Absorbent Mixtures Optimisation for COD and Ammonia Nitrogen Reduction in Stabilised Leachate

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ABSTRACT: This paper describes the optimisation of mixed media for Chemical Oxygen Demand (COD) and Ammonia Nitrogen (NH_3-N) removal from stabilised leachate by feldspar (FE), zeolite (ZE), activated carbon (AC), and cockle shells (CS) mixtures using D-optimal mixture design. Linear equations characterised the optimal mixture. The optimum mitigation of COD and NH_3-N in landfill leachate was favourable at 12.5 mg/L, 9.72 mg/L, 6 mg/L, and 11.79 mg/L of adsorbent mixed dosage for FE, ZE, AC, and CS, respectively, with the desirability value of 0.886. The predicted R-squared values for NH_3-N (0.9839) and COD (0.8972) were in close agreement with the adjusted R-squared values of 0.9940 and 0.9900 for COD and NH_3-N, respectively, which validates the obtained regression models. The Lack of Fit F-values of 0.6015 (COD) and 0.4565 (NH_3-N) are insignificant, indicating that the models accurately predict the removal. The Fourier transform infrared spectroscopy (FTIR) revealed that the predominant hydroxyl group consisted of –OH at spectra 3306.18 and 3338.74. The study also revealed that the D-optimal mixture design has extremely high application potential as it produces a good mixture design based on the remediation of contaminants from stabilised leachate.

KEYWORDS: Adsorbent, COD, D-optimal, leachate, mixture, NH_3-N

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I. INTRODUCTION

Landfill leachate is a complex mixture of soluble organic and inorganic compounds produced by waste layers that use excess water to infiltrate landfills (Daud *et al*., 2016; Daud *et al*., 2017). In general, the leachate has a high concentration of dissolved organic matter, COD, inorganic macro constituents, halogenated hydrocarbons, ammonia (NH4-N), xenobiotic natural substances, suspended solids, and a substantial concentration of heavy metals in addition to inorganic salts (Peng, 2017; Daud *et al*., 2018). Leachate from landfills can pollute water bodies if it is not effectively managed. Due to their potential impact on plants, other terrestrial animals, the aquatic biota, and human health, there has been a need for stricter regulatory criteria regarding the indiscriminate disposal of polluting waste materials in recent years. (Arkles, 2011).

On a fundamental level, liquid or vapour molecules and the boundary layer of the solid phase are considered to interact along two distinct spectra, ranging from hydrophobic (averse to water) to hydrophilic (loves water). Water droplet formation on material surfaces suggests that the forces of attraction exerted within bulk liquid exceed the forces of attraction between the surface boundary and the liquid (Adeleke *et al*., 2017). Hydrophilic surfaces have a contact angle of fewer than 30 degrees with water. Hydrophobicity intensifies when the contact angle between water droplets and a surface is greater than 30 degrees. Standard contact angles range from 30° to approximately 90°, whereas hydrophobic materials have contact angles between 90° and 120° (Adeleke *et al*., 2017).

Activated carbon derived from organic materials found in nature is used in one of the most common wastewater treatment methods, adsorption, to remove soluble and insoluble organics, inorganics and biological pollutants. The hydrocarbons are eliminated by heating the raw material to a high temperature without oxygen during the production process. The char is then oxidised through steam at quite a high temperature (800-900 °C) to yield a high porosity with an extensive surface area. Activated carbon is considered hydrophobic and an adaptable adsorbent, notably for removing organic constituents, It has insufficient adsorption capacity for to remove of ammonium nitrogen (Hor *et al*., 2016). Similarly, hydrophilic natural zeolite has been widely utilised in treating industrial wastewater containing ammonia and other inorganic constituents (de Magalhães *et al*., 2022). Zeolites are naturally occurring tetrahedral crystalline molecules composed of alumino-silicates (Hu, 2017). The high utilisation of the

