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Biosorption of Oil and Heavy Metal Ions from Produced Water Using Sesame Residues

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ABSTRACT: With the ever-increasing use of water for municipal and industrial purposes, it has become necessary to appraise water quality on a continuous basis. Crude oil production is accompanied by generation of large volumes of produced water. The produced water contained dissolved and dispersed oil which is hazardous to both human health and aquatic lives. Hence, the objective of this paper was to evaluate the removal of oil, cadmium and lead ions from produced water by sesame pod and stalks collected from farm-site in Bartak Village of Alkaleri Local Government Area, Bauchi State, Nigeria. Effects of loading rate, stirring speed and sorption time were studied. The results of EDS spectroscopy revealed that sesame pod contained 65.21% C; 18.22% Ca; 13.11% Si; 1.22% K; 0.02% Ag; 1.29% Mg; 0.12% Sr; 0.31% Cu; 0.11% Zn; 0.01% Zr; 0.05% S; 0.31% Rb and 0.02% Na while sesame stalk contained 69.35% C; 13.58% Ca; 14.29% Si; 1.13% K; 0.02% Ag; 1.03% Mg; 0.32% Sr; 0.13% Cu; 0.01% Zn; 0.15% Zr; 0.38% S; 0.13% Rb and 0.14% Na respectively. Biosorption study with the two biosorbent (sesame pod and stalk) showed that both can be used in the removal of oil, cadmium and lead ions from produced water given up to 96.7% oil removal for sesame pod and 97.2% removal for sesame stalk at an equivalent dosage of 1.0 g (for both sesame pod and stalk) per liter produced water after 30minutes equilibrium time and initial oil concentration as high as 435.5 mg/l. Finally, the prepared sesame pod and stalk biosorbents are characterized significantly by their high ability to adsorb oil and suspended solids from produced water, as a result, reduces the economic cost of water treatment.

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The oil and gas industry is considered as one of the eight most water-intensive industries due to the high volumes of water that are required for oil production, and the subsequent amount of wastewater that is generated. Produced water (PW) is a water from underground formations that is brought to the surface during oil or gas production (Munirasu *et al*., 2015). Billions of gallons of produced water generated globally on annual basis (Peng *et al*., 2020) could be linked to more than 65,000 global onshore and offshore oil and gas fields (Davidson *et al*., 2014). During oil and gas explorations, produced water (trapped in subsurface formations) is brought to the surface which contains heavy metals (such as copper, cadmium, lead, chromium, mercury, silver, nickel and zinc) as part of dissolved inorganic matter (Shammaei, *et al*., 2018). The geology of formation and age of wells are major factors that determine heavy metals concentrations in produced water. These heavy metals should be properly managed when the produced water is spilled on ground surface or discharged into water bodies because they damage the ecosystem (Udeagbra *et al*., 2020).

Treatment of oil spills and oil contaminated water remains one of the major challenges to environmental scientists and technologists. Among the existing techniques used for oil treatment, sorption is a popular technique because it is cheap, simple and effective (Rodriguez *et al*., 2020). Oil removal by biological waste materials have been reported by several authors [Muhammad *et al*., (2012); El-Nafaty *et al*., (2013); Lia and Jiang (2015); El-Araby *et al*., (2017) Mehdi *et al*., (2020); Adil, *et al*., (2020);

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Tagreed *et al.*, (2020); Udeagbra *et al.*, (2020) and Lekan *et al.*, (2020)]. During the 1970s, increasing environmental awareness and concern led to search for new technique to replace the expensive/hazardous chemical treatment methods. These demands have led to increasing interest in biosorption. The use of biosorbent has been proposed as an alternative, as it has proven effective on low concentrations. Hence, the objective of this paper was to evaluate the removal of oil, cadmium and lead ions from produced water by sesame pod and stalks collected from farm-site in Bartak Village of Alkaleri Local Government Area, Bauchi State, Nigeria.

MATERIALS AND METHODS

Sample Collection and Preparation: Sesame pod and stalks were collected from a farm-site in Bartak village of Alkaleri local government area, Bauchi State, Nigeria. Crude oil was obtained from Kaduna Refinery and Petrochemical Company (KRPC), Kaduna-Nigeria. 1, 1, 1-trichloroethane was purchased from Chuzz Bond International, Jos-Nigeria. All chemicals and reagents were of analytical grade. Distilled water was obtained from Gubi Dam Water Treatment Plant Laboratory, Bauchi-Nigeria. Oven was used to dry the sorbent materials (Manufactured by Ragaterm, Italy). Separating funnels were used to extract out the oil from water and DR/2000 Spectrophotometer (HACH, Colorado, and U.S.A) was used to test the presence of oil in the extract. Hanna pH meter was used to determine the pH of the mixtures. A JJ-4 six couplet digital electric mixer (Search Tech Instrument, England) was used for the sorption study. Laboratory mortar and pestle were used to convert the sesame pod and stalk to powder and sieves were used to classify it into different sizes (212-63 microns).

iosorbent Preparation: Sesame pod and stalk were first washed with water several times and then sun-dried. The dried sesame pod and stalk were ground to particle sizes between 2-3 mm to remove all the colour pigments in a reflux condenser. The n-hexane treated seseame pod and stalk were later washed with distilled water and dried in an oven at 70^0C for 24 hours. These were further crushed and sieved through 212-63 microns sieve and then stored in an air tight sealed plastic containers as SPB (Sesame Pod Biosorbent) and SSB (Sesame Stalk Biosorbent) respectively.

Characterization: The raw sesame pod biosorbent (SPB) and sesame stalk biosorbent (SSB) were characterized using FTIR, SEM and EDS. Perkin Elmer Spectrum 100 FTIR spectrometer was used for the infra-red spectroscopic studies at wave numbers 4000-400 cm^{-1}. The X-ray diffractometry study was done on a BRUKER AXS D8 Advance (Cu-Kα radiation $\lambda K\alpha_1$=1.5406A) 40kV. The Hitachi X-650 Scanning Electron Microscope (Tungsten Filament, EHT 20.00 kV) and LEO 1450 Scanning Electron Microscope (Tungsten Filament, EHT 20.00 kV) were used for the SEM imaging. The chemical compositions were determined using energy dispersive spectroscopy (EDS) while surface areas and pore sizes were determined using TriStar 3000 V6.05 A BET equipment.

The spectrograms are presented in Figures 1, 2 and 3 respectively.

Simulation of the produced water: The produced water was synthesized in the laboratory by mixing 435.5 mg of crude oil with 1 litre of distilled water. The pH of the produced water was measured and recorded with the aid of a pH meter. Atomic absorption spectrophotometric study (AAS) was conducted on the simulated produced water to determine the amount of cadmium and lead ions in the mixture, and the results were recorded.

Experimental Design: In this current study, design-expert software (Version 13.0) was used for the experimental design. The response surface methodology (RSM) is a set of statistical and mathematical tool for designing experiments and optimizing the effects of process variables. The correlation of three independent variables (i.e biosorbent dosage, X_1; stirring speed, X_2; and contact time, X_3) and dependent variables (residual oil, Y_1; residual cadmium ion, Y_2; and residual lead ion, Y_3) was investigated through CCD at three different levels denominated as (-1, 0, +1). The layout can be viewed as three-level partial factorials. A 2k factorial CCD was performed to build a total of 20 experiments with eight cube points plus six center points and six axial points for optimization of the three variables that exhibited significant effects on oil removal capacity of both sesame pod and stalk. To determine how each independent variable affected responses and model quality, analysis of variance (ANOVA) with Fisher's exact test and p-values was conducted. The matrix design for the experiment is presented in Table 1.

Batch adsorption experiments: The experiments were carriedout by taking 500 ml of 435.5 mg/l laboratory synthesized produced water and different quantities of the prepared sorbent materials (0.10, 0.55, 1.0 and 1.31 grams) each in a 1000 ml glass beakers. The different adsorbent dosages were obtained using the design-expert software by means of response surface methodology (RSM) as given in Table 1. The flasks were then agitated at various stirring speeds (50-250) rpm and at various contact time (10-40) minutes. The stirring speed and the contact time were also obtained using central composite design. With the aid of a jar test set-up, the mixtures were agitated at the given time and stirring speeds. The biosorbents and sorbates were then separated using a 63micron sieve. After separating the biosorbent from the mixture, the residual oil in the mixtures were then extracted and measured with the aid of a UV/VIS spectrophotometer and an AAS analysis was also carried-out to determine the amount of residual cadmium and lead ions in the various samples respectively. Same procedure was followed for all the 20 runs obtained from CCD for each of the two adsorbents (Sesame pod and stalk).

Table 1: Experimental Design for Removal of Oil and Heavy Metals from Produced Water

Run	Dosage (g/l)	Time (min)	Speed (rpm)	Residual oil (mg/l)	Cadmium ion (mg/l)	Response Lead ion (mg/l)
1	0.10	30.00	50.00			
2	0.55	38.52	150.00	-	-	-
3	0.55	17.50	150.00	-	-	-
4	1.00	5.00	250.00	-	-	-
5	0.55	17.50	150.00	-	-	-
6	0.55	17.50	150.00	-	-	-
7	0.55	17.50	150.00	-	-	-
8	0.10	5.00	50.00	-	-	-
9	0.10	30.00	250.00	-	-	-
10	0.55	17.50	150.00	-	-	-
11	1.00	30.00	250.00	-	-	-
12	0.10	5.00	250.00	-	-	-
13	1.31	17.50	150.00	-	-	-
14	0.55	3.52	150.00	-	-	-
15	0.55	17.50	318.18	-	-	-
16	1.00	30.00	50.00	-	-	-
17	0.55	17.50	150.00	-	-	-
18	1.00	5.00	50.00	-	-	-
19	0.21	17.50	150.00	-	-	-
20	0.55	17.50	18.18	-	-	-

RESULTS AND DISCUSSIONS

FTIR Analysis: FTIR analysis was used to identify the characteristic functional groups on the surface of biosorbents and the spectra of sesame pod and stalk (as shown in Fig. 1a and 1b). FTIR apparatus type shimadzu (4000-400 cm^{-1}) was carried out to identify the functional groups and structure in the surface of the bio-wastes that might be involved in the adsorption process.

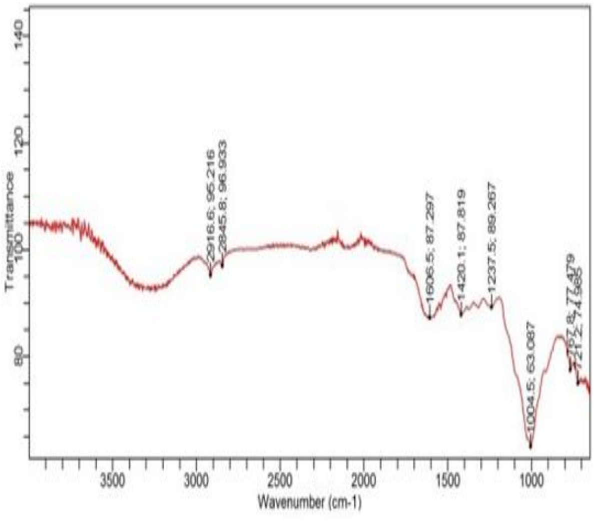

Fig 1: FTIR Spectrum of Sesame Pod Biosorbent (SPB)

From the FTIR spectra in Figures 1a and 1b, it can be seen that many peaks exist indication of many functional groups on the surface of the SPB and SSB. A shift at (Figure 1a) wave number 1004.5 cm^{-1} was observed and was assigned to Si-O-Si silicon stretching while the absorption at 1237.5 cm^{-1} was assigned to C-N amine stretch. The shift at 1420.1 cm^{-1} was assigned to organic sulfate stretch. Shift at 1606.5 was assigned to secondary amine NH stretch while the shift at 2845.8 cm^{-1} was assigned to Si-H symmetric stretch and the shift at 2916.6 cm^{-1} was assigned to methyl ester C-H stretch. For the stalk (Figure 1b), the band shift at 1233.7 cm^{-1} to 1315.8 cm^{-1} was assigned to P=O stretching while the shift at 1597.2 cm^{-1} was assigned to N-H amide stretch and the shift at 1638.2 was assigned to N-H bending stretch respectively.

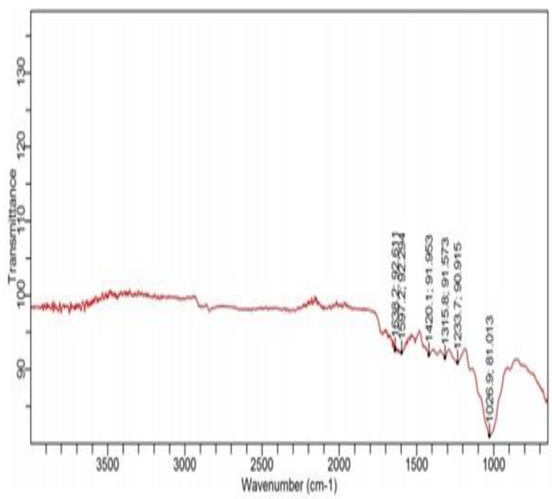

Fig2: FTIR Spectrum of Sesame Stalk Biosorbent

SEM Analysis: Scanning Electron Microscopy under 1500 magnification was used to determine the surface morphology and microporous structure of the biosorbents. Figure 2a and 2b shows the SEM of SPB and SSB. As seen from the Figure, both SPB and SSB have semi-permeable bio-membrane with an intricate poly-porous structure with a pore diameter of 50 µm(pod) and 80 µm (stalk) respectively. The SEM clearly indicates that sesame stalk are more porous than sesame pod. The microporous structure of the biosorbents is responsible for the sorption of oil and heavy metal ions from the produced water.

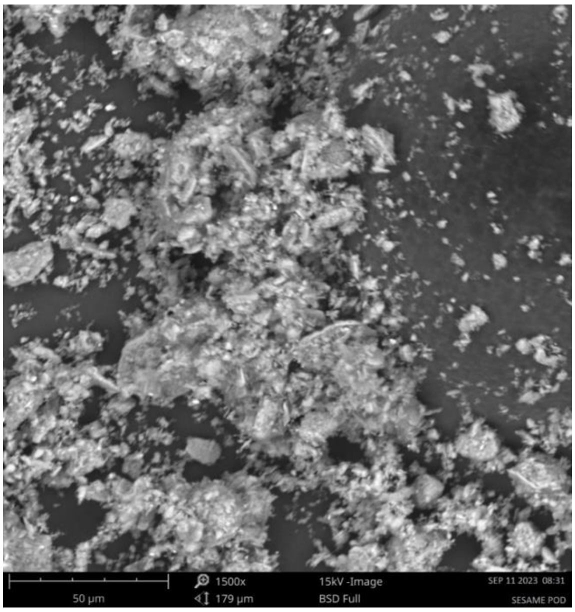

Plate 1: SEM of Sesame Pod Biosorbent (SPB)

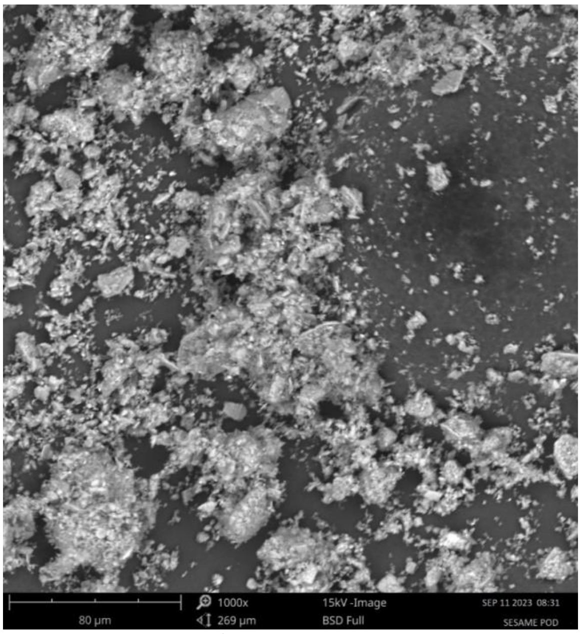

Plate 2: SEM of Sesame Stalk Biosorbent (SSB)

EDS Analysis: An electron dispersion spectrophotometric analysis was carried out to determine the elemental content. The various elements present and their compositions are presented in Table 2 and 3 for SPB and SSB. As seen from the Table 1, Carbon has the highest percentage composition (65.21%) followed by Calcium (18.22%), and then Silicon (13.11%). The percentage composition of Magnesium was found to be 1.29% while that of Potassium was 1.22%. Other elements present include Rubidium (0.31%), Copper (0.31%), Strontium (0.12%), Zinc (0.11%), Sulphur (0.05%), Sodium (0.02%) and Zirconium (0.01%).

Table 2: Elemental Analysis of Sesame Pod Biosorbent

Element	Weight, g	Atomic, %	Weight, %
C	4.25	65.21	68.39
Ca	0.15	18.22	13.21
Si	0.26	13.11	15.29
K	0.49	1.22	1.13
Ag	0.08	0.02	0.01
Mg	0.12	1.29	1.03
Sr	0.06	0.12	0.32
Cu	0.04	0.31	0.11
Zn	0.07	0.11	0.12
Zr	0.05	0.01	0.01
S	0.16	0.05	0.11
Rb	0.07	0.31	0.13
Na	0.09	0.02	0.14
Totals	5.89	100	100

Table 3 present the EDS analysis of sesame stalk biosorbent. As seen from the Table, the elemental analysis revealed that SSB contained Carbon, Calcium, Silicon, Potassium, Silver, Magnesium, Strontium, Copper, Zinc, Zirconium, Sulfur, Rubidium, and Sodium. Among the different elements present, Carbon appeared to have the highest percentage (69.35%).

Table 3: Elemental Analysis of Sesame Stalk Biosorbent

Element	Weight, g	Weight, %	Atomic, %
C	4.86	62.21	69.35
Ca	0.16	21.22	13.58
Si	0.27	12.11	14.29
K	0.45	1.72	1.13
Ag	0.10	0.03	0.02
Mg	0.15	1.68	1.03
Sr	0.07	0.12	0.32
Cu	0.05	0.35	0.13
Zn	0.08	0.01	0.01
Zr	0.06	0.34	0.15
S	0.14	0.51	0.38
Rb	0.03	0.31	0.13
Na	0.09	0.02	0.14
Totals	6.51	100	100

Sesame pod and stalk have an average pore diameter of diameter of 2.138 nm and 2.84 nm, a pore volume of 1.341 cc/g, 1.981 cc/g and a BET surface area of 2.256 m^2/g and 2.034 m^2 /g as revealed by BET analytical equipment.

