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Potential of Oil-free-Cake Dry Seed Kernels of Desert Date (*Balanites aegyptiacus* (L.) Delile) for simultaneous Removal of Pb (II), Cu (II) and Cd (II) ions from Battery Industry Effluent

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ABSTRACT: This study was carried out to investigate the potential of oil-free-cake dry seed kernels of desert date (*Balanites aegyptiacus* (L.) Delile) for simultaneous removal of Pb (II), Cu (II) and Cd (II) ions from Battery Industry Effluent using standard methods in a batch sorption process.. The battery effluent was mimicked by dissolving known concentration of metal ions in distilled water. The optimum conditions for the simultaneous removal of Pb (II), Cu (II) and Cd (II) ions were: pH (6), contact time (105 min) and adsorbent dosage (6.5 g). The results obtained showed that the biosorbent was effective for the simultaneous removal of Pb (II), Cu (II) and Cd (II) ions with removal efficiencies of up to 87.7%, 78.6% and 61.6% respectively. The consistency of the model-predicted optimum conditions were confirmed by conducting experiments under those conditions. It was found that the experimental removal efficiencies under optimum conditions were very close (less than a 5% error) to the model-predicted value. The three parameter isotherm equations (Redlich-Peterson and Sips) provide better fitting than the two-parameter isotherm equations (Freundlich and Langmuir), which can be explained by the fact that these have three adjustable parameters. The best fitted was achieved with the Redlich–Peterson equation. The results of the sorption kinetic study showed that the data fitted well with the pseudo-second order model for Pb (II), Cu (II) and Cd (II) ions. In conclusion, desert date oil-free cake exhibits great potential as an efficient sorbent for removal of metal ions.

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Heavy metals contamination exists in waste effluents of different factories such as metal plating, mining operation, tanneries processes, ceramic panting, paint manufacturing, catalyst, alloy industries, wire conducting, galvanizing iron, polymer stabilizer, storage batteries manufacturing, semi-conductors, pesticides and wood preservation pigment factories (Al-jlil, 2010). Owing to the toxic and adverse effects of the heavy metals, these industries are advised by various regulatory bodies to treat wastewaters systematically so that the metal contents in effluent from their industries can be minimized in their wastes. Various conventional treatments have been applied for removing heavy metal ions such as chemical precipitation, ion exchange, filtration and reverse osmosis (Sri et al., 2018), but most of these methods are only suitable for large scale treatments and incur high cost to be practiced. Generally, all these treatments lead to certain disadvantages such as incomplete removal of heavy metals ions, high-energy requirements and production of toxic sludge. Numerous approaches have been studied for the

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development of more effective methods in removing heavy metal pollution and the adsorption process is found to be more practicable over other techniques. Adsorption process is one of the easiest, safest and more cost-effective methods for heavy metal removal from industrial effluents and this process is already established as a simple operation and an easy-handling process (Siti et al., 2013). Activated carbon is a potential adsorbent for the removal of several organic and inorganic pollutants but due to its high cost and (10-15%) loss during regeneration; alternative low-cost adsorbents have attracted the attention of several investigators to provide an alternate for the high cost activated carbon. Therefore, the need for cheaper or low-cost adsorbents has become the focus of many scientists. Various low-cost materials have been used; they include drumstick, cocoa shell, solid agricultural waste, clay and marine algae (Mangale et al., 2012; Theivarasu et al., 2011; Shabudeen, 2011; Akpomie et al., 2012). From the above, it is evident that bio-waste materials and/or agricultural by-products are efficient biosorbent for oil, dye and heavy metal removals. However, types and availability of bio-waste materials varies from location to location. In view of this, there arouse the need to carry out research into the use of a locally available agricultural by-product in our environment as potential biosorbent for the removal of heavy metal ions from wastewater. The desert date (*Balanites aegyptiaca*) seed cakes are the secondary by-product generated after oil extraction from desert date (*Balanites aegyptiaca*) seed, which are poorly utilized. Recently, desert date (*Balanites aegyptiaca*) seed oil is being utilized as biodiesel (Gutti et al., 2012); however, the residual desert date (*Balanites aegyptiaca*) seed kernel cake imposes a disposal problem. Although, this cake has been found suitable for water treatment and used as animal feeds (Morkaz et al., 2011). However, its use as biosorbent could result in diversification of its areas of application and more so, a supplement to conventional means of removal of heavy metal ions from industrial effluent. Therefore, this research evaluates the potential of oil-free-cake dry seed kernels of desert date (*Balanites aegyptiacus* (L.) Delile) for simultaneous removal of Pb (II), Cu (II) and Cd (II) ions from Battery Industry Effluent.

MATERIALS AND METHODS

Sample collection and pretreatment: Dried seeds of desert date *(Balanites aegyptiaca)* were purchased from a vendor at Tirwun market in Bauchi, Bauchi State-Nigeria. The sample was spread under shade and sorted to remove unwanted materials. The seeds were then manually crushed using hammer to remove the seed kernel from the husk shell and the kernel milled into powder using a pestle and mortar.

Oil extraction and sorbent preparation: The seed kernel oil of desert date (*Balanites aegyptiaca)* was extracted according to the method adopted by Mortadha et al., (2015). The solvent extraction was performed using soxhlet apparatus and n-hexane as the solvent. One hundred grams (100g) of the ground seed kernel was placed into a porous thimble of a soxhlet extractor. Volume of 250 mL of n-hexane (with boiling point of 75 – 80°C) was used as solvent for 4 hours repeatedly until all the oil was extracted. A rotary evaporator was used to remove the excess solvent from the extracted oil. The oil was kept without further treatment until needed for further analysis. The residue from the oil extraction was thoroughly washed with distilled water to remove unwanted solvent and dried in an oven at 50°C overnight (Abdulsalam et al., 2014). The dried kernel was stored in an airtight container for further analysis.

Determination of the percentage yield of oil from oil seed: The percentage yield of the oil extracted was determined according to method adopted by Ogala et al., (2018). The oil obtained from the extraction process was transferred into a measuring cylinder which was placed over a water bath and allowed for 30 minutes at 75°C so as to ensure complete evaporation of the solvent and then weigh using weighing balance (Krishna, Kss-55) and recorded. Using equation (1) the percentage yield was calculated.

$$\%Yield = \frac{W_1}{W_2} \times 100 \qquad (1)$$

Where, W_1= weight of oil extracted, W_2= weight of sample used

Physicochemical analysis of the oil-free cake: The quality assessment of the desert date *(Balanites aegyptiaca)* oil-free cake was analyzed by evaluating the physicochemical properties such as the ash content and moisture content. The ash content was determined according to the method described by Pearson (1981). A clean dried crucible was weighed and 5 g of sample was placed on the empty crucible. The sample was heated in a Muffle furnace at 500°C for 7 hours. The procedure was carried out in triplicate and mean calculated. The ash content was calculated using equation 2:

$$\%\, Ash\ content = \frac{W_1 - W_2}{W_1} \times 100 \qquad (2)$$

Where W_1= weight of crucible + sample before heating, W_2= weight of sample + crucible after heating

Moisture content, expressed as percentage by mass, was determined by adapting the Association of Official Analytical Chemist method 934.06 (AOAC, 1990). A clean empty dried petri dish was weight and then 5 g of the sample of the seed kernel cake was added. The petri dish containing the sample was then placed in an oven preset at 105°C for 24 h. This also was done in triplicate and the mean calculated. The moisture content was calculated using equation 3.

$$\%\ \text{Moisture content} = \frac{\text{a}-\text{b}}{\text{a}} \times 100 \qquad (3)$$

Where a = weight of petri dish + sample before drying in oven, b = weight of dish + sample after drying.

Characterization of the sorbent: The sorbent was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The functional groups present in the adsorbent before and after treating the effluent was determined by FTIR (NicoletTM 6700). Surface morphology was observed by SEM (Phenom ProX, manufactured by Phenom World Einhoven, Netherlands) micrographs. Further, the phase was identified by XRD.

Preparation of Synthetic Solutions (Mimicking a Typical Battery Effluent: Analytical grade reagents were used in preparing stock solutions from which the various working solutions were obtained by diluting to required concentration. The stock solution of the different metallic salts were prepared by dissolving 4.56, 2.397 and 3.250g of $Pb(NO_3)_2$, $CuSO_4$, and $CdSO_4$ respectively in 1000 cm^3 of distilled water.

Experimental Design Using RSM: The experiment was designed using Design Expert Software (Version 6.0.8) whereby the effect of adsorbent dosage, pH and contact time on the heavy metal ions sorption onto desert date oil-free cake adsorbent was studied.

The response surface methodology (RSM) technique involving central composite design (CCD) was utilized to optimize the three main sorption parameters selected, to achieve maximum ion removal.

Table 1 shows the experimental ranges and levels of the independent variables. The experimental data matrix was determined using Design Expert v6.0.8 and the obtained models were statistically analyzed using analysis of variance (ANOVA).

The interactions between variables were studied using 3D surface plots.

Table 1: Experimental ranges and levels of the independent variables

	Name	Units	-1 Level	+1 Level
A:	Adsorbent Dosage[a]	g	3	10
B:	pH[b]		3	9
C:	Contact Time	min	30	180

Source: [a]Naiya *et al.,* 2009; [b]Feng *et al.,* 2011; [c]Kumar and Gaur, 2011

Batch adsorption experiment: All adsorption tests were carried out in 250 mL conical flask containing 100 mL of the battery effluent. The tests were conducted by varying three factors, pH, contact time and adsorbent dosage, on Pb (II), Cu (II) and Cd (II) simultaneous biosorption. All the samples were agitated at 150 rpm at room temperature in orbital Shaker (Bioevopeak, model SHK – 00310III). Samples were collected at the predetermined time interval of 30, 105, and 180 min, respectively and filtered through filter paper (Whatman No.1 0.45µm). The filtrates were examined for metal ion concentration using the Atomic Absorption Spectrometer (AAS). The amount of metal ion adsorbed (q_e) and the percent removal ($\%R$) were calculated using equations (4) and (5), respectively.

$$qe = V\frac{Co-Ce}{m} \qquad (4)$$

$$\%R = \frac{Co-Ce}{Co}100 \qquad (5)$$

Where q_e is the amount of metal ion adsorbed (mg/g), C_o and C_e are the initial and equilibrium liquid-phase concentrations of the metal ion (mg/L) respectively, V is the volume of the solution (L) and m is the weight of the adsorbent used (g).

RESULTS AND DISCUSSION

Properties of the Desert Date Seed Kernel: Table 2 showed the physicochemical properties of the desert date seed obtained. As it can be observed from the table, the oil yield from the seed was 45%, bright yellow in color and liquid at room temperature.

Table 2: Physicochemical analysis of the desert date seed

Properties	Obtained Value
Oil content (%)	45
Moisture content (%)	6.2
Oil color	Bright Yellow
Ash content (%)	4.77

The seed contains low moisture content (6.2 %) as compared to other studies reported by Haftu (2015). This means, the seed kernel of desert date can be stored for an extended time under suitable condition without deteriorating. The moisture content of the oil is low, an indication that its stability is guaranteed. Oil seeds deteriorate as a result of high moisture content; this happens when heat is generated by oxidation reaction and increases the temperature of the stored seed thereby accelerating deterioration even to the point of charring the seed. Moisture content gives an indication of a food shelf life and nutritive value, hence low moisture content is a requirement for long storage life (Zang et al., 2017).

The ash content of the seed kernel was 4.77 % this value is in agreement with previous studies conducted by Ajayi and Ifedi (2014). This is the measure of the total amount of minerals present in the seed. The mineral content of a food is a measure of the amount of specific inorganic components present and ash is the inorganic residue remaining after the water and organic matter have been removed. Desert date seed kernel ash content is high when compared with cotton seed (4.56%) as reported by Muhammad et al., (2012). This shows a reasonable amount of mineral content in the seed kernel.

Characterization of the Adsorbent: SEM-XRD analysis: The surface morphology of the oil-free cake before and after the simultaneous biosorption were investigated using SEM. Plate 1 shows the surface morphology of oil-free cake before and after the simultaneous biosorption of Pb (II), Cu (II) and Cd (II).

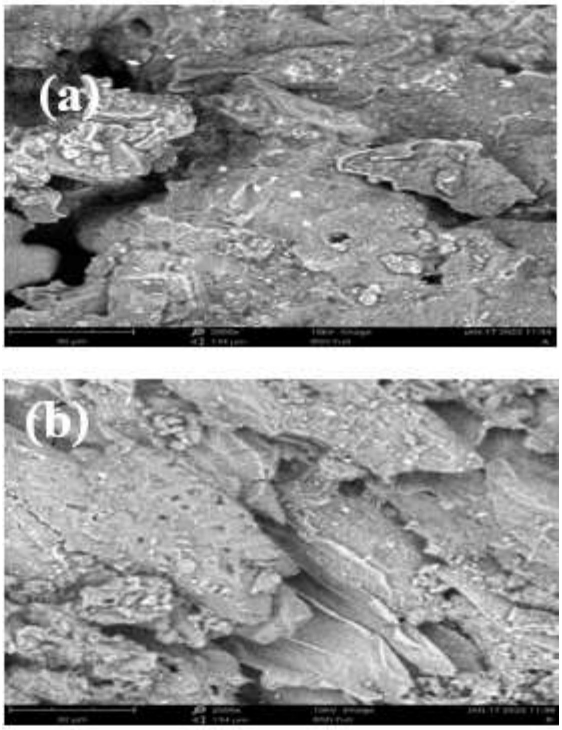

Plate 1: SEM image of oil-free cake **(a)** before simultaneous biosorption of Pb (II), Cu (II) and Cd (II)ions, 30µm and **(b)** after simultaneous biosorption of Pb (II), Cu (II) and Cd (II)ions, 30µm

The morphological characterization of oil-free cake after the simultaneous biosorption of Pb (II), Cu (II) and Cd (II) was significantly different from those before biosorption. The pores on the biomass surface became smooth after the simultaneous biosorption. This change can be explained by accumulation of metal ions on the surface by electrostatic attraction effect, this is in line with work of Peng et al., (2018). The XRD spectrum of the oil-free cake biosorbent before and after is shown in figures 1 and 2 respectively. Figure 1 showed broad peak which indicate the amorphous nature of the biosorbent. The amorphous nature suggests that the metal ions can easily penetrate the surface of oil-free cake for their sorption which is desirable for an effective removal (Folasegun and Kovo, 2014). While in Figure 2, a sharp peak was observed indicating crystalline nature which indicates that the adsorption process has resulted in changes in the surface structure of the aforementioned biosorbent.

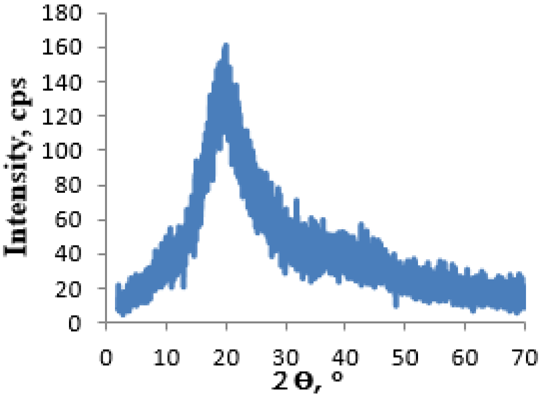

Fig 1: XRD pattern of oil-free cake before simultaneous biosorption of Pb (II), Cu (II) and Cd (II) ions

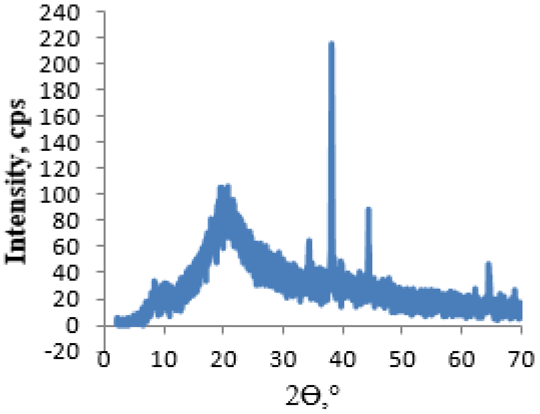

Fig 2: XRD pattern of oil-free cake after simultaneous biosorption of Pb (II), Cu (II) and Cd (II) ions

FTIR Analysis: The functional groups on the biosorbent surface and their interaction during the simultaneous biosorption process of Pb (II), Cu (II) and Cd (II) were investigated through FTIR spectrum analysis. Figure 3 and 4 show the peaks corresponding to the functional groups of oil-free cake before and after the biosorption of metal ions. The broad and strong peak at 3278.2 cm^{-1} was assigned to the overlapping of O–H and N–H stretching, indicating the existence of hydroxy stretching and carboxylic groups on the surface on oil-free cake (Mubeen et al., 2019).

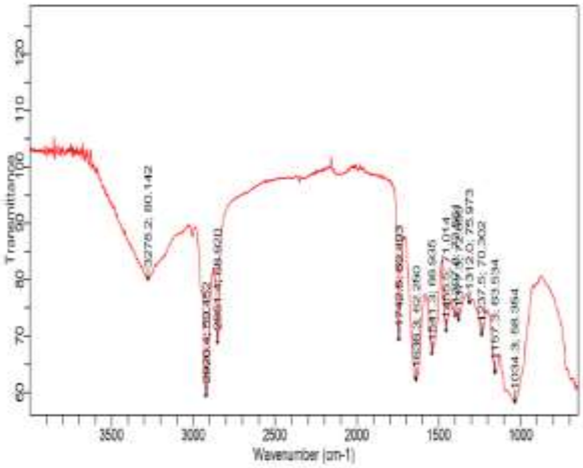

Fig 3: FTIR pattern of oil-free cake before simultaneous biosorption of Pb (II), Cu (II) and Cd (II) ions

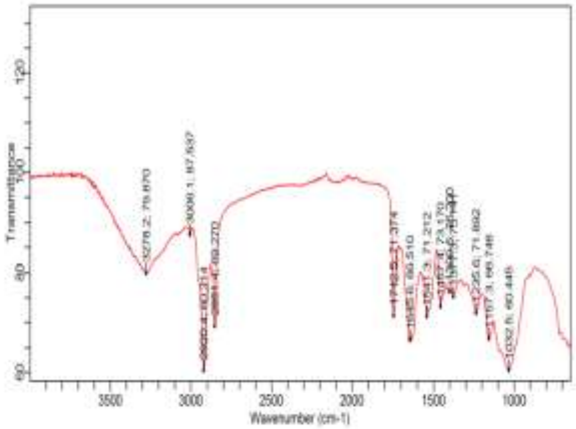

Fig 4: FTIR pattern of oil-free cake after simultaneous biosorption of Pb (II), Cu (II) and Cd (II) ions

The peaks at 3006.1, 2920.4 and 2851.4 cm^{-1} respectively were attributed to the C–H stretching vibration of aliphatic groups and at 1742.5 cm^{-1} was attributed to the presence of C=O stretching. The peaks at 1636.3 and 1541.3 cm^{-1} represented the presence of C=C stretching. The peak found at 1455.5 cm^{-1} was assigned to the C–H bonding. The peaks observed at 1237.5 cm^{-1} was attributed to the C–O stretching. The sulfoxide band was assigned to the peak observed at 1034.3 cm^{-1}. The numerous characteristic peaks observed on the surface indicate the complex nature of the biosorbent. Table 3 shows no changes in the vibrational frequency of the functional groups after the simultaneous biosorption of Pb (II), Cu (II) and Cd (II). This clearly indicates the simultaneous biosorption of Pb (II), Cu (II) and Cd (II) on the biosorbent by physical forces instead of chemical combination (Vijyakumar et al., 2012).

Table 3: Infrared vibration wavenumber and functional groups observed on unloaded, Pb (II), Cu (II) and Cd (II) loaded oil-free cake

Wavenumber (cm^{-1})		Functional Groups
Unloaded Oil-free cake	Loaded Oil-free cake	
1034.3; 58.343	1032.5; 60.445	S=O stretching
1157.3; 63.534	1157.3; 66.746	C-O stretching
1237.5; 70.302	1235.6; 71.892	C-O stretching
1455.5; 71.014	1457.4; 73.170	C-H stretching
1541.3; 66.935	1541.3; 71.212	C=C stretching
1636.3; 62.250	1645.6; 66.510	Asymmetric C=C stretching
1742.5; 69.493	1742.5; 71.374	C=O stretching
2851.4; 68.920	2851.4; 69.270	C-H symmetric stretching
2920.4; 59.452	2920.4; 60.314	C-H asymmetric stretching
-	3006.1; 87.537	C-H stretching
3278.2; 80.142	3278.2; 79.870	O-H stretching

Model Development for Pb (II), Cu (II) and Cd (II) Removal: A CCD matrix was used to investigate the interaction effects of three important factors, including adsorbent dosage, contact time, and pH, on the simultaneous removal of Pb (II), Cu (II) and Cd (II) from battery industry effluent. The experimental design and the responses are shown in Table 4. Based on the obtained results, the following polynomial equations for Pb (II) and Cu (II) removal were developed while for Cd (II) ion, no model equation was developed which suggesting the heavy metal ion concentration is low or the efficiency of the biosorbent is high as such the percentage removal is very closed.

$$\text{Pb (II) Removal \%} = +87.68+1.68A+0.82B+7.39C-6.39C^2-6.69AB-8.43BC$$

$$\text{Cu (II) Removal \%} = +82.49+2.41A+1.10B-0.29C+2.43B^2-13.56C^2-5.11AB-5.34AC-5.00BC$$

Where A, B, and C are the coded values for the selected influential parameters, namely, adsorbent dosage, contact time and pH, respectively. Table 5 shows the ANOVA for the polynomial equations and the corresponding regression coefficients for the removal models of Pb (II) and Cu (II). The significance of the obtained models can be determined based on the p-value, the correlation of determination (R^2), and the results of the lack of fit test (Zhu et al., 2017). Both models showed p-values (Prob > F) less than 0.0500, suggesting their significant. The lack of fit test showed the variation of responses around the fitted model. The insignificant lack of fit indicated that the model did not fit the data well. The model fit the real data better for Cu (II) than for Pb (II). The values of R^2 and adjusted R^2 were 0.8590 and 0.7565 for Cu (II), and those for Pb (II) were 0.6281and 0.4565 respectively.

The coefficient of variance (CV) refers to the ratio of standard deviation to mean. The CV values were 10.09 and 8.13 for Pb (II) and Cu (II) models, respectively. A model is reproducible if the CV value is less than 10 (Haftu, 2015). Adequate precision (AP) is defined as the ratio of signal to noise. An AP ratio higher than 4 is desired. The AP values of the models were 9.554 and 11.123 for Pb (II) and Cu (II), which showed a good signal and indicated that the models can be used to navigate the design space.

Table 4: Experimental design for simultaneous biosorption of Pb (II), Cu (II) and Cd (II) on Desert date oil-free cake. CCD: central composite design.

Run	Independent Factors			Responses		
	Adsorbent Dosage	**Contact Time**	**pH**	**Pb (II) Removal%**	**Cu (II) Removal%**	**Cd (II) Removal%**
1	3	30	3	75.96154	79.09091	76.74419
2	6.5	105	6	87.74038	78.63636	61.62791
3	10	30	9	93.14904	70.22727	71.80233
4	10	30	3	80.52885	87.95455	89.24419
5	10	180	3	94.83173	88.40909	72.38372
6	6.5	231.13	6	74.87981	62.5	64.82558
7	3	180	9	91.94712	38.18182	66.56977
8	3	30	9	86.17788	76.36364	71.80233
9	12.39	105	6	97.23558	88.86364	46.80233
10	6.5	105	6	84.25481	82.27273	50.87209
11	0.61	105	6	74.75962	79.54545	55.81395
12	10	180	9	94.95192	80.45455	51.74419
13	6.5	105	6	87.25962	79.31818	56.68605
14	3	180	3	98.07692	91.81818	79.94186
15	6.5	105	6	87.01923	82.5	51.45349
16	6.5	105	6	81.73077	77.04545	56.39535
17	6.5	105	11.05	45.79327	53.86364	39.24419
18	6.5	105	0.95	91.34615	83.40909	90.40698
19	6.5	105	6	87.13942	77.5	65.11628
20	6.5	105	6	81.97115	78.63636	52.32558

Table 5: Analysis of variance (ANOVA) for Pb (II), Cu (II) and Cd (II) simultaneous biosorption models.

Response	Source	Sum of squares	Df	Mean Square	F Value	p-Value Prob > F	Comments
Pb (II) Removal (%)	Model	1607.96	6	267.99	3.66	0.0237^{s}	SD=8.56
	A	38.68	1	38.68	0.53	0.4803	Mean=84.84
	B	9.23	1	9.23	0.13	0.7283	CV=10.09
	C	503.75	1	503.75	6.88	0.0211	R^2=0.6281
	C^2	357.40	1	357.40	4.88	0.0457	$R^2_{(Adj)}$=0.4565
	AB	357.59	1	357.59	4.88	0.0457	AP=9.554
	BC	568.31	1	568.31	7.76	0.0154	
	Residual	952.08	13	73.24			
	Lack of Fit	694.11	7	99.16	2.31	0.1641^{n}	
	Pure Error	257.98	6	43.00			
Cu (II) Removal (%)	Model	2612.65	8	326.58	8.38	0.0010^{s}	SD=6.24
	A	79.32	1	79.32	2.03	0.1815	Mean=76.83
	B	16.66	1	16.66	0.43	0.5268	CV=8.13
	C	0.78	1	0.78	0.020	0.8901	R^2=0.8590
	B^2	85.20	1	85.20	2.19	0.1674	$R^2_{(Pred)}$=-0.4728
	C^2	1596.18	1	1596.18	40.94	< 0.0001	AP=11.123
	AB	209.19	1	209.19	5.37	0.0408	
	AC	228.20	1	228.20	5.85	0.0340	
	BC	200.00	1	200.00	5.13	0.0447	
	Residual	428.82	11	38.98			
	Lack of Fit	219.04	5	43.81	1.25	0.3902^{n}	
	Pure Error	209.78	6	34.96			

s: significant; n: insignificant; df: degree of freedom; SD: standard deviation; CV: coefficient of variance; R^2: correlation of determination; AP: adequate precision.

Effect of Factors on the Removal Percentages of Pb (II), Cu (II) and Cd (II): Three-dimensional surface plots present the effects and interactions of independent variables, namely; adsorbent dosage, contact time, and pH, on the removal percentages of Pb (II) (Figure 5), Cu (II) (Figure 6) and Cd (II) (Figure 7) as the responses. The interaction of pH and adsorbent dosage shown in Figures 6a and 7a indicates the significant influence of both factors on the simultaneous removal of Pb (II) and Cu (II). For both adsorbates, the removal percentages increased with increasing adsorbent dosage. This result was due to the presence of additional active sites and large biosorbent surface area that is readily available for adsorption (Mondal et al., 2019). The removal percentage was increased slightly by increasing the residence time from 30 min to 180 min. These results confirmed that the initial adsorption rate was very rapid due to the availability of large surface area and the presence of unused sites on the biosorbent surface (Lingamdinne et al., 2018). While for Cd (II) (Fig. 8a) both factors have no effect on the removal percentage.

The outcome of the developed empirical models is shown via cube plot (Fig. 5d, 6d & 7b). The axis represents all the experimental design factors from low to high range whereas the coordinate point represents the outcome. The values depicted inside the cube represent the predicted removal efficiency of Pb (II), Cu (II) and Cd (II) by the process variable taken under study. Minimum Pb (II) removal (61.21%) was achieved for low ranges of adsorbent dosage, pH and contact time while maximum removal was achieved by high range of adsorbent dosage, contact time and at neutral pH (93.08%) (Fig. 5d). Similar results were obtained for Cu (II) removal, wherein minimum removal (58.56%) is obtained at low ranges of adsorbent dosage, pH and contact time whereas maximum removal (86.27%) at high ranges (Fig. 6d). while in figure 8b, both the minimum and maximum removal percentages are the same at low and high ranges of adsorbent dosage, pH and contact time.

Optimization and Validation: The optimum values of the operation variables, predicted maximum responses and the error percentages are presented in Table 6. The maximum removal percentages for Pb (II), Cu (II) and Cd (II) were predicted to be 84.8%, 84.1% and 63.6%, respectively. Verification experiments were conducted under the optimum conditions, and the removal percentages were 87.7%, 78.6% and 61.6% for Pb (II), Cu (II) and Cd (II) respectively; these findings are similar to the predicted values with an error rate of < 5% and indicated the suitability and accuracy of the suggested models. The metal uptakes obtained under the optimum conditions were 166.7, 6.7 and 83.2 mg/g for Pb (II), Cu (II), and Cd (II) respectively. From the results obtained, there were significant reductions in the concentrations of Pb (II), Cu (II) and Cd (II) ions at the various conditions considered. However, the residual metal concentrations were above the limits permissible by the regulatory authority.

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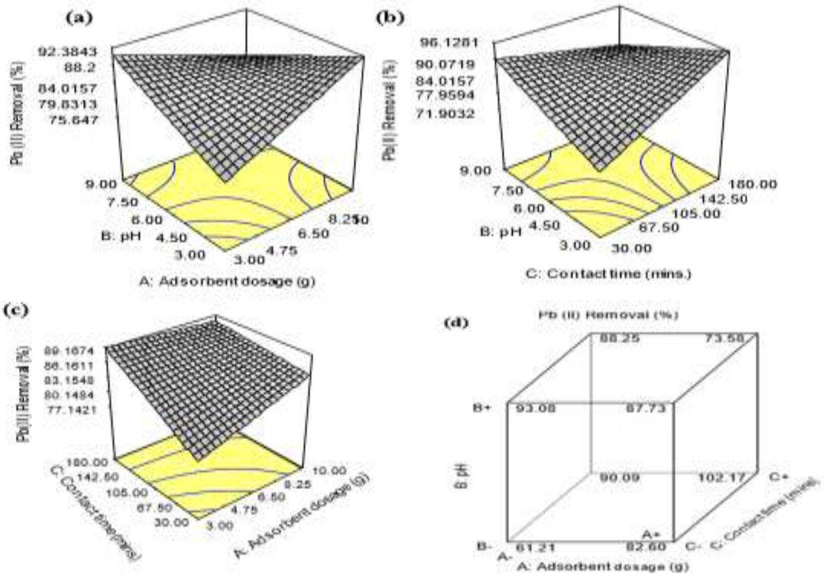

Fig 5: Combined effect of process variables (**a**) pH and adsorbent dosage, (**b**) pH and contact time, (**c**) contact time and adsorbent dosage on Pb (II) removal with interaction effect of dual factors, (d) removal percentage at each factorial point

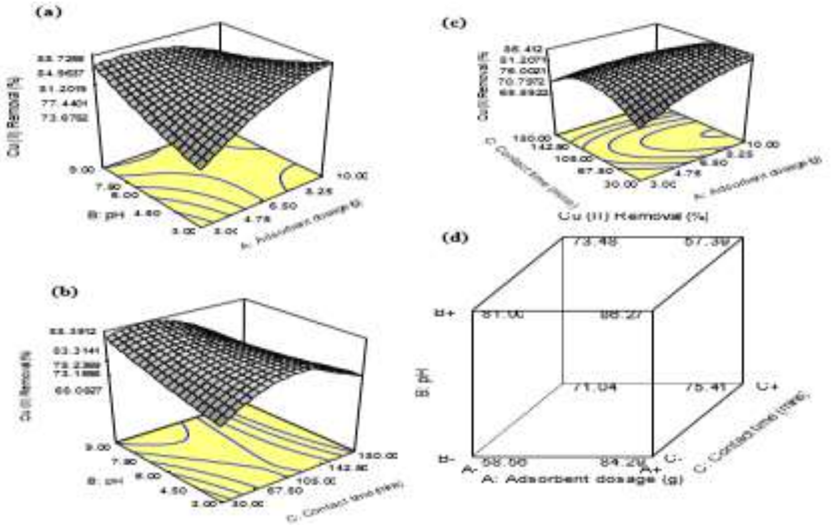

Fig 6: Combined effect of process variables (**a**) pH and adsorbent dosage, (**b**) pH and contact time, (**c**) contact time and adsorbent dosage on Cu (II) removal with interaction effect of dual factors, (d) removal percentage at each factorial point

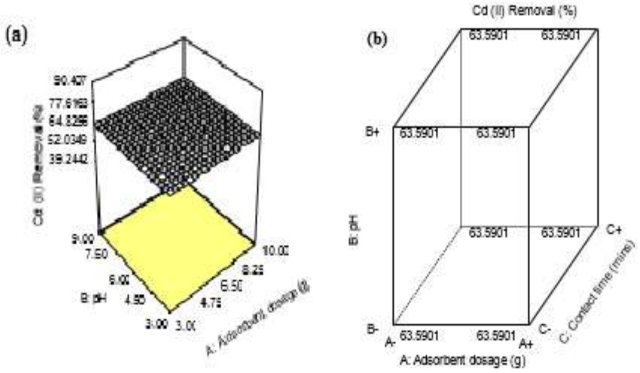

Fig 7: Combined effect of process variables (**a**) pH and adsorbent dosage on Cd (II) removal with interaction effect of dual factors, (b) removal percentage at each factorial point

Table 6: Predicted and experimental maximum values of Pb (II), Cu (II) and Cd (II) removal percentages achieved in optimum conditions

Heavy Metal	Adsorbent Dosage (g)	Contact Time (min)	pH	Removal %		% Error
				Predicted	Experimental	
Pb (II)	6.50	105.00	6.00	84.8377	87.74038	3.31
Cu (II)	6.50	105.00	6.00	84.1499	78.63636	-7.00
Cd (II)	6.50	105.00	6.00	63.5901	61.62791	-3.18

Table 7: Biosorption capacities of various biosorbents.

Biosorbent	Adsorbate	q_{max} (mg/g)	Reference
Desert date oil-free cake	Pb(II) Cu(II) Cd(II)	166.7 6.7 83.2	Present study
Cashew nut shell	Zn(II)	24.98	Kumar et al., (2012)
Orange peel	Pb(II) Cd(II) Ni(II)	113.5 63.35 9.82	Feng et al., (2011)
Multi-metal binding biosorbent (tea waste, maple leaves and mandarin peel)	Cd(II) Cu(II) Pb(II) Zn(II)	31.73 41.06 76.25 26.63	Abdolali et al., (2014)

Further experimental runs might reduce the contaminant rate to the desired level. A comparison between maximum adsorptive capacities of desert date oil-free cake biosorbent and some other biosorbents is shown in Table 7. The study showed that the biosorbent considered compared favorably with most results obtained from previous studies (Kumar et al., 2012; Feng et al., 2011; Abdolali et al., 2014). Therefore, desert date oil-free cake is effective biosorbents for the simultaneous removal of Pb (II), Cu (II) and Cd (II) ions from Battery effluent.

Adsorption Isotherm Study: The sorption equilibrium data were tested with two and three-parameter models such as Langmuir, Freundlich, Redlich-Peterson and Sips isotherms. The model parameters for each isotherm, their respected correlation coefficients (R^2)

and non-linear chi-square, (χ^2) values are shown in Tables 8 and 9. Comparing the values of R^2 obtained from the two-parameter models, the Langmuir isotherm best fitted for Pb (II), Cu (II) and Cd (II) on the oil-free cake, with R^2 values of 0.7598, 0.7154 and 0.5963 respectively. This fitting indicated that the sorption of metal ions had monolayer coverage on the sorbent surface (Mubeen *et al.*, 2019). The maximum sorption capacity was higher for Pb (II) than that for Cu (II) and Cd (II). The values of R_L were less than zero, confirming the irreversibility and not acceptable sorption of Pb (II), Cu (II) and Cd (II) onto the oil-free cake.

Table 8: Isotherm constants of two-parameter models for Pb (II), Cu (II) and Cd (II) ions simultaneous biosorption onto oil-free cake

	Langmuir Isotherm Coefficient				**Freundlich Isotherm Coefficient**		
Heavy metals	q_o (mg/g)	b (L/mg)	R^2	R_L	K_F $[(mg/g)/(L/mg)]^{1/n}$	1/n	R^2
Pb (II)	1.5466	-0.1048	0.7598	-0.0529	2.5276	0.0402	0.0023
Cu (II)	0.0863	-4.5079	0.7154	-0.0268	0.1261	-0.1590	0.0128
Cd (II)	0.6748	-0.0508	0.5963	-0.1707	6.7391	-0.3943	0.0724

Table 9: Isotherm constants of three-parameter models for Pb (II), Cu (II) and Cd (II) ions simultaneous biosorption onto oil-free cake

Models	Parameters	Pb (II)	Cu (II)	Cd (II)
Redlich-Peterson	K_R (L/g)	141.1951	4.1354	12.626
	a_R (L/mg)	82.0170	39.1910	174.5100
	g	0.7429	19.229	0.1307
	χ^2	5.4998	1.212×10^{-06}	1.1816×10^{-05}
Sips	K_s (L/g)	46.1567	0.0227	0.0062
	a_s(L/mg)	11.8902	0.1312	0.0028
	β_s	76.0000	83.5530	2.8114
	χ^2	5.6382	0.3634	3.0126

Table 10: The Pseudo-first order, Pseudo-second order And Elovich kinetic parameters for biosorption of Pb (II), Cu (II) and Cd (II) onto desert date oil-free cake

Model	Equation	Parameters	Pb (II)	Cu (II)	Cd (II)
Pseudo-first order	$\log(q_e - q_t) = \log(q_e) + k_1 t$	q_e (mg/g)	20.0217	1.0414	10.2542
		k_1 (1/min)	0.00004	0.0002	0.00010
		R^2	0.00740	0.1736	0.05070
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{q_e k_2} + \frac{1}{q_e} t$	q_e (mg/g)	2.4131	0.0825	1.3578
		k^2 (g/(min.mg))	0.3079	-0.1862	0.0607
		R^2	0.7078	0.9067	0.5294
Elovich kinetic model	$q_t = \frac{1}{\beta} \ln \alpha\beta + \frac{1}{\beta} \ln t$	A	-5.730×10^{-8}	-1.303×10^{-5}	-6.6018×10^{-5}
		B	-3.6887	-31.250	-2.5548
		R^2	0.0185	0.2036	0.0945

Similarly, for the three-parameter models in Table 9, Redlich-Peterson's model showed better fit to the experimental adsorption data than the Sips. The non-linear regression chi-square (χ^2) value are 5.4998, 1.212×10^{-06} and 1.182×10^{-05} for Pb (II), Cu (II) and Cd (II) respectively, closer to zero than any other models.

The values of Redlich-Peterson's exponents are 0.7429, 19.229 and 0.1307 for the Pb (II), Cu (II) and Cd (II) ions, respectively.

The foregoing analysis of isotherm models shows that the better fit for Pb (II), Cu (II) and Cd (II), biosorption is produced by three-parameter isotherm models rather than two-parameter isotherm models.

Adsorption Kinetic Study: In this study, three different kinetics models were investigated, namely the pseudo-first order, the pseudo-second order, and the Elovich kinetic models, to test the experimental data.

The parameters for each kinetic model and its respected correlation coefficients (R^2) are shown in Table 10. A plot of the best fitted kinetic model is shown in Figure 9. The experimental results fitted well with the pseudo-second order model.

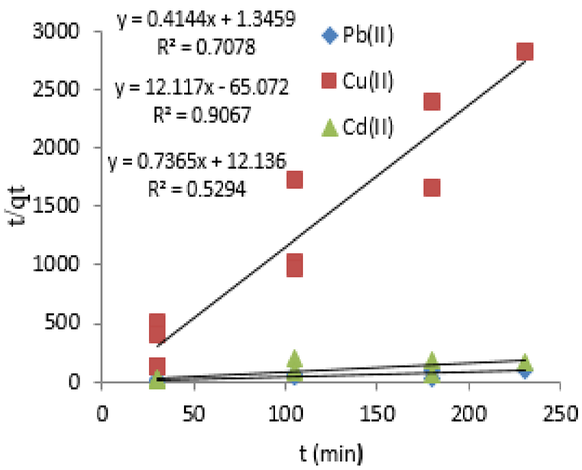

Fig 9: Linear fitting of biosorption of Pb (II), Cu (II) and Cd (II) by desert date oil-free cake to the pseudo-second order kinetic models

Conclusion: The study has demonstrated that oil-free-cake dry seed kernels of desert date (*Balanites aegyptiacus* (L.) Delile) can be effective as biosorbent for the simultaneous removal of metal ions from industrial effluent. This will benefit waste water management in battery, textile and related industries. In conclusion, the outcome of the study is an indication of a clear pathway to tackling those concerns arising from the presence of heavy metal ions in the environment.

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