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adsorbent in the treatment of wastewater is due to the zeolite's ion-exchange mechanism for the adsorption of pollutants. The structural porosity of zeolites provides sites for the adsorption of contaminants. Chabazite, clinoptilolite, and analcime are examples of commonly employed zeolite minerals. Natural zeolite, which has been utilised concurrently with activated carbon, consists primarily of 65.06% SiO2, 12.01% C, 10.23% Al2O3, 4.18% K2O, and some trace components such as Fe2O3, K2O, and CaO. In addition, these two adsorbents have become expensive due to their renown uses in industrial remediation. As a result, there is a growing need for additional alternative adsorbents for sustainability. Absorbents comprised of natural materials, some of which are wastes or their derivatives, have been studied to address the cost issue, such as coconut fibre (Bispo *et al*., 2018), soybean (Yu, *et al*., 2016), banana peel (Anastopoulos, *et al*., 2017), feldspar (Moideen, *et al*., 2020), and cockle shells. (Daud *et al*., 2017), among others.

Feldspar is another material with a similar chemical composition that is utilised as an adsorbent in novel ways. Feldspar minerals constitute approximately 60 percent of the earth's crust, making them one of the most common mineral groups. Feldspar is abundant in every crystalline rock. The sodium, potassium, and calcium aluminosilicates that make up their densely packed tetrahedral crystalline framework give them their structure. Many industries use them as raw materials for the production of glass, ceramics, and paint, among other domestic and industrial materials. It is composed chemically of 53.9% SiO2, 11.0% C, 15.6% Al2O3, 10.12% K2O, and some trace components such as Fe2O3, Na2O, MgO, and CaO. Feldspar can be used effectively for wastewater treatment on its own or as a partial replacement for conventional zeolite media (Hu, 2017). Daud *et al*. (2016) investigated the ability of a mixture of feldspar and zeolite to remove ammoniacal nitrogen and COD from landfill leachate. The results showed that the optimal removal has been achieved at a mixing ratio of 20:20 for zeolite and feldspar at pH 6.5 and 150rpm shaking speed.

CS, also known as "Kerang" in Malaysia, is a small, edible marine bivalve mollusc belonging to the Arcidae family that inhabits sandy beaches. The CS has a spherical exterior with radiating ribs. The consumption of CS (Anadaragranosa) varies from country to country (Ibrahim *et al*., 2016), but is universally accompanied by the generation of solid waste from the discarded shells. According to studies, cockle shells contain (96.28 per cent) of CaO nearly the same proportion as limestone (97.67 per cent). Therefore, it can relatively be presented as a suitable adsorbent, which is the most significant benefit. Several studies on the application of CS in waste water treatment have been conducted. Ibrahim et al. (2016) reported the use of crushed cockle shells (Anadara granosa) for the treatment of contaminated river water, and the results demonstrated that it could reduce chemical oxygen demand by an adsorption capacity of 5.32 mg g-1, with physio-sorption being more pronounced based on the Freundlich isotherm model fitting.

While significant research has been conducted on the use of various adsorbents for the mitigation of stabilised leachate, few studies have investigated the use of cockle shell and feldspar as replacements for activated carbon and zeolite, respectively, in landfill effluent treatment. A mixture of activated carbon, zeolite, feldspar, and cockle shell would provide effective media for the removal of COD and Ammonia Nitrogen, as well as an efficient method for treating landfill leachate. This could prevent or reduce groundwater contamination by landfill leachate. Moreover, during the preparation of combined adsorbent media for wastewater treatment, the composition of the mixture must be optimised in order to obtain a final product with significant removal properties (Ab Ghani *et al*., 2017). Several statistical experimental design techniques, including factorial design, response surface, and combined and mixed experimental design, have been utilised for optimisation work (Daud *et al*., 2018). The D-optimal mixture experimental design is one of the most efficient methods for addressing a variety of optimisation issues. Additionally, it offers an effective output of the influencing factors. In contrast to the classical one-factor-at-a-time approach, D-optimal mixture design tool reduces the amount of time, effort, and resources required to conduct investigations (Ghafari, *et al* 2009; Hauwa, *et al* 2018). The D-optimal mixture design method can simultaneously process numerous variables using a lower number of observations. It has been proven effective in experimental studies of the relationship between variables in optimisation operations (Ghafari *et al*., 2009). However, it has rarely been used for media mixture optimisation in wastewater treatment. Therefore, the present study investigated leachate treatment utilising the D-optimal mixture design as a tool for optimising the mixtures of activated carbon, cockle shells, feldspar, and zeolite media.