Effects of SPB Dosage: The batch adsorption experiment was carried out using the design matrix presented in Table 1. Effects of biosorbent dosage (Sesame Pod), contact time and stirring speed were determined and the results are presented in Table 4. As shown in Table 4, the results indicated that run 13, 14, 15, 19 and 20 are out-layers and therefore were not considered in choosing the best treatment option. From the results obtained, it could be observed that there was a reduction in the concentrations of the residual oil with increase in the concentration of the bio-sorbent dosage (Sesame pod). At run 1, when the amount of the bio-sorbent was 0.1 g, the residual oil was found to be 310 mg/L, which is equivalent to 28.8% removal. Runs 16 and 18 gave residual oil removal of 15 mg/L and 28 mg/L respectively which were within the acceptable limit of 30 mg/L set up by the Department of Energy and Climate Change (DECC) for oil in produced water discharged into seas. In addition, the residual cadmium and lead ions were 0.015 and 0.018 mg/L respectively which were slightly above the maximum limit of 0.005 mg/l for cadmium ion in drinking water set up by World Health Organization (WHO). However, the residual Pb^{2+} for run 16 was found to be below the 0.015 mg/L set by WHO. Therefore, run 16 was chosen as the best treatment option. Table 4 present the results obtained on biosorption of oil, cadmium and lead ions from produced water using sesame pod biosorbent (SPB).

Table 4: Effects of SPB loading rate on oil, lead and cadmium ions removal from produced water

Run	Dosage (g)	Time (Min)	Stirring speed (rpm)	Residual oil (mg/L)	Residual Cadmium ion (mg/L)	Residual lead ion (mg/L)
1	0.10	30.00	50.00	310.00	2.146	1.269
2	0.55	38.52	150.00	118.00	0.425	0.534
3	0.55	17.50	150.00	120.00	0.427	0.536
4	1.00	5.00	250.00	30.00	0.018	0.013
5	0.55	17.50	150.00	120.00	0.422	0.537
6	0.55	17.50	150.00	120.00	0.422	0.537
7	0.55	17.50	150.00	120.00	0.422	0.537
8	0.10	5.00	50.00	311.00	2.150	1.272
9	0.10	30.00	250.00	309.00	2.143	1.266
10	0.55	17.50	150.00	120.00	0.422	0.537
11	1.00	30.00	250.00	32.00	0.012	0.010
12	0.10	5.00	250.00	305.00	2.149	1.275
13	1.31	17.50	150.00	45.00	0.017	0.012
14	0.55	3.52	150.00	100.00	0.425	0.539
15	0.55	17.5	300.00	110.00	0.423	0.535
16	1.00	30.00	50.00	15.00	0.015	0.011
17	0.55	17.50	150.00	120.00	0.422	0.537
18	1.00	5.00	50.00	28.00	0.018	0.015
19	0.21	17.50	150.00	320.00	2.146	1.249
20	0.55	17.50	18.18	123.00	0.425	0.538

Table 5: ANOVA for Response 1(residual oil) using SPB

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	1.857E+05	3	61913.41	36.97	< 0.0001	Significant
A-Dosage	1.857E+05	1	1.857E+05	110.89	< 0.0001	
B-Time	36.32	1	36.32	0.0217	0.00011	
C-Speed	7.12	1	7.12	0.0043	0.00012	
Residual	26794.71	16	1674.67			
Lack of Fit	26787.21	11	2435.20	1623.47	< 0.0001	Significant
Pure Error	7.50	5	1.50			
Cbor Total	2.125E+05	19				

Analysis of variance (ANOVA) for SPB results: To determine how each independent variable affected responses and model quality, analysis of variance (ANOVA) with Fisher's exact test and p-values was conducted. Table 5 present the ANOVA for the first response (residual oil) using SPB. As seen from Table 5, the p-values for all the three independent variables (dosage, time and speed) are significant i.e <0.0001. Figure 3, 4 and 5 shows the 3D-surface plots showing the interactions of dosage and contact time on oil, cadmium and lead ion removal at constant stirring speed of 200 rpm. As seen from the 3D diagram in Figure 3, at constant stirring speed of 200 rpm, there is a decrease in the concentration of the residual oil from 265 mg/L to about 28 mg/L when the biosorbent dosage is increased from 0.1 g to 1.0 g, that is an increase in the concentration of the biosorbent leads to a decrease in the amount of residual oil in the produced water. Similarly, from the 3D-diagram in Figure 4, a decrease in the concentration of cadmium ion was observed when the concentration of the SPB was increased. At 0.1 g of the SPB, the residual Cd^{+2} was 1.6 mg/l but when the SPB dosage was increased to 1.0 g, the residual Cd^{+2} was found to be 0.012 mg/l which amount to 96.8% removal. Similar result was observed from the 3D-diagram in Figure. The concentration of Pb^{+2} decreased from 1.68 mg/l to 0.035 mg/l when the SPB dosage was increased from 0.1 to 1.0 g respectively. Optimum SPB dose was found to be 1.0 g of the adsorbent per liter of the produced water. A similar observation was previously reported with (Agarwal *et al*., 2016) and (Adil *et al*., 2020).

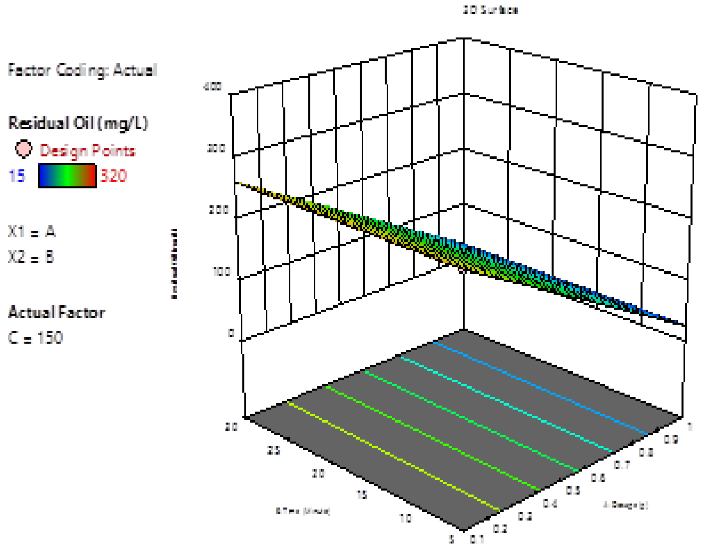

Fig 3: 3D Surface plot showing the effect of dosage and contact time on oil removal for sesame pod biosorbent.

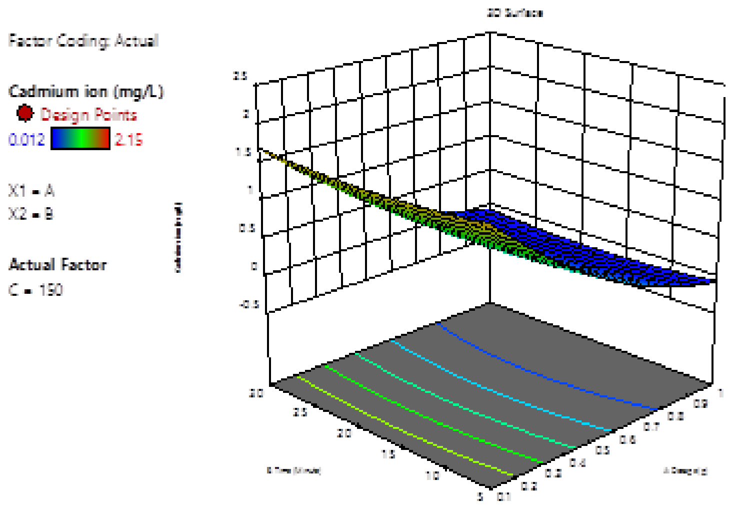

Fig 4: 3D Surface plot showing the effects of dosage and contact time on Cadmium ion removal using SPB

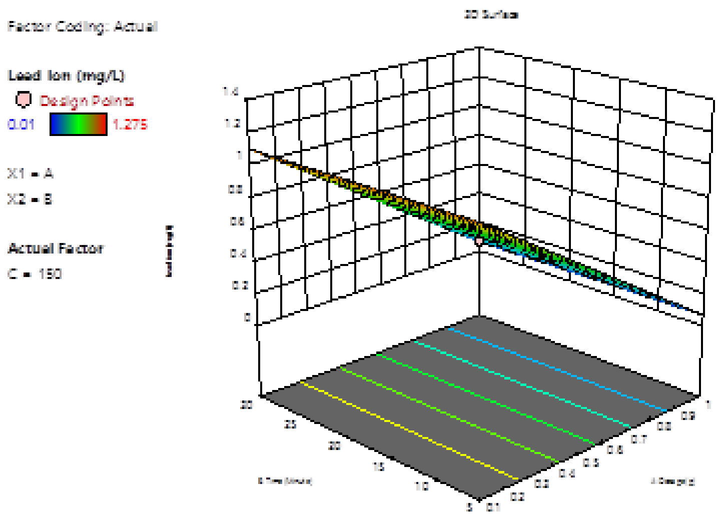

Fig 5: 3D Surface plot showing the effect of dosage and contact time on Lead ion removal using SPB.

Table 5: Validation of the Experimental results for SPB

	Dosage (g)	Time (min)	Speed (rpm)	Residual oil (mg/l)	Residual cadmium ion (mg/l)	Residual lead ion (mg/l)
1st	1.0	5.37	245	26	0.014	0.065
2nd	1.0	5.37	245	27	0.013	0.062
3rd	1.0	5.37	245	25	0.012	0.065

Optimization of the SPB experimental results: The experimental results were optimized using design expert software and thereafter validated in the laboratory at replicate determination. Table 5 present the validation of the experimental results for sesame pod biosorbent. The average of the three validated results gave a residual oil of 26.0 mg/L which is within the maximum limit of oil in produced water discharged into the environment given by DECC. Percentage error of 3.68% was observed between the validated results and the optimized results

Effects of Sesame Stalk Biosorbent (SSB) Dosage: Table 6 present the results obtained on biosorption of oil, cadmium and lead ions from water using sesame stalk biosorbent (SSB). As seen from the results in Table 6, there was an increase in oil removal as the concentrations of the bio-sorbents were increased for the sesame stalk biosorbent. For sesame stalk, the residual oil was found to be 295 mg/L at 0.1 g dose of the bio-sorbent, which is equivalent to 32.3% oil removal. At run 11, this was found to decrease up to a concentration of 12 mg/L (97.24% oil removal) at a concentration of 1.0 g of the sesame stalk bio-sorbent which was within the acceptable limit set up by the Department of Energy and Climate Change (DEEC). The regulatory limit for concentration of oil in produced water discharged into sea is set at a concentration of 30 mg/L performance standard. At run 18, the residual oil was found to be 18 mg/L while the residual cadmium and lead ions were 0.026 mg/L and 0.023 mg/L respectively. The residual lead ion at run 18 fall within the standard limit of 0.05 mg/L set up by WHO hence run 18 was chosen as the best treatment option. Similar findings were reported by Veil (2019) and Wong *et al.* (2020). Furthermore, from the Table, it can be observed that the amount of organic biosorption increased with an increased in biosorbent dosage. This result can be explained by the fact that for optimum biosorption, extra sites must be available for biosorption reaction, whereas by increasing the biomass concentration, number of sites available for biosorption increased; this is in agreement with the results published by different authors such as (Ibrahim *et al.*,2017), (Eletta *et al*., 2019) and (Abdel-shafy *et a*/., 2020).

Analysis of variance (ANOVA) for SSB results: Table 7 present the analysis of variance (ANOVA) for the first response (residual oil) using SSB. As seen from Table 5, the p-values for all the three independent variables (dosage, time and speed) are significant i.e <0.0001. Figure 6, 7 and 8 present the 3D-Surface plot showing the interaction effects of adsorbent dosage and contact time on the removal of oil, cadmium and lead ions from produced water at constant stirring speed of 200 rpm using sesame stalk biosorbent.

Table 6: Effect of SSB loading rate on oil, cadmium and lead ion removal from produced water

Run	**Dosage (g)**	**Time (min)**	**Stirring speed (rpm)**	**Residual oil (mg/L)**	**Residual Cadmium ion (mg/L)**	**Residual lead ion (mg/L)**
1	0.10	30.00	50.00	295.00	2.34	1.94
2	0.55	38.52	150.00	132.00	1.191	0.551
3	0.55	17.50	150.00	105.00	1.195	0.552
4	1.00	5.00	250.00	23.00	0.025	0.024
5	0.55	17.50	150.00	105.00	1.195	0.552
6	0.55	17.50	150.00	105.00	1.195	0.552
7	0.55	17.50	150.00	105.00	1.195	0.552
8	0.10	5.00	50.00	308.00	2.346	1.843
9	0.10	30.00	250.00	301.00	2.341	1.838
10	0.55	17.50	150.00	105.00	1.195	0.552
11	1.00	30.00	250.00	12.00	0.020	0.021
12	0.10	5.00	250.00	315.00	2.343	1.842
13	1.31	17.50	150.00	40.00	0.022	0.024
14	0.55	3.52	150.00	111.00	1.196	0.555
15	0.55	17.50	318.18	103.00	1.188	0.551
16	1.00	30.00	50.00	16.00	0.021	0.020
17	0.55	17.50	150.00	105.00	1.195	0.552
18	1.00	5.00	50.00	18.00	0.26	0.023
19	0.21	17.50	150.00	300.00	2.343	1.841
20	0.55	17.50	18.18	108.00	1.197	0.553

Table 7: ANOVA for Response 1(Residual oil) using SSB

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	1.845E+05	3	61494.57	32.25	< 0.0001	Significant
A-Dosage	1.845E+05	1	1.845E+05	96.76	< 0.0001	
B-Time	1.61	1	1.61	0.0008	0.0003	
C-Speed	2.29	1	2.29	0.0012	0.0012	
Residual	30505.10	16	1906.57			
Lack of Fit	30505.10	11	2773.19			
Pure Error	0.0000	5	0.0000			
Cor Total	2.150E+05	19				

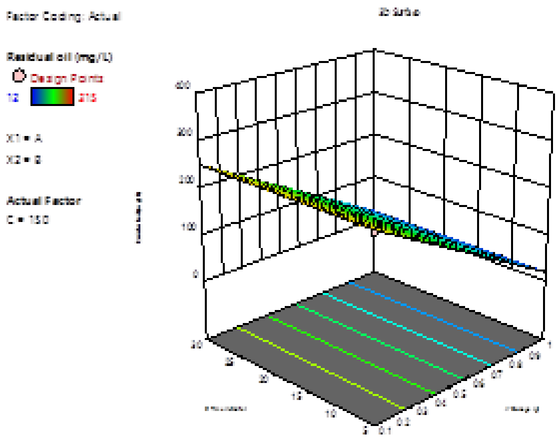

Fig 6: 3D surface plot showing the effect of dosage and contact time on oil removal using SSB.

As shown in Figure 6, when the stirring speed is kept constant (200rpm), an increase in biosorbent dosage leads to an increase in the percentage of oil removal. In other word, a decrease in the residual oil with increase in the concentration of the sesame stalk biosorbent was observed until equilibrium is reached. When the SSB dosage was 0.1 g, the residual oil was 256 mg/l, as the concentration of the biosorbent dosage was increased to 1.0 g, the residual oil was found to be 22 mg/L which clearly indicates that SSB plays a vital role in the adsorption of the oil. In other word, an increase in the SPB dose causes a decrease in residual oil. Also from Figure 7, it can be observed that at constant stirring speed of 200 rpm, when the concentration of the SSB was increased from 0.1 g to 1.0 g, the concentration of the residual cadmium ion decreases from 2.26 mg/L to 0.32 mg/L which is equivalent to 85.8% removal, hence an increase in SSB dosage causes a decrease in the concentration of the residual Cd^{+2}.

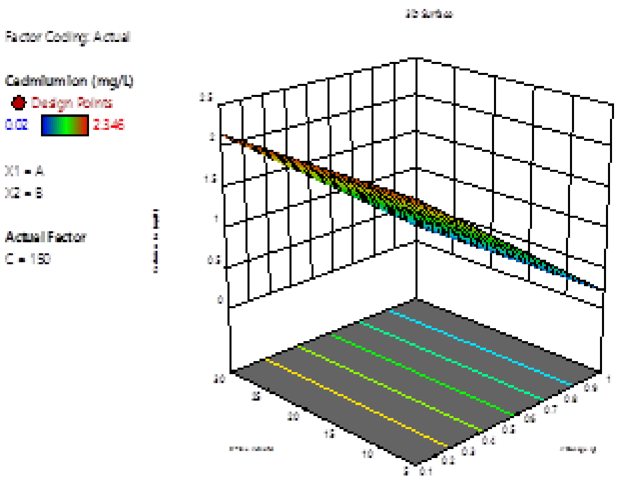

Fig 7: 3D Surface plot showing the effect of dosage and contact time on cadmium ion removal using SSB.

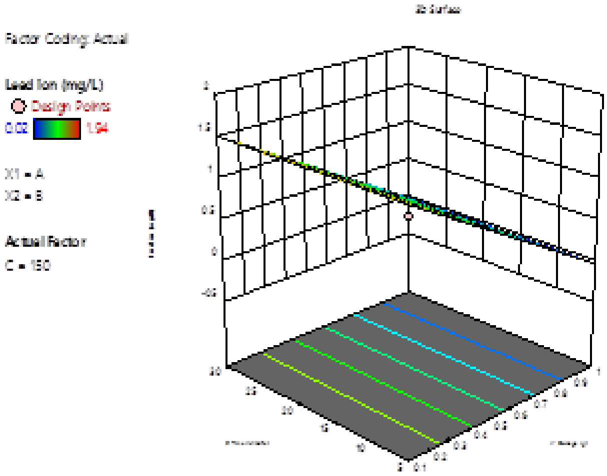

Fig 8: 3D Surface plot showing the effect of dosage and contact time on lead ion removal using SSB.

Table 8: Validation of the Experimental Results for SSB

	Dosage (g)	Time (min)	Speed (rpm)	Residual oil (mg/L)	Residual cadmium ion (mg/l)	Residual lead ion (mg/l)
1st	1.0	30	50	19	0.025	0.016
2nd	1.0	30	50	20	0.023	0.016
3rd	1.0	30	50	20	0.025	0.016

Also, by critically looking at Figure 8, it can be observed that, an increase in the concentration of the SSB dosage from 0.1 g to 1.0 g causes a reduction in the concentration of the residual Pb^{+2} from 1.53 mg/L to 0.016 mg/L when the stirring speed is kept constant at 200 rpm. The results clearly showed that SSB is a good adsorbent which can be used in the removal of oil and heavy metal ions from produced water. These findings agree with that of (Agarwal *et al.*, 2016) and that of (Adil *et al*., 2020).

Optimization of the SSB experimental results: The experimental results were optimized using design expert software and thereafter validated in the laboratory at replicate determination. Table 8 present the validation of the experimental results for sesame stalk biosorbent. The average of the three validated results gave a residual oil of 19.67 mg/L which is within the maximum limit of oil in produced water discharged into the environment given by DECC. Percentage error of 5.61% was observed between the validated results and the optimized results

Conclusions: Biosrbents were prepared from sesame pod and stalk using standard methods. Their utilization and optimization for the removal of oil, Cd^{+2} and Pb^{+2} from produced water was tested at different adsorbent dosage, reaction time and stirring speed. The biosorbents have active functional groups, porous structure, large surface area and various metallic elements as revealed by the characterization results. Batch experimental results showed the efficacy of both biosorbents to remove oil, cadmium and lead ions from produced water. The optimization results revealed an optima removal of oil, Cd^{+2} and Pb^{+2} at 1.0 g dosage of the SPB and SSB while stirring speed was insignificant. There were excellent agreements between experimental and predicted data which proved developed models to be efficient.

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