faculty of Science, Alexandria University, Alexandria, Egypt

Abstract

The combined effects of metal ion concentration (X), hydrogen ion concentration (pH) and biomass dose (BD), on the biosorption of Cadmium Cd(II) were investigated. Two different plant biomasses; rice straw (Oryza sativa) and dragon tree leaves (Dracaena draca) were studied.

The optimum conditions were found at (X)=10 ppm, (pH)=7 and (BD)=0.5 g. Under these conditions, desirability values of 0.996 and 0.997 for rice straw and dragon tree leaves were obtained, showing that the calculated model may represent the experimental model and give the desired conditions. The samples before and after biosorption experiments were characterized by Energy Dispersive X-Ray Spectroscopy.

Keywords: Optimization; Cadmium; *Oryza sativa*; *Dracaena draca*; Response surface methodology

Introduction

The availability of water resources are becoming increasingly scarce; the consumption and exploitation of water resources, along with exponential increase in population have caused water pollution [1]. Toxic metals of particular concern in treatment of industrial wastewaters include: mercury, lead, cadmium, zinc, copper, nickel, and chromium [2]. So this study focuses on Cadmium (Cd(II)) that is attracting wide attention of environmentalists as one of the most toxic heavy metals. Currently methods that are being used to remove heavy metal ions include chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical technologies. These methods are usually inadequate and expensive [3].

Biosorption is an emerging technology that is used to sequester toxic heavy metals and is particularly useful for the removal of contaminants from industrial effluents [4]. The biosorbent term refers to material derived from microbial biomass, seaweed or plants that exhibit adsorptive property [5]. Many biosorbents have been used in biosorption processes such as bacteria, fungi, algae [6] and agricultural wastes such as rice husk [7], Pequi Fruit Skin [8], *Psidium guajava* leaves powder [9], sugarcane bagasse, maize corncob, Jatropha oil cake [10] and cork waste [11].

The utilization of agricultural waste materials is increasingly becoming important concern because these wastes represent unused resources and, in many cases, present disposal problems [6]. So the use of natural biomaterials, especially crop wastes as biosorbents, is a promising alternative due to their relative abundance and their low commercial value [12]. Nearly 3 Million tons of rice straw is burned annually in the field of Egypt every year causing "Black cloud" [13]. However, no available literatures about using waste of ornamental plants as natural biosorbent.

In this work, the Central Composite Design (CCD), which is a type of Response Surface Methodology (RSM), was employed for Optimization the biosorption of Cd(II) using two different dried plant biomasses: rice straw (*Oryza sativa*) and dragon tree leaves (*Dracaena draca*); a common ornamental plant in Egyptian gardens. Samples before and after biosorption of Cd(II) were characterized using Energy Dispersive X-Ray Spectroscopy.

Materials and Methods

Biosorbent preparation

Plant biomasses were dried, then were washed with tap water to remove any dust or foreign particles attached to them and finally rinsed with deionized water. The washed biomasses were dried at 60°C for 48 hours and grounded to powder then sieved through a siever; mesh size ≤ 0.5 mm for biosorption experiments.

Reagents and equipments

Cadmium standard solution with initial concentration 1000 ppm was used to prepare experimental concentration of 10 and 100 ppm using deionized water. pH adjustment of the solutions was made by HNO_3 and NaOH utilizing a pH/mV hand-held meter (Crison pH meter, PH 25).

Biosorption experiments

Response surface methods are used to examine the relationship between response variable (RF%) and the studied factors (X, pH and BD). RSM is applied to optimize the studied factors that produce the best response and model a relationship between the factors and the response [14]. All data were analyzed using MINITAB®16 software. A2^3 full factorial central composite design with two coded levels was performed. For statistical calculation, the variables were coded according to Eq. (1):

$$x_i = X_i - X_0 / \Delta X \qquad (1)$$

Where x_i is the dimensionless coded value of the variable Xi, X0 the middle value of X_i, and ΔX the step change.

***Corresponding author:** Alaa El Din Mahmoud, Environmental Sciences Department, Faculty of Science, Alexandria University, Alexandria, Egypt, Tel: +1285849461; E-mail: alaa-mahmoud@alexu.edu.eg

Received June 09, 2015; **Accepted** July 06, 2015; **Published** July 08, 2015

Citation: Mahmoud AED, Fawzy M (2015) Statistical Methodology for Cadmium (Cd(II)) Removal from Wastewater by Different Plant Biomasses. J Bioremed Biodeg 6: 304. doi:10.4172/2155-6199.1000304

Batch experiments were conducted with the following conditions: 0.5 g of each biomass and 100 ml of Cd(II) solution with an agitation speed 300 rpm (round per minute) at room temperature. The influence of three factors i.e., initial metal ion concentration (X), hydrogen ion concentration (pH) of the solution, biomass dose (BD) have been investigated. The range and the levels of the variables investigated in this research are given in Table 1.

Then samples were collected after 2 hours to reach equilibrium in biosorption. Control samples were prior to batch biosorption experiment to determine initial metal concentration and all samples were conducted in triplicate. The metal ions contents in all the samples prior to and after batch biosorption experiments were analyzed by Varian Inductively Coupled Plasma (ICP-AES).

Removal efficiency (RF%) of biosorbent was calculated using the following equation

$$\text{Removal effeciency\%} = \frac{\text{Ci} - \text{Cf}}{\text{Ci}} \times 100 \tag{2}$$

Where: C_i= Initial concentration of metal in solution, before the sorption analysis (mg/l), C_f= Final concentration of metal in solution, after the sorption analysis (mg/l).

Characterization of biosorbents

Energy Dispersive X-Ray Spectroscopy (EDAX): EDAX spectra can be collected from a specific point on the sample, giving an analysis of a few cubic microns of material. Each biosorbent was characterized by EDAX before and after Cd(II) biosorption.

Results and Discussion

Biosorption experiments

Batch experiments were conducted as tabulated in Table 2, '+1' for the higher level and '−1' for the lower level of the studied factors. Removal efficiency percentage (RF%) were calculated according to Eq.(1).

Regression coefficients (Coef) and the associated standard errors (SE Coef) of results are shown in Table 3. Results revealed that all the studied factors together with their interactions were significant at 95% confidence limits (P>0.05). The response variable (Cd(II) removal %) was fitted by the following equation:

$$\begin{aligned} Y = A + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_1x_2 + \\ a_5x_1x_3 + a_6x_2x_3 + a_7x_1x_2x_3 \end{aligned} \tag{3}$$

Where: Y: Estimated of the response, A: represents the global mean (constant), a: Coefficients and x: Experimental Factors.

At X=10 ppm, pH=7 and BD=0.5 g, the highest percentage of Cd(II) removal by rice straw was 82.60% while that for dragon tree leaves was 79.60% (Table 2).

It worth noting that the effect of all the studied main factors (X, pH, BD) was identical for both biosorbents. As such, our results demonstrated that the factor (X) had the largest effect on biosorption process by rice straw and dragon tree leaves (Table 3). Results also showed that Cd(II) biosorption was favored at low metal concentration values (X=10 ppm). This is in line with [15,16]. In the current work, the biosorption percentage was decreased as the metal ion concentration from 10 to 100 ppm. This is may be because the biomass surface area available for metal biosorption was higher the ratio of active adsorption sites to the initial Cd(II) ions is larger, resulting in higher removal efficiency [17]. This is in agreement with many researchers [6,11].

Factor	Low level	High level
X(mg/l)	10	100
pH	2	7
BD(g)	0.1	0.5

Table 1: High and low levels of the studied factors.

The second important main factor in the biosorption process was pH. Results indicated that as the pH value increases, Cd(II) biosorption increases by both biosorbents (Table 3). At lower pH values, the H_3O^+ ions compete with the metal ions for the active sites on the biosorbent [18]. In our work, the optimum higher pH value for Cd(II) biosorption was 7. The hydrolysis of Cd(II) ions occur beyond pH=7 as reported in [10].

In this account, the third main factor in the biosorption process was BD. Results indicated that as (BD) increases, Cd(II) biosorption increases by both biosorbents (Table 3). An increase in the biomass dosage generally increases the amount of solute biosorbed, due to the increased surface area of the biosorbent, which in turn increases the number of binding sites [19-21]. Data obtained from the response surface plots of both biosorbents are illustrated in Figures 1-3. These plots are used to visualize the relationship between response (%RF) and the level of each studied factors. Every one of them is mapped against two experimental factors while the third is fixed at two different levels [22].

Figure 1 illustrated the removal efficiency of Cd(II) by both biosorbents over (pH) and (BD). At constant metal ion concentration (100 ppm, 10 ppm), a remarkable increase in Cd(II) removal was attained as pH increases till reaching its maximum at pH=7 for both biosorbents. However, a slight increase in Cd(II) removal was observed as (BD) increases till reaching its maximum at BD=0.5 g.

Figure 2 illustrated the removal efficiency of Cd(II) by both biosorbents over (X) and (BD). When keeping pH constant (7, 2) for both biosorbents, a remarkable increase in Cd(II) removal was attained as (X) decreases till reaching its maximum at X=10 ppm for both biosorbents. However, a slight increase in Cd(II) removal was observed as BD increases till reaching its maximum at BD=0.5 g for both biosorbents.

Figure 3 illustrated the removal efficiency of Cd(II) by both biosorbents over (X) and (pH). At constant biomass dose (0.5 g, 0.1 g), a remarkable increase in Cd(II) removal was attained as (X) decreases till reaching its maximum at X=10 ppm for both biosorbents. However,

Factors			Rice straw	Dragon tree leaves
X	pH	BD	RF-R2 Average (%)	RF-D2 Average (%)
-1	-1	-1	31.00	48.38
-1	-1	1	61.99	67.63
-1	1	-1	72.78	76.06
-1	1	1	82.30	79.40
1	-1	-1	7.79	13.03
1	-1	1	28.09	35.32
1	1	-1	27.27	45.44
1	1	1	60.91	55.16

Table 2: Experimental factorial design results for Cd(II) biosorption(X: metal ion concentration, pH: hydrogen ion concentration, BD: biomass dose).

Biosorbents	Rice straw					Dragon tree leaves				
Term	Effect	Coef	SE Coef	T	*p*	Effect	Coef	SE Coef	T	*p*
Constant		46.51	1.652	28.16	0.000		52.55	0.5781	90.90	0.000*
Main Factors										
X	-31.00	-15.50	1.652	-9.39	0.000	-30.63	-15.32	0.5781	-26.49	0.000*
pH	28.60	14.30	1.652	8.66	0.000	22.93	11.46	0.5781	19.83	0.000*
BD	23.61	11.81	1.652	7.15	0.000	13.65	6.83	0.5781	11.81	0.000*
Two Factors Interaction										
X.pH	-2.45	-1.22	1.652	-0.74	0.480	3.20	1.60	0.5781	2.77	0.024*
X.BD	3.36	1.68	1.652	1.02	0.339	2.36	1.18	0.5781	2.04	0.076
pH.BD	-2.03	-1.02	1.652	-0.61	0.556	-7.12	-3.56	0.5781	-6.16	0.000*
Three Factors Interaction										
X.pH.BD	8.70	4.35	1.652	2.63	0.030	0.83	0.42	0.5781	0.72	0.491

* P>0.05

Table 3: Response surface regression for Cd(II) removal by rice straw and dragon tree leaves (T: t-test, *p*: probability value).

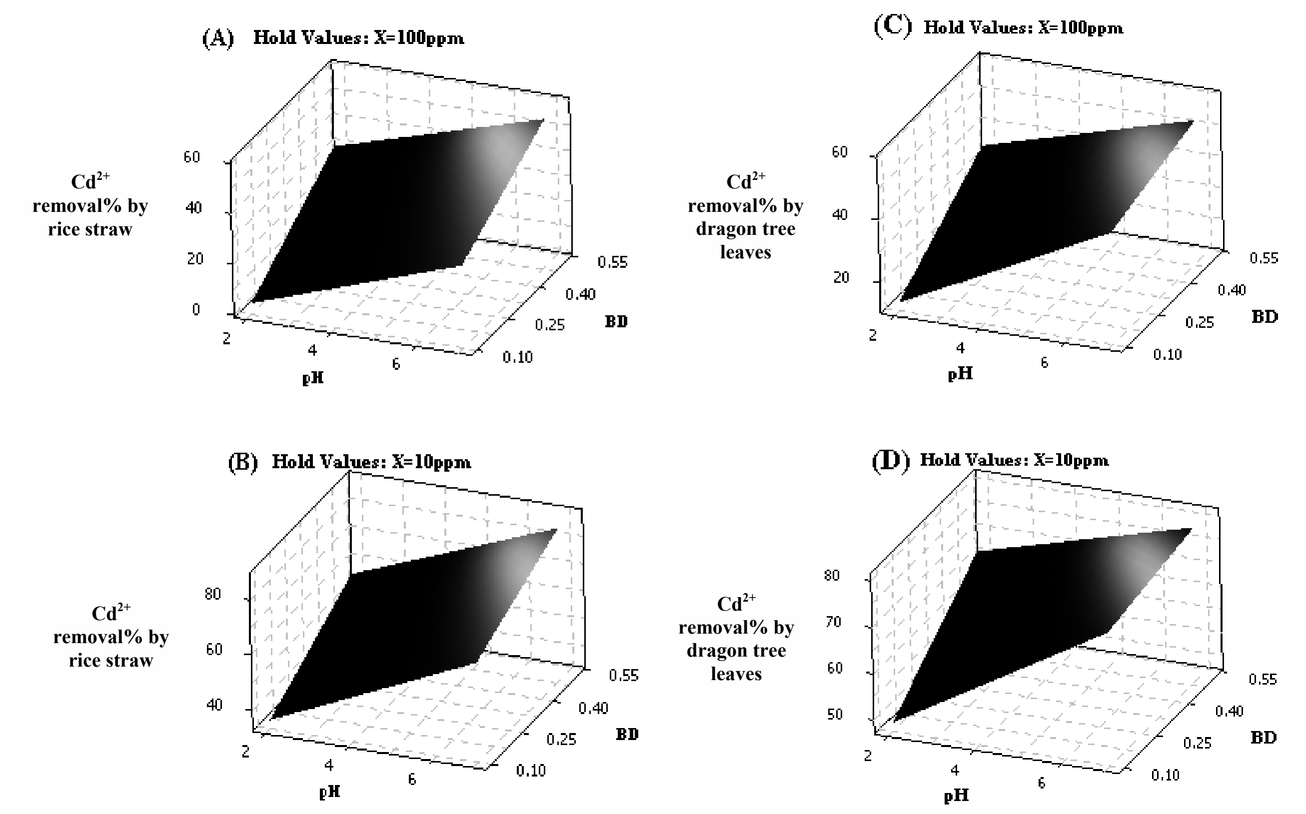

Figure 1: Response surface plots showing the effect of (pH) and (BD) on Cd(II) removal percentage by rice straw at (A) 100 ppm and (B) 10 ppm and dragon tree leaves at (C) 100 ppm and (D) 10 ppm.

a slight increase in Cd(II) removal was observed as pH increases till reaching its maximum at pH=7.

Analysis of variance (ANOVA - Table 4) showed the sum of squares used to estimate the factors' effect and the F-ratios defined as the ratio of the respective mean-square-effect and the mean-square-error. The significance of the present biosorption models as assessed by F-values and P-values indicated that the studied factors and their interactions (X.pH.BD) except (X.pH, X.BD, pH.BD) are statistically significant in the case of rice straw and the studied factors and their interactions except (X.BD and X.pH.BD) are statistically significant in the case of dragon tree leaves.

Characterization of biosorbents

The results of EDAX (Figure 4) showed that raw biosorbents did not contain any Cd(II) ions on their surfaces and these ions appeared only after batch biosorption experiments.

Response optimization

After Response Surface Methodology was carried out, Minitab's Response Optimizer was used to get the optimized factors and responses. The goal for the studied factors (X, pH, BD) was to maximize them as listed in Table 5.

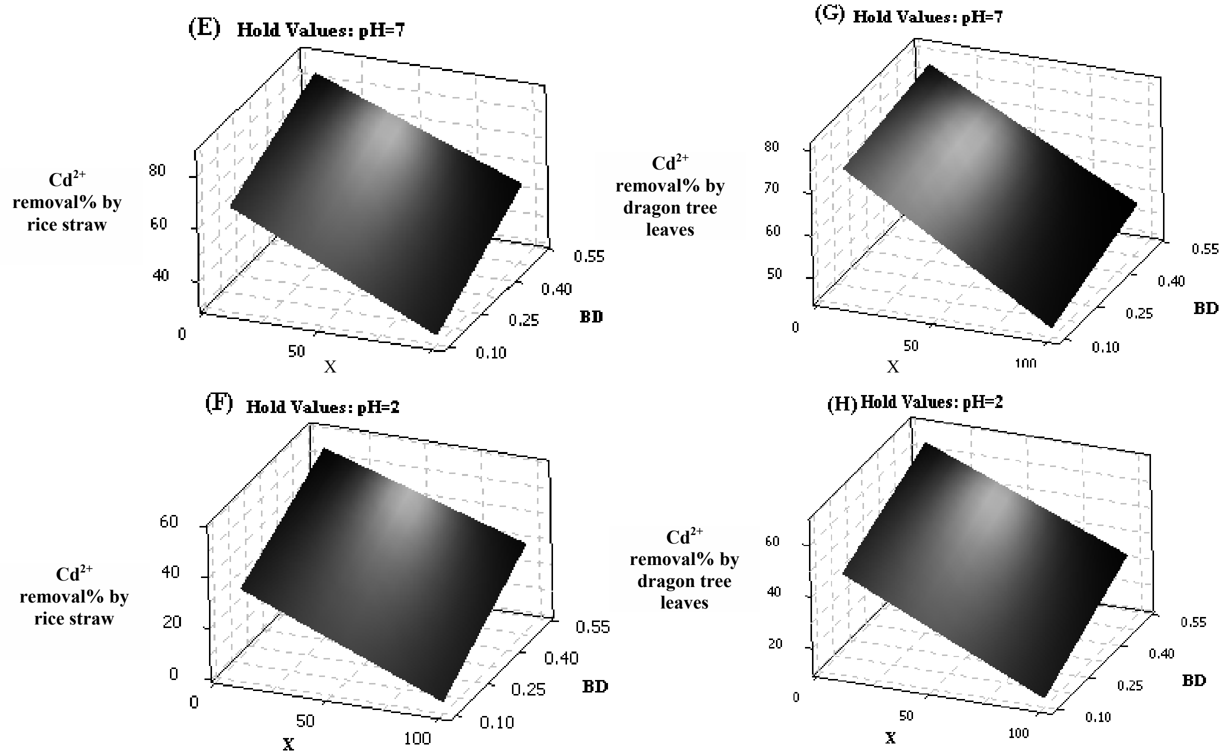

Figure 2: Response surface plots showing the effect of (X) and (BD) on Cd(II) removal percentage by rice straw at (E) pH=7 and (F) pH=2 and dragon tree leaves at (G) pH=7 and (H) pH=2.

	Rice straw					Dragon tree leaves				
Source	DF	Seq SS	Adj MS	F	P	DF	Seq SS	Adj MS	F	P
Main Effects	3	9346.4	3115.48	71.37	0.000	3	6601.06	2200.35	411.45	0.000
X	1	3844.9	3844.93	88.09	0.000	1	3753.16	3753.16	701.82	0.000
pH	1	3271.6	3271.55	74.95	0.000	1	2102.59	2102.59	393.17	0.000
BD	1	2230.0	2229.96	51.09	0.000	1	745.32	745.32	139.37	0.000
2-Way Interactions	3	85.5	28.50	0.65	0.603	3	266.08	88.69	16.58	0.001
X.pH	1	23.9	23.94	0.55	0.480	1	40.97	40.97	7.66	0.024
X.BD	1	45.1	45.06	1.03	0.339	1	22.23	22.23	4.16	0.076
pH.BD	1	16.5	16.50	0.38	0.556	1	202.88	202.88	37.94	0.000
3-Way Interactions	1	302.7	302.67	6.93	0.030	1	2.78	2.78	0.52	0.491
X.pH.BD	1	302.7	302.67	6.93	0.030	1	2.78	2.78	0.52	0.491
Residual Error	8	349.2	43.65			8	42.78	5.35		
Pure Error	8	349.2	43.65			8	42.78	5.35		
Total	15	10083.8				15	6912.70			

Table 4: Analysis of Variance.

	Goal	Lower	Target	Upper	Predicted Responses	Desirability
Rice straw (RF-R2)	Maximum	7.65	82.60	82.60	82.30	0.996
Dragon tree leaves (RF-D2)	Maximum	12.81	79.60	79.60	79. 39	0.997

Table 5: Parameters of Response Optimization.

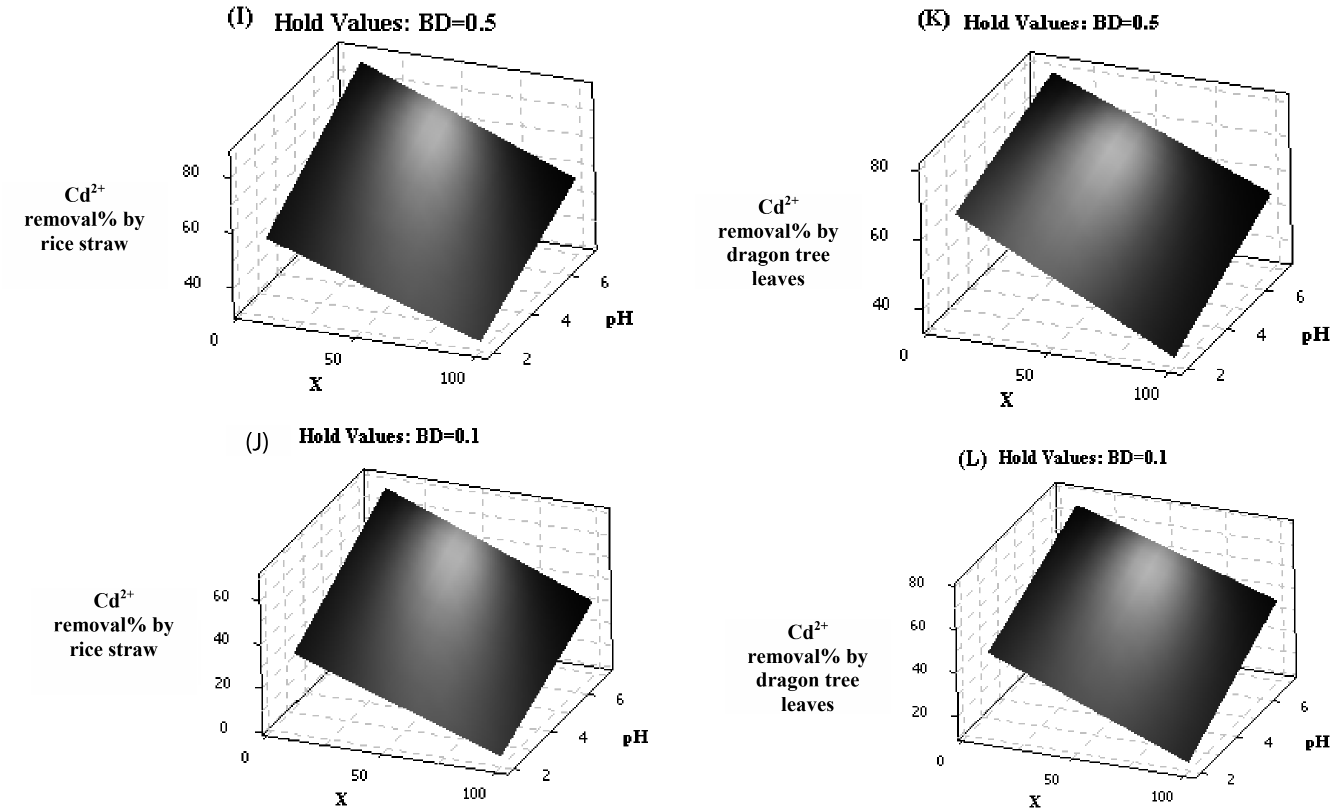

Figure 3: Response surface plots showing the effect of (X) and (pH) on Cd(II) removal percentage by rice straw at (I) BD=0.5 and (J) BD=0.1 and dragon tree leaves at (K) BD=0.5 and (L) BD=0.1.

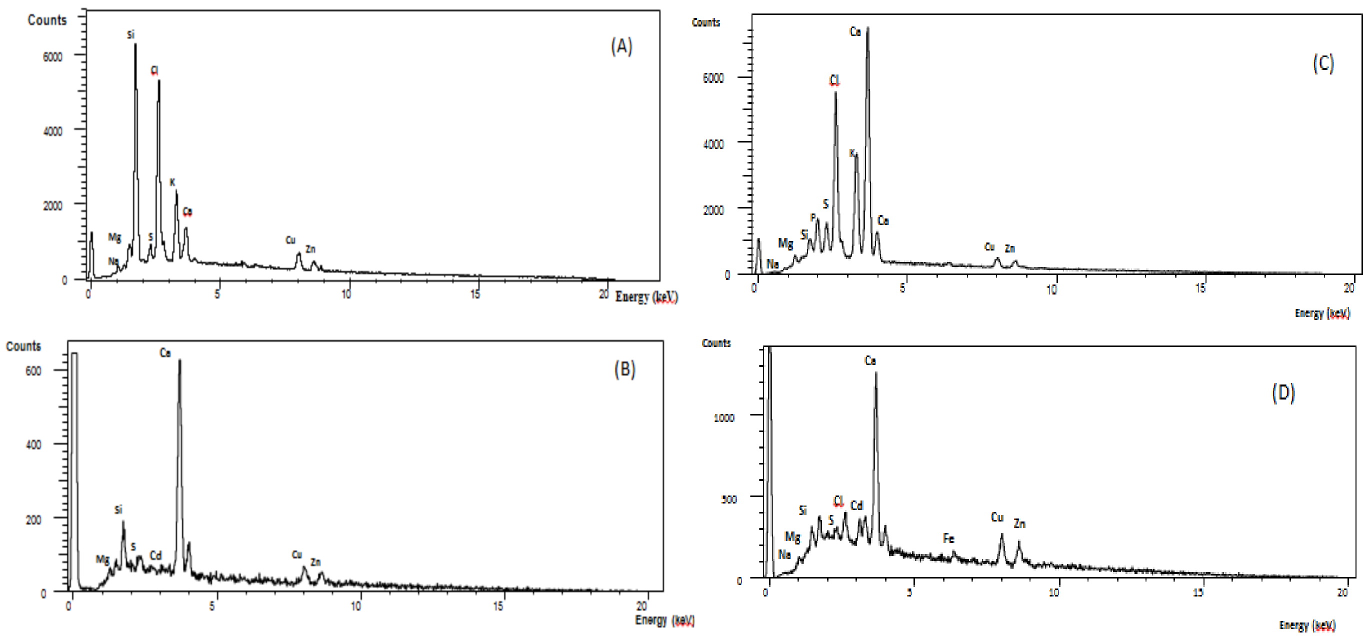

Figure 4: EDAX images of; (A) Raw rice straw, (B) Rice straw after Cd(II) biosorption, (C) Dragon tree leaves and (D) Dragon tree leaves after Cd(II) biosorption.

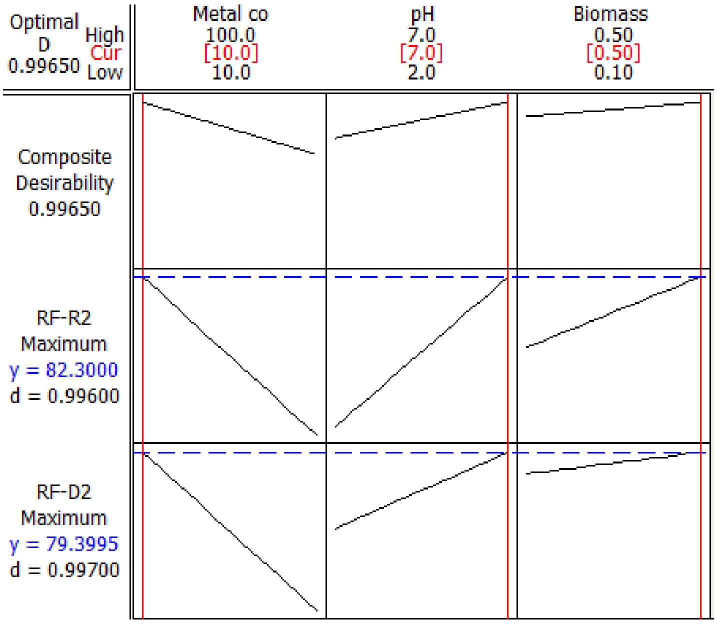

Figure 5: Optimization Plot for Cd(II) Removal% by rice straw (RF-R2) and dragon tree leaves (RF-D2).

All results had relatively high desirability scores of rice straw and dracaena draca were 0.961 and 0.970, respectively as listed in Table 5 because the predicted response of them were 82.30 and 79.39 which were quite close to the targets of each one of 82.60 and 79.60, respectively and optimization plot was shown in Figure 5. Desirability is an objective function that ranges from zero outside of the limits to one at the goal [23,24]. The composite desirability (D) of 0.99650 combined the individual desirabilities and it is high as it is closer to 1 and the best removal percentage of Cd(II) obtained at X=10 ppm, pH=7 and BD=0.5 g for each biosorbent where the vertical lines on the graph represent the current factor settings, the horizontal datch lines represent the current response values

Conclusion

It may be concluded that:

- The most significant effect for Cd(II) biosorption by rice straw and dragon tree leaves was ascribed to (X).
- Main factors exert more effect than interaction factors by both biosorbents.
- Ion exchange and complexation processes are the mechanisms of biosorption that occurred in rice straw and dragon tree leaves, respectively.
- EDAX confirmed biosorption process by the changes occurred on the surfaces of both biosorbents.
- Desirability values (0.996 and 0.997) indicated the calculated model can represent the experimental model and give the desired conditions for both biosorbents.