II. MATERIALS AND METHODS

A. *Leachate sampling*

Using clean 20-L high-density polyethylene plastic containers, the leachate sample was manually collected at the Simpang Renggam municipal landfill (situated at latitude 1° 53'41.64" north and longitude 103° 22'34.68" East), transported to the laboratory, and stored at 4°C in a cold room. Within 24 hours, leachate was characterised in accordance with the standard methods for analyzing water and wastewater (Goff *et al*., 2014). All chemicals employed in the characterisation of leachate were of analytical grade.

B. *Media preparation*

As mixed media types, feldspar, zeolite, activated carbon and cockle shells designated as FE, ZE, AC and CS respectively were used in the experiment. All granular media types were washed thoroughly, rinsed with deionized water, and dried at 105 °C for 24 hours before being pulverized with a Fritsch model grinder and sieved to a particle size of 0.150 mm. The feldspar was purchased on average for 0.12RM per kilogram purchased from CCS Corporation Sdn Bhd in Selangor, Malaysia. Pure zeolite (Brand: Mechastone) was purchased for approximately 0.4RM per kilogram from Pt. Anugerahalam Sendirian Berhad (SDN BHD), Malaysia. The GAC was purchased for 4RM per kilogram from Cabot Malaysia Sdn Bhd in Negeri Sembilan. The CS was obtained from a commercial restaurant as wasted material at Parit Raja, Malaysia (Latitude 1°51’31.632" N and Longitude 103°6’27.604" E). The CS was taken to the laboratory, brushed and thoroughly washed with tap water, distilled water rinsed and allowed to air-dry for twenty-four hours. All samples were dried in an oven at 105 °C and cooled by air to ambient temperature before being ground into a powder to a size of 0.150 mm.

III. EXPERIMENTAL DESIGN

Using the RSM optimisation method, experiments on mixture composition were conducted at room temperature. The D-optimal design utilised in this study is a subset of RSM. The media were classified according to their hydrophobic and hydrophilic natures so that two media with potentially identical properties could be substituted for one another in the design. Using a video contact angle (VCA-Optima) device, the contact angle was determined by placing a substance on the sample holder and adjusting until the specimen was just under the tip of the needle. The liquid was then discharged through the dropper and dropped onto the specimen, followed by a click on the autofast icon to freeze the picture and assess the contact angles.

Fourier transform infrared (FTIR) spectroscopy was utilised to identify the functional groups in the sample media. The sample was examined with a Perkin Elmer Spectrum 100 FT-IR spectrometer after and before the sorption process of pollutants. A spectrum scan was performed between 400 and 4000 cm^{-1}. Before beginning the analysis, after cleaning the crystal tray with ethanol, the infrared field was provided. The sample was placed on the crystal load, the pressure arm as well as the force gauge were activated to push the sample down against the crystal, and then a laser beam was directed at it. Evaluations were conducted on the functional groups using the wave bands that were obtained within 30 seconds.

The subsequent analyses were performed in 250 ml conical flasks bearing 100 mL of effluent, and different amounts of the absorbent combination depending on the D-optimal design run were added and agitated at a maximum speed of 150 rpm for 105 minutes at room temperature through the use of an orbital shaker (model Daiki) with the solution pH adjusted to 7 using HCl and NaOH (Hauwa *et al*., 2018). The samples were collected, filtered with 0.45 µm filter paper, and then analyzed for ammonia nitrogen and chemical oxygen demand (COD), which are the major contaminants in the leachate. Standard method No. 5220 A (closed reflux method) was employed to determine the COD of every filtered sample (Goff *et al*., 2014).

The samples were dropped into digestion glass vials containing the digestion solution, with a blank reference serving as a control, and prior to introducing the mixture into a preheated COD digester, it was thoroughly homogