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Design and Application of Biosorbent (*Opuntia fragalis* Leaves) for the Removal of Heavy Metal from Human Blood Plasma

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ABSTRACT

Environmental pollution is a potential threat to human health mainly because of the non-biodegradable and hazardous heavy metals. Among these heavy metals, lead is of considerable concern. Various methods adopted for removal of heavy metals include chemical precipitation, membrane separation, ion exchange and adsorption. In case of adsorption, the generally used adsorbents like activated carbon, silica, alumina, etc. are expensive. This has prompted the use of natural materials as biosorbents in order to develop cheaper alternatives, which can be disposed of without regeneration due to their lower cost. This study seeks to investigate the efficiency of *Opuntia fragalis* leaves as biosorbents for the removal of Pb (II) ions from Human plasma using Response Surface Methodology (RSM). The effect of adsorption factors; adsorbent dose (A), concentration of Pb (II) ions (B), pH of solution (C) and contact time (D) was optimized. The percentage removal of Pb (II) ions increased as the biosorption factors increased. The optimal removal of Pb (II) ions was attained at 95%. The surface chemistry of the biosorbent was analyzed using Scanning Electron Microscope, revealed an appreciable level of porosity and ability of biosorbent to adsorb Pb (II) ions from human plasma. The FTIR results showed that –C-Br, -C-N, -C-O, -C-C, -N-H and –OH functional groups were responsible for Pb (II) ions adsorption from human plasma. The lack of fit model have p-value greater than 0.05 with F-value of 0.27, implies non-significant lack of fit relatively due to the pure error and 97% lack of fit is caused by noise. The kinetics of the adsorption processes were investigated and data were subjected to Pseudo first order, Pseudo second order and Elovich models. The adsorption process fits into Pseudo second order model with R^2 = 0.9991. The equilibrium data was analyzed using isotherm models and Langmuir isotherm model with R^2 = 0.8932 indicated Pb (II) ions uptake from human plasma occurred on the same pore space without having interactions amongst themselves thereby exhibiting monolayer adsorption.

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1. Introduction

Environmental pollution of heavy metals has become a worldwide challenge and a keen attention has been given to them because of their level of toxicity, non-biodegradability, and accumulation in the food chain. Heavy metals, even at minute level, are very harmful for human beings. Thus, the removal of heavy metals from water systems is a very critical and has attracted a considerable attention [1].

Lead is considered as one of the key toxic pollutants because of its carcinogenic characteristics for humans. The permissible limit of lead (II) in drinking water is 0.05 mg/L. The maximum discharge limits for Pb (II) in waste water is 0.05 mg/L and sewage sludge applied to agriculture land is 420 mg/L as set by the Environment Protection Agency. Toxic levels of lead in human beings have been associated with encephalopathy seizures and mental retardation. Lead poisoning causes severe damage to the kidneys, nervous system, reproductive system, liver and brain [2].

The several methods used for the treatment of contaminated solutions include Precipitation, adsorption with activated carbon, ion exchange, membrane processes, oxidation and reduction. However, technical and economic factors limit sometimes the feasibility of such process. The promising method for heavy metal removal from wastewater is biosorption. Biosorption is an economically feasible means for the removal and/or recovery of heavy binding abilities of various biological materials. Recently, there has been an intensive study on the use of seeds, pods, and bark of plants called as biomass in the removal of heavy metals. *Opuntia fragalis* leaves has been identified as biosorbent capable of removing exceptional high metal concentration, shows genetic ability of plant to remediate polluted soil, water and bio fluids [3].

In addition, studies have been carried out to ascertain the optimum conditions necessary for efficient removal of these metals from polluted sites using Response Surface Methodology (RSM). RSM is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables on the response. RSM generates an experimental design for model preparation. An experimental design is a specific set of experiments defined by a matrix composed of the different level combinations of the variables studied [4][5].

The aim of the present study was to explore the use of an ecofriendly biosorbent produced from *Opuntia fragalis* leaves for the removal of Pb (II) ions from Human plasma and also to subject the optimized data to adsorption isotherm and kinetic models.

2. Materials and Methods

2.1. Materials

Lead (II) trioxonitrate, Nitric acid, Sodium hydroxide, Deionised water, *Opuntia fragilis* leaves, Human blood plasma, All the solutions were prepared with distilled water. Also, all the chemical reagents were of an analar grade.

2.2. Sample Collection

In this study, biosorbent prepared from *Opuntia fragalis* leaves for the biosorption of Pb (II) ions was collected from the botanical garden of Biological Science, Ahmadu Bello University, Nigeria. The blood sample was sourced from the Department of Haematology, Ahmadu Bello University Teaching Hospital (ABUTH), Nigeria and screened for heavy metal content using Atomic Absorption Spectroscopy (AAS).

2.3. Biosorbent Preparation

Opuntia fragalis leaves were repeatedly and carefully washed with a running tap water and distilled water was used to wash again to remove dirt particles, cut into small sizes and dried at 60°C for 24 hours. The dried plant was grounded, sieved and stored in a plastic container prior to experimental use.

2.4. Preparation of Human Blood Plasma

The blood was drawn into tubes to full volume containing anticoagulant (~1.80 mg citrate phosphate dextrose adenine per cm^3 blood) to ensure perfect mixing of the substances. The tubes were carefully inverted ten times to ensure even mixing of blood and anticoagulant, and store at ambient temperature. After, centrifugation three distinct layers were observed from the top to bottom; plasma, leucocytes and erythrocytes. The plasma was carefully aspirated at physiological temperature (37°C) and care was taken not to distort the cell layers. Inspection of plasma for turbidity was carried out and turbid sample was centrifuged again to remove remaining insoluble matters [5]. Thereafter, the human plasma was characterized for the presence of heavy metal of interest using AAS.

2.5. Characterisation of Biosorbent

2.5.1Fourier Transform Infrared (FT-IR) Spectroscopy

The biosorbent was characterized for the presence of functional groups responsible for adsorption of Pb (II) ions from human plasma by using Perkin Elmer, USA FTIR spectrophotometer. To determine the FT-IR spectra of the biosorbent before and after biosorption, Perez Meteus *et al.,* method was used [6]. Biosorbent/lead ions films were prepared by mixing with KBr, the films containing the specimen were inserted into the apparatus, and the infrared spectrum was recorded in the range 400–4000 cm^{-1}.

2.5.2 Scanning Electron Microscopy (SEM)

To investigate the morphology of the biosorbent before and after adsorption and the distribution of the lead ions onto the biosorbent using an electron microscope (Hitachi, Japan). To obtain microscopic images of the biosorbent, the specimens were bonded to the aluminum substrates using a double-sided adhesive. Aluminum plate was then coated with gold using BAL-TEC SCD 005 coating system (Baltec AG, Balzers, Liechtenstein) and the samples were imaged using Scanning Electron Microscopy.

2.6. Experimental Design

In this study, the design of experiment was used to optimize the following factors; adsorbent dose, initial concentration of Pb (II) ions, pH and contact time. Percentage removal of Pb (II) ion seeks to be the response. Table 1 showed the factors that affect the removal of Pb (II) ions from human plasma. The prepared stock solutions were diluted to get appropriate concentrations of interest and spiked into the blood plasma. The adjusted pH of interest was achieved by using 0.01M of HCl and NaOH. The loaded mixtures on the mechanical shaker comprising of the adsorbent and human plasma containing spiked Pb (II) ions concentration was shaken for the allotted experimental time at constant speed of 250 rpm at 37°C [7]. After shaking and filtered with filter paper. The filtrate was digested and analyzed for the presence of Pb (II) ions. The percentage removal of Pb (II) ions was calculated using equation 1

$$\% \text{ Removal of } Pb^{2+} = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

Where: C_o = Initial concentration, C_t = Concentration after shaking for time, t

2.7. Statistical Analysis

In order to investigate the interaction of biosorbent dose, Pb (II) ions concentration, pH and contact. The Central Composite Design (CCD) was used by Design expert-10 statistical software (Table 1). Mathematical relationships between variable factors were established. The mathematical models were fitted to the least squares method and evaluated with modified coefficient of variation. In order to evaluate the significance of the coefficients of the models, regression analysis at the significance level of 0.05 was used.

A quadratic model for the adsorption of Pb (II) ions from human plasma as influenced by factors affecting adsorption during the experimental runs is expressed in equation 2

$$Y = \beta o + \sum_{i=1}^{n} \beta i X i + (\sum_{i=1}^{n} \beta ii X\, i)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta ij X i X j + € \qquad (2)$$

Where: Y = Predicted response, βo = Constant coefficient, βi = Linear coefficient, βii = Quadratic coefficient, βij = Interaction coefficient, xi and xj = Factors and € = Random error.

Coefficient of determination (R^2) was used to express a comparison between the qualities of data gotten from predicted model with data gotten from experimental runs [8]. The adequacy and significance of the predicted model was adequately explained using Fisher variation ratio (F-value) [9].

2.8. Digestion of Filtrate

Accurately, 3 cm^3 of the filtrate was measured into 5 Pyrex flask separately and 10 cm^3 of concentrated HNO_3 and 5 cm^3 of H_2O_2 (2:1) was added. The mixture was allowed to stand for 10 minutes and digested at 70°C for 2 hours covered with a lid until a clear digested solution was obtained and the volume of mixture reduced to semi dryness. Then, make up to 100cm^3 mark using distilled water. The concentration of Pb (II) ions in the filtrate was obtained by Atomic Adsorption spectroscopy (AAS) method (AA240FS Varian)[10].

3. Results and Discussion

3.1. Scanning Electron Micrograph

Figure 1 and Figure 2 show the plates of SEM results of the biosorbent before and after adsorption of Pb (II) ion. Figure 1 shows numerous surface porosities of the biosorbent in its original state. Figure 2 shows the SEM micrographs of a loaded biosorbent with Pb (II) ions. It shows appreciation of the porosity of the biosorbent and qualitative assessment of their ability to adsorb Pb (II) ions. The prepared biosorbent have many pores which were clearly found on the surface was the main factor responsible for high removal of Pb (II) ions from human plasma.

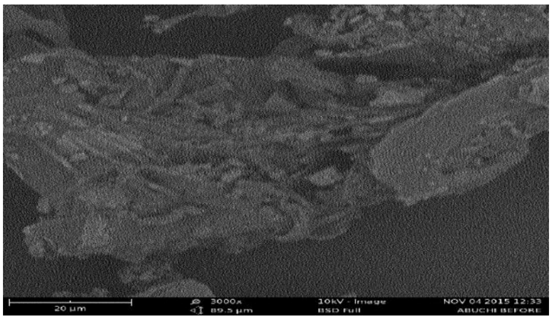

Figure 1. SEM micrograph of biosorbent before Pb^{2+} biosorption from human plasma.

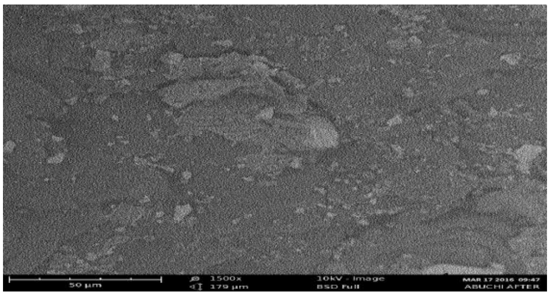

Figure 2. SEM micrograph of biosorbent after Pb^{2+} biosorption from human plasma.

3.2. FTIR Characterisation and Contribution of Functional Groups to Pb^{2+} Binding

The FTIR spectra of biosorbent and biosorbent loaded with Pb (II) ions were compared to ascertain the functional groups responsible for the removal of Pb (II) ions from human plasma are presented in Figure 3 and Figure 4. The spectra showed generally a shift in the peaks from 538.16 cm^{-1}, 644.25 cm^{-1}, 1062.81 cm^{-1}, 1332.86 cm^{-1}, 1631.83 cm^{-1} and 3306.76 cm^{-1} in biosorbent to peak 1149.61 cm^{-1}, 1319.35 cm^{-1}, 1411.94 cm^{-1}, 1481.38 cm^{-1}, 1635.69 cm^{-1} and 3402.64 cm^{-1} in biosorbent loaded with Pb (II) ion respectively. The shift in frequency indicated that Pb (II) ion was bonded onto the surface of biosorbent. The spectral interpretation of unloaded biosorbent and biosorbent loaded with Pb (II) ions indicated that –C-Br, -C-N, -C-O, -C-C, -N-H and –OH was involved in Pb (II) ions biosorption.

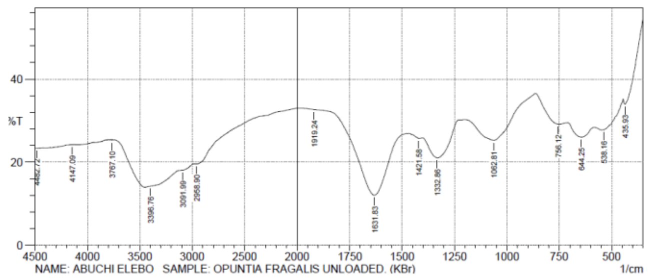

Figure 3. *FTIR spectra of biosorbent before Pb^{2+} biosorption from human plasma.*

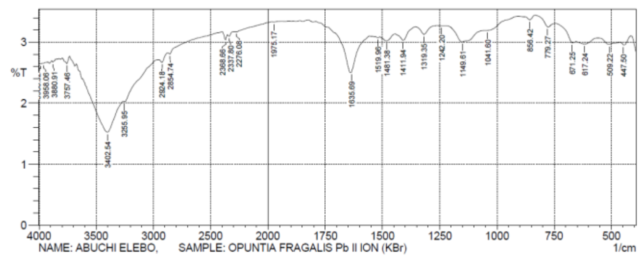

Figure 4. *FTIR spectra of biosorbent after Pb^{2+} biosorption from human plasma.*

Table 1. *Factors and their corresponding levels.*

Coded levels	Adsorbent Dose (mg/g)	Initial Conc. (mg/L)	pH.	Contact time (Sec)
	A	B	C	D
-α	0.5	10	2	20
-1	1.0	20	4	40
0	1.5	30	6	60
+1	2.0	40	8	80
+ α	2.5	50	11	100

Table 2. *Experimental runs with coded variables and responses.*

Run	A	B	C	D	% Pb^{2+} Removal
1	-α	+α	-α	0	91.53
2	0	0	-1	-α	92.05
3	-1	-1	+1	-1	93.55
4	+1	+1	0	+α	96.69
5	+α	-α	+α	+1	95.09
6	-1	+α	-1	0	99.32
7	-α	0	-α	+1	99.69
8	+1	-α	+α	+α	99.72
9	0	-1	+1	-1	99.88
10	+α	+1	0	-α	99.62
11	-1	0	-1	+α	88.90
12	-α	-α	+α	-α	91.77
13	0	-1	+1	0	92.63
14	+1	-1	-α	+1	91.74
15	+α	+α	0	-1	90.07
16	-α	0	-1	+α	93.34
17	-1	-1	+1	-1	94.14
18	+α	-α	+α	+1	94.88
19	+1	+1	0	+α	95.60
20	0	+α	-α	-α	96.29
21	-1	0	-1	-1	97.03
22	-α	-1	+α	0	97.07
23	0	-α	+1	-α	97.05
24	+1	+1	0	+1	97.03
25	+α	+α	-1	0	97.02
26	+1	0	-α	+α	97.02
27	-α	-1	+α	-1	97.03
28	-1	-α	+1	+1	87.52
29	0	+1	0	-α	91.32
30	+α	+	-1	+α	89.34

Table 3. *Analysis of variance (ANOVA) for the regression model equation, values of regression coefficients and their significant tests.*

Source	Sum of Squares	df	Square	F-Value	p-vaue	Verdict
Model	381.58	10	38.16	11.89	< 0.0001	Significant
A-DOSE	84.74	1	84.74	26.40	< 0.0001	
B-CONC.	15.64	1	15.64	4.87	0.0371	
AD	25.78	1	25.78	8.03	0.0092	
CD	15.57	1	15.57	4.85	0.0375	
C^2	143.33	1	143.33	44.65	< 0.0001	
A^3	42.91	1	42.91	13.37	0.0012	
CD^3	20.99	1	20.99	6.54	0.0173	
B^3CD	22.60	1	22.60	7.04	0.0139	
B^3D^2	21.69	1	21.69	6.76	0.0157	
BC^3D	17.07	1	17.07	5.32	0.0301	
Residual	77.04	24	3.21			
Lack of Fit	50.28	21	2.39	0.27	0.9728	not significant
Pure Error	26.76	3	8.92			
Cor Total	458.62	34				

$R^2 = 0.8320$ $R^2_{adj} = 0.7620$ $R^2_{pred} = 0.6341$ Adeq Precision = 11.541

4. Model and Statistics

Various percentage of Pb (II) ions biosorption from human plasma is presented in Table 2. The linear, quadratic and polynomial models were adequate and significant to depict the relationship between percentage removal of Pb (II) ions from human plasma and biosorption factors. The designed coded form of the model for Pb (II) ions biosorption is presented equation 3. The signs in the model equations showed how positively and negatively the coefficients affect the biosorption process. Table 3 shows the lack of fit value, significance and not significance of the model. P-value less than 0.05 of the models was arrived, depicting significance. The lack of fit P-value of all models was greater than 0.05 with F-value of 0.27 depicts a non-significant lack of fit due to pure error and 97% lack of fit was caused by noise. A lack of fit that is not significant is good because the model needs to fit. Adeq precision 11.541 measured the signal divided noise ratio is desirable, since its greater 4 indicated adequate signal. The predicted and actual values of percentage biosorption of Pb (II) ions is shown in Figure 10, indicates a good fit of experimental model. The closer the points to the straight line, the closer the coefficient of determination (R^2) to unity. $R^2 = 0.8548$ validates the experimental variables as shown in Table 4. Deviation of plots from point of reference (perturbation curves) was also used to validate experimental variables as deviation from reference points indicated good correlation as shown in Figure 9. The response surface equation of Pb (II) ions is given in equation (3)

$$\%\ Removal\ of\ Pb^{2+} = +94.70 + 8.0A - 1.93D + 3.7AD + 12.57CD - 7.73C^2 - 7.02A^3 - 26.3CD^3 + 63.76B^3CD + 14.76B^2 - 52.52BC^3D \quad (3)$$

5. Effect of Process Parameters on Biosorption

A. Biosorbent dose

The percentage removal of Pb (II) ions from human plasma increased with biosorbent dose depicting a sharp deviation from the centre of the graph as presented in Figure 9. This could be as a result of increasing available active sites for the participating ions [11]

B. Initial concentration

Pb (II) ions initial concentration was varied from 10 – 50 mg/L at constant adsorption parameters. The percentage efficiency of biosorbent for the removal of Pb (II) ions from human plasma increased as the metal ions concentration increased with a slight deviation from the centre point of the graph as presented in Figure 9 [11]. This could be inferred to the fact that more Pb (II) ions compete for adsorption sites thereby affecting the increased rate of removal [13].

C. pH

pH played a vital role in detecting the optimum pH for Pb (II) ions removal from human plasm. The Pb (II) ions biosorption was keenly affected mostly by pH thereby creating a broad deviation at the centre of the graph as presented in Figure 9 [14]. However, the percentage of Pb (II) ions removal increased with increasing pH at optimum value of 7. This could be due to a reduced competition between hydrogen ions and Pb (II) ions for available active sites [15], [16], [17].

D. Contact time

The efficacy of the biosorbent is dependent on its ability to remove more Pb (II) ions as time increases [18]. The percentage removal of Pb (II) ions increased with contact time having a gentle deviation at the centre point as presented in Figure 9. This could be as a result of the fact that fewer active sites were available for adsorption and thickness of boundary layers increased too [19].

5.1 Interactive effects of response surface on adsorption

The 3-D representation of the interactive effect of time and initial Pb (II) ions concentration, pH and Pb (II) ion concentration, time and pH and Pb (II) ion concentration on the removal of Pb (II) ions from human plasma are presented in Figure 5, 6, 7 and 8 respectively. The Pb (II) ions bi increased with the adsorption factors; this could be due to the present of more active available sites for the adsorption of Pb (II) ions from human plasma [20].

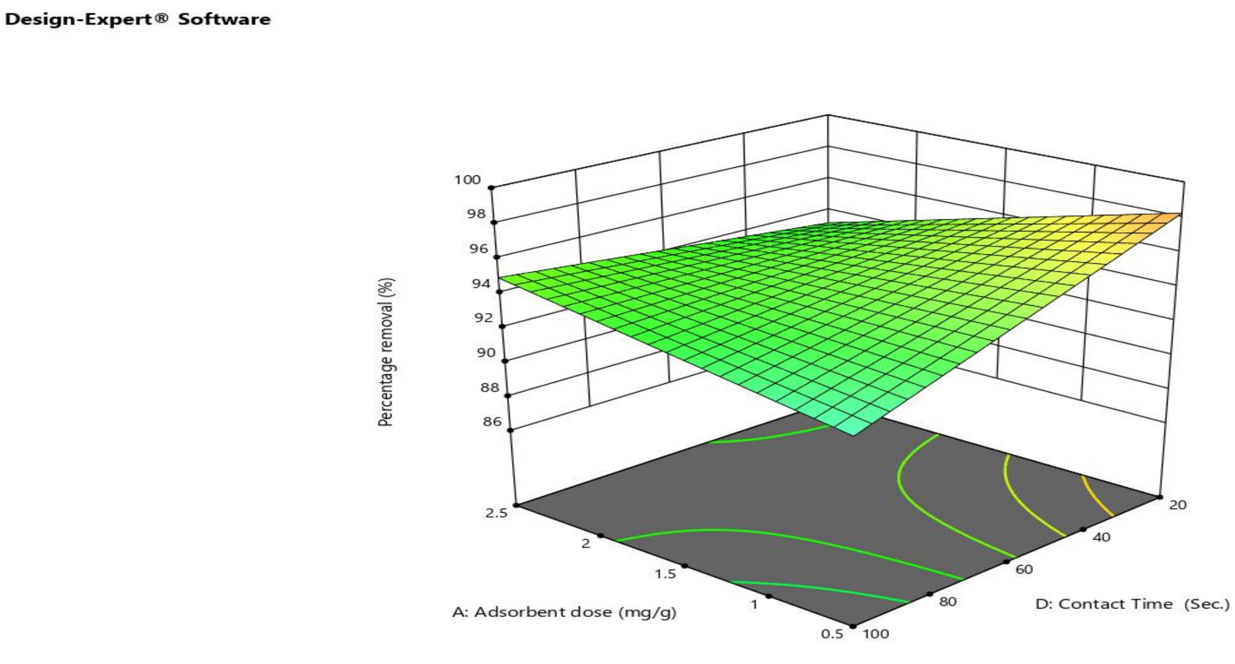

Figure 5. *Effect of Adsorbent dosage and Time on Pb (II) ions removal from human plasma.*

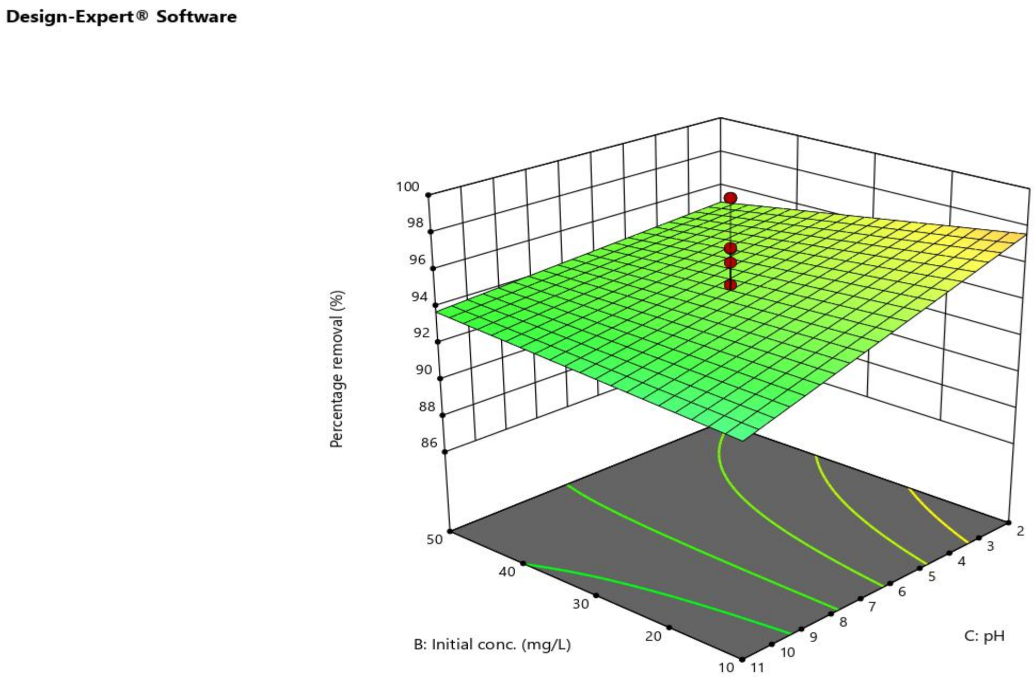

Figure 6. *Effect of Concentration and pH on Pb (II) ions removal from human plasma.*

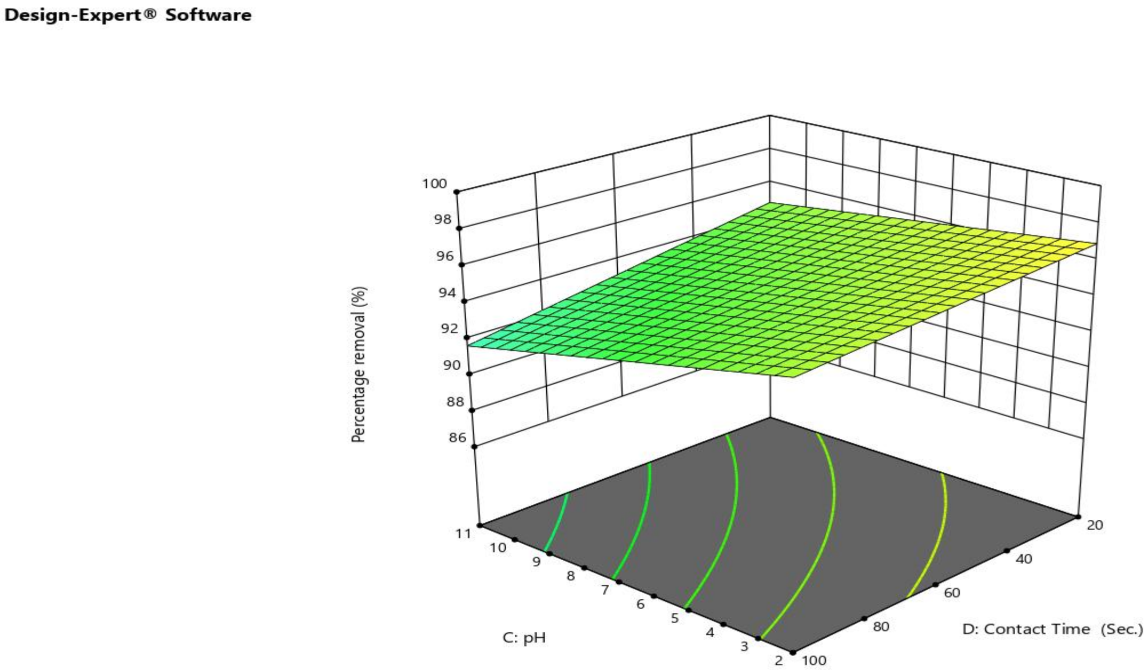

Figure 7. *Effect of pH and Time on Pb (II) ions removal from human plasma.*

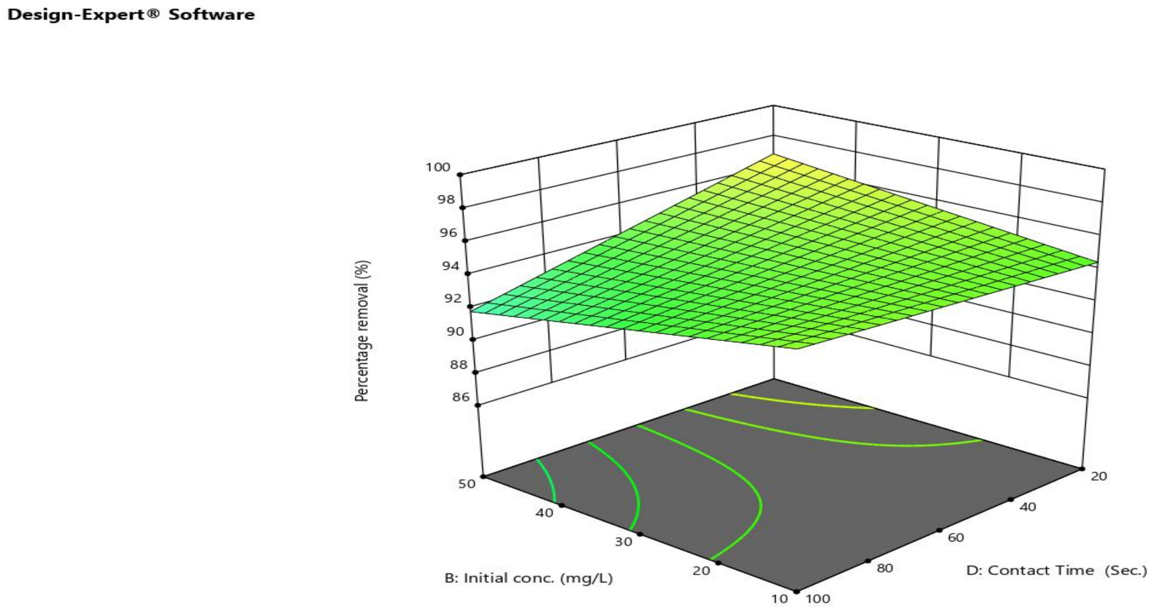

Figure 8. *Effect of Concentration and Time Pb (II) ions removal from human plasma.*

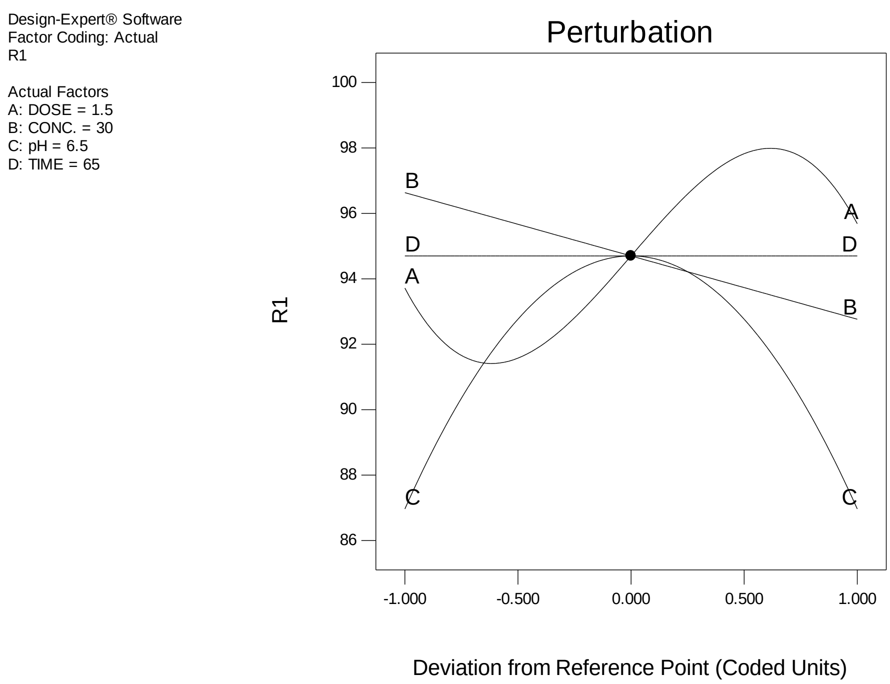

Figure 9. *Deviation of Pb (II) ions adsorption from reference point.*

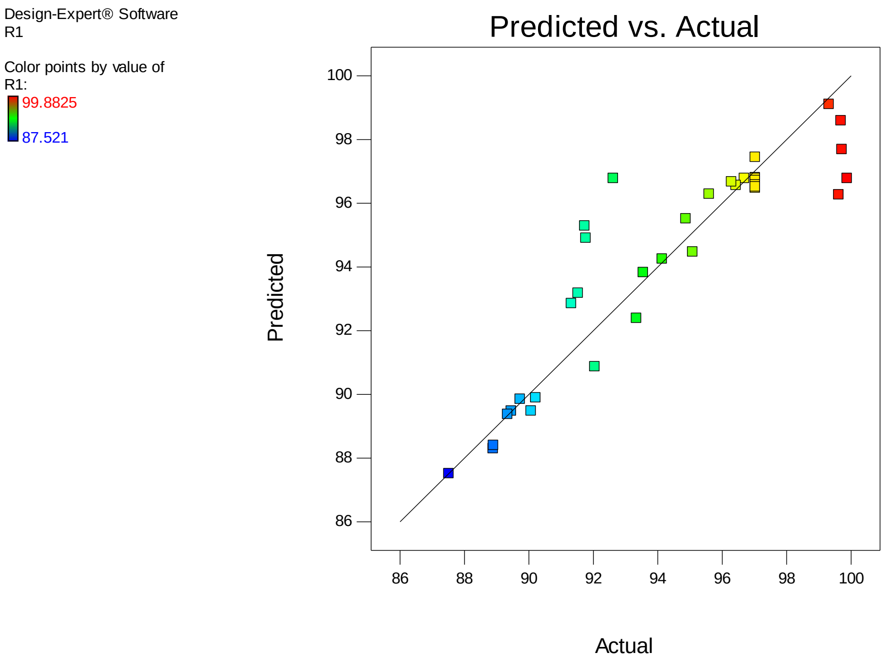

Figure 10. *Predicted versus actual value of Pb (II) ions removal from human plasma.*

Table 4. *Validation of results.*

Run order	Actual Value	Predicted Value
1	91.53	93.18
2	92.05	90.87
3	93.55	93.82
4	96.69	96.78
5	95.08	94.47
6	99.32	99.1
7	99.69	98.59
8	99.72	97.68
9	99.88	96.78
$R^2 = 0.8548$		

6. Equilibrium Adsorption Isotherms

In this study data gotten from experiment were analysed using Langmuir, Freundlich and Temkins isotherms.

6.1. Langmuir Isotherm

Langmuir isotherm is based on the assumption that all the adsorption sites are energetically identical (monolayer adsorption) and adsorption occurs on a structurally homogeneous adsorbent. In its formulation, binding to the surface is primarily by physical forces [21]. The Langmuir equation is shown in equation (4)

$$\frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^o} \quad (4)$$

where q_e is the amount of Pb (II) ions adsorbed from human plasma per unit mass (mgg^{-1}), Q^o is the maximum amount of Pb (II) ions adsorbed from human plasma. K_L is the binding energy of adsorbent in the binding sites (Lmg^{-1}), C_e is the equilibrium concentration of Pb (II) ions (mgL^{-1}). Furthermore, R_L which is a dimensionless constant referred to as separation factor or equilibrium parameter as presented in equation 5.

$$R_L = \frac{1}{1+K_L C_o} \quad (5)$$

Where C_o is the initial concentration and K_L is the adsorption energy, The values of R_L indicate the nature of the isotherm. $R_L>1$ means unfavourable adsorption, $R_L= 1$ means a linear shape isotherm, $0<R_L<1$ and $R_L= 0$ mean favourable and irreversible adsorption isotherm respectively [22].

Table 5 is the correlation parameter of Langmuir isotherm of Pb (II) ion removal from human plasma. Q^o (0.1468 mgg^{-1}) and K_L (-8.9174 Lm^{-1}) are the biosorption capacity and energy of biosorption respectively. The result implies that this model is suitable to explain removal of Pb (II) ions from human plasma. Since these constants are indicative of the surface binding energy and monolayer coverage [23]. This also suggested that some sites on the surface of the biosorbent played a role in Pb (II) ion decontamination from human plasma. R_L (-0.0028) value indicated that removal of Pb (II) ions by biosorbent was effective and favorable and R^2 (0.8932) value indicated that the biosorption process fits Langmuir isotherm due to good correlation between $\frac{C_e}{q_e}$ and C_e as shown in Figure 11.

6.2. Freundlich Isotherm

The Freundlich Isotherm model describes an empirical relationship between different adsorption sites with corresponding adsorption energy [24]. Freundlich equation is presented in equation 6

$$In q_e = In K_f + \left(\frac{1}{n}\right) In C_e \quad (6)$$

Where, qe (mgg^{-1}) is the amount of Pb (II) ions adsoreded per unit mass, K_f (Lmg^{-1}) is the Freundlich constant measuring adsorption capacity, Ce (mgL^{-1}) is the residual concentration, n is constant related to the intensity of adsorption. Table 5 is the Freundlich isotherm constants and correlation coefficient of Pb (II) ion adsorbed from human plasma. The 1/n (-0.7309) value indicated that the removal of Pb (II) ions is a normal biosorption (physisorption) signifying higher adsorption of Pb (II) ion, n (-1.3682) value indicated that the removal of Pb (II) ions from human plasma by biosorbent was favourable (since 1/n<1) with K_f (0.1334 Lmg^{-1}) indicated significant amount of Pb (II) ions adsorbed per site. R^2 (0.2916) value indicated that sorption data didn't fit into Freundlich isotherm due to poor correlation between Inq_e and InC_e as shown in Figure 12.

6.3. Temkins Isotherm

This isotherm explains that the adsorption heat energy of all the molecules resident in the adsorption sites decrease linearly as a result of the adsorbent and adsorbate interactions [28]. The Temkins isotherm in its simplified form is presented in equation 7

$$q_e = \frac{RT}{b_T} \text{In}A_T + \frac{RT}{b_T}\text{In}C_e \quad (7)$$

where $\frac{RT}{b_T}$ = B, q_e is amount of Pb (II) ions adsorbed and C_e is the residual concentration, T is the absolute temperature (K) and R is the gas constant (8.314 J mol^{-1} K^{-1}).

Table 5 is the correlation parameter of Temkins model of Pb (II) ions removal from human plasma. A_T (0.9581 Lg^{-1}) value explained the interaction between Pb (II) ions and biosorbent is held by low binding energy, b_T (-10237.81) value indicated low heat of biosorption [28]. R^2 (0.1122) value entails that detoxification of Pb (II) ions from human plasma didn't fit into Temkins isotherm due to poor correlation between as q_e and InC_e as shown in Figure 13.

Table 5. *Correlation parameters for Langmuir, Freundlich and Tempkins Isotherms for Pb (II) ions adsorption from human plasma.*

Langmuir Isotherm				Freudlich Isotherm			Tempkins Isotherm		
R^2	K_L	Q^o	R_L	R^2	N	K_f	R^2	A_T	b_T
0.8932	-8.9174	0.1468	-0.0028	0.2916	-1.3682	0.1334	0.1122	0.9581	-10237.81

6.4. Kinetics Models

Monitoring the effect of time is vital in most sorption process. The knowledge of kinetic in sorption processes is important in order to have a clear understanding of the interaction between liquid and solid phases and to predict the reaction time [25]: [26]. Pseudo first order, Pseudo second order and Elovich models were explored in the study.

6.4.1. Pseudo First Order Model

Pseudo first order equation or Lagergren kinetics equation [27] is widely used for the adsorbent-adsorbate interaction and given in linearized form as presented in equation 8.

$$log\ (q_e - q_t) = log\ q_e - \frac{k_1}{2.303}t \quad (8)$$

where q_t (mgg^{-1}) is the Pb (II) ions adsorbed per unit mass at time t, K_1 ($Lmin^{-1}$) is the Pseudo first order rate constant, t (min) is the time taken and q_e (mgg^{-1}) is the Pb (II) ions adsorbed per unit mas at equilibrium. Table 6 is the correlation parameters of Pseudo first order model of Pb (II) ion removal. The K_1 (0.0316 L/min) and qe (0.039 mg/g) are rate constant and amount of Pb (II) ion adsorbed per biosorbent respectively suggested that significant amount Pb (II) ion could be detoxified within a short time [29]. R^2 (0.5238) value indicated that the removal of Pb (II) ion onto biosorbent fits slightly into pseudo first order model due to good correlation between $log\ (q_e - q_t)$ and t as shown in Figure 14.

6.4.2. Pseudo Second Order Model

[30] suggested the Pseudo second order kinetic as presented in equation 9

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

Where K_2 is the pseudo second order rate constant (gmg^{-1}.min), q_e (mgg^{-1}) is the amount of Pb (II) ions adsorbed per unit mass of adsorbent and q_t is the amount of Pb (II) ions adsorbed per unit mass of adsorbent at time t. Table 6 is the correlation parameters of Pseudo second order model of Pb (II) ions removal from human plasma. The qe (0.5585 mgg^{-1}) value indicated that large amount of Pb (II) ions were removed by biosorbent within limited time [29]. R^2 (0.9991) suggested that the decontamination of Pb (II) ion by biosorbent fits into pseudo second order model due to good correlation between $\frac{t}{q_t}$ and t as shown in Figure 15.

6.4.3. Elovich Model

This model explains the heterogeneous nature of the active sites undergo chemisorption with different activation energies [31]. The linearized equation as presented in equation 10

$$q_t = \frac{1}{\beta}\ In(\alpha\beta) + \frac{1}{\beta}\ In(t) \quad (10)$$

Where α is the initial adsorption rate (mgg^{-1}.min), β is desorption constant during any experiment. Table 6 is the Correlation parameters of Elovich model on Pb (II) ion removal from human plasma. R^2 (0.9156) value indicated that the removal of Pb (II) ion by biosorbent fits into Elovich model due to good correlation between q_t and $In(t)$ as shown in Figure 16 which indicated chemisorption

Table 6. *Rate constants and correlation coefficient values of Pseudo first order, Pseudo second order and Elovich model for Pb (II) ion adsorption from human plasma.*

Pseudo first order			Pseudo second order			Elovich model		
R^2	q_e	K_1	R^2	q_e	K_2	R^2	α	B
0.5238	0.039	0.0316	0.9991	0.5585	0.3849	0.9156	1.3016	16.6113

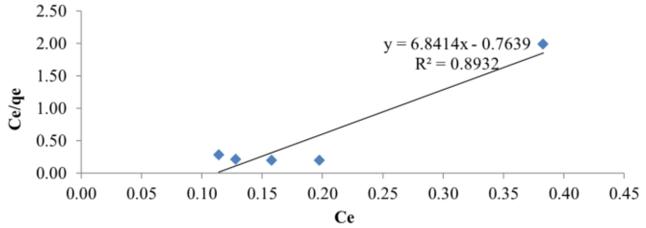

Figure 11. *Langmuir isotherm of Pb (II) ion adsorption from human plasma.*

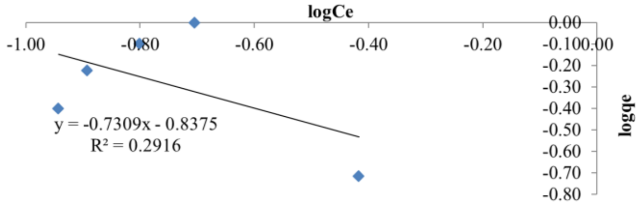

Figure 12. *Freundlich isotherm of Pb (II) ion adsorption from human plasma.*

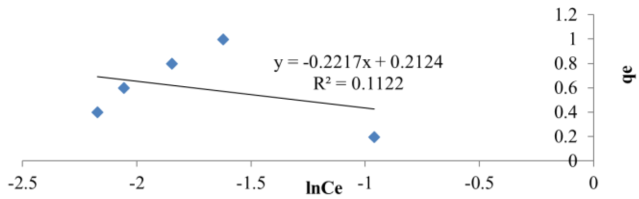

Figure 13. *Tempkins isotherm of Pb (II) ion adsorption from human plasma.*

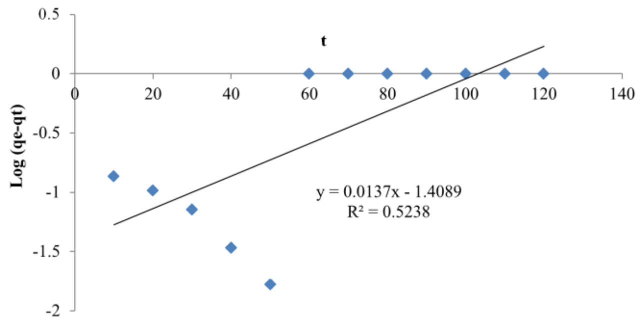

Figure 14. *Pseudo first order of Pb (II) ion adsorption from human plasma.*

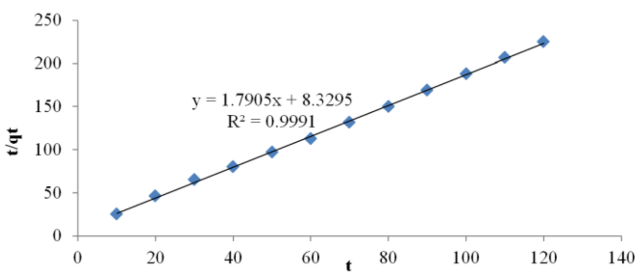

Figure 15. *Pseudo second order of Pb (II) ion adsorption from human plasma.*

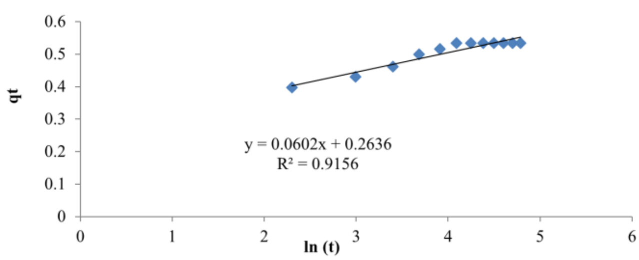

Figure 16. *Elovich model of Pb (II) ion adsorption from human plasma.*

7. Conclusion

In this study, Pb (II) ions removal from Human plasma onto natural low-cost, abundant and locally available adsorbents, *Opuntia fragalis* was studied at ambient temperature. The adsorption parameters were optimized using Central Composite Design. The Pb (II) ions removal from human plasma was wholly dependent on the quantity of biosorbent dose, initial concentration of Pb (II) ions, pH and contact time. The adsorption mechanisms and characteristic parameters for the present application were also explored as an important objective using various isotherm and kinetic models. The optimum conditions for Pb (II) ions removal by *Opuntia fragalis* leaves were found to be; pH = 4, equilibration time = 100 min. Optimum dosages = 1.5 g and initial concentration = 50mg/L. Amongst the three parameter isotherms; Freundlich, Temkin and Langmuir isotherms. The Langmuir isotherms were found to be the best-fitted isotherm models to describe the experimental data with R^2 = 0.8932. The applicability of all isotherm models implies that both monolayer adsorption and heterogeneous surface conditions exist under the experimental conditions. However, experimental data were subjected to Pseudo first order, Pseudo second order and Elovich kinetics models. Amongst these kinetic models, the experimental data showed best fit with Pseudo-second order model with considerably higher correlation coefficients (R^2) of 0.9991. The results indicated that the biosorbent exhibited good surface chemistry suitable for enhancing the activity in the biosorption process with high percentage removal of lead ions. Therefore, *Opuntia fragalis* leaves should be preferred for Pb (II) ions removal from Human plasma.

Recommendations

1. Thermodynamic studies should be carried out for a comprehensive understanding of the biosorption process on biosorbent prepared from *Opuntia fragalis.*
2. The experiment should be extended to the effect of particle sizes on the biosorption of heavy metals from human plasma.
3. Desorption studies should be carried out.

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