References

1. Singh R, Chadetrik R, Kumar R, Bishnoi K, Bhatia D, et al. (2010) Biosorption optimization of lead(II), cadmium(II) and copper(II) using response surface methodology and applicability in isotherms and thermodynamics modeling. Journal of Hazardous Materials 174: 623-634.
2. Mousavi HZ, Hosseynifar A, Jahed V, Dehghani SAM (2010) Removal of Lead from aqueous Solution using waste Tire Rubber Ash as an Adsorbent. Brazilian Journal of Chemical Engineering 27: 79-87.
3. Reddy DHK, Seshaiah K, Reddy AVR, Rao MM, Wang MC (2010) Biosorption of Pb2+ from aqueous solutions by Moringa oleifera bark: Equilibrium and kinetic studies. Journal of Hazardous Materials 174: 831-838.
4. Reddy KO, Maheswari CU, Reddy DJP, Guduri B, Rajulu AV (2010) Properties of ligno-cellulose ficus religiosa leaf fibers. International Journal of Polymers and Technologies 2: 29-35.
5. Nasr M, Mahmoud A, Fawzy M, Radwan A (2015) Artificial intelligence modeling of cadmium(II) biosorption using rice straw. Applied Water Science: 1-9.
6. Sulaymon AH, Mohammed AA, Al-Musawi TJ (2012) Competitive biosorption of lead, cadmium, copper, and arsenic ions using algae. Environmental Science and Pollution Research: 1-13.
7. Krishnani KK, Meng X, Christodoulatos C, Boddu VM (2008) Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. Journal of Hazardous Materials 153: 1222-1234.
8. Seolatto AA, Silva Filho CJ, Mota DLF (2012) Evaluation of the Efficiency of Biosorption of Lead, Cadmium, and Chromium by the Biomass of Pequi Fruit Skin (Caryocar brasiliense Camb.). Chemical Engineering Transactions 27: 1974-9791.
9. Varma DSNR, Srinivas C, Nagamani C, PremSagar T, Rajsekhar M (2010) Studies on biosorption of Cadmium on Psidium guajava leaves powder using statistical experimental design Journal of Chemical and Pharmaceutical Research 2: 29-44
10. Garg U, Kaur MP, Jawa GK, Sud D, Garg VK (2008) Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass. Journal of Hazardous Materials 154: 1149-1157.
11. Lopez-Mesas M, Navarrete ER, Carrillo F, Palet C (2011) Bioseparation of Pb(II) and Cd(II) from aqueous solution using cork waste biomass. Modeling and optimization of the parameters of the biosorption step. Chemical Engineering Journal 174: 9-17.
12. Barka N, Abdennouri M, El Makhfouk M, Qourzal S (2013) Biosorption characteristics of cadmium and lead onto eco-friendly dried cactus (Opuntia ficus indica) cladodes. Journal of Environmental Chemical Engineering.
13. Bakker R, Elbersen W, Poppens R, Lesschen JP (2013) Rice Straw and Wheat Straw - Potential feedstocks for the Biobased Economy. Wageningen UR, Food & Biobased Research.

14. Pavan FA, Gushikem Y, Mazzocato AC, Dias SLP, Lima EC (2007) Statistical design of experiments as a tool for optimizing the batch conditions to methylene blue biosorption on yellow passion fruit and mandarin peels. Dyes and Pigments 72: 256-266.

15. Saadat S, Karimi-Jashni A (2011) Optimization of Pb(II) adsorption onto modified walnut shells using factorial design and simplex methodologies. Chemical Engineering Journal 173: 743-749.

16. Amarasinghe B, Williams R (2007) Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. Chemical Engineering Journal 132: 299-309.

17. Singh N, Gadi R (2012) Bioremediation of Ni(II) and Cu(II) from wastewater by the nonliving biomass of Brevundimonas vesicularis. Journal of Environmental Chemistry and Ecotoxicology 4: 137-142.

18. Arief VO, Trilestari K, Sunarso J, Indraswati N, Ismadji S (2008) Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies. CLEAN-Soil Air Water 36: 937-962.

19. Lichtfouse E, Schwarzbauer J, Robert D, Mudhoo A, Garg V, et al. (2012) Heavy Metals: Toxicity and Removal by Biosorption. Environmental Chemistry for a Sustainable World, Springer Netherlands pp. 379-442

20. Garg UK, Kaur M, Garg V, Sud D (2007) Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. Journal of Hazardous Materials 140: 60-68.

21. Badr N, Al-Qahtani KM (2013) Treatment of wastewater containing arsenic using Rhazya stricta as a new adsorbent. Environmental Monitoring and Assessment 185: 9669-9681.

22. Sarkar M, Majumdar P (2011) Application of response surface methodology for optimization of heavy metal biosorption using surfactant modified chitosan bead. Chemical Engineering Journal 175: 376-387.

23. Amini M, Younesi H, Bahramifar N (2009) Statistical modeling and optimization of the cadmium biosorption process in an aqueous solution using Aspergillus niger. Colloids and Surfaces A: Physicochemical and Engineering Aspects 337: 67-73.

24. Amini M, Younesi H, Bahramifar N, Lorestani AAZ, Ghorbani F, et al. (2008) Application of response surface methodology for optimization of lead biosorption in an aqueous solution by Aspergillus niger. Journal of Hazardous Materials 154: 694-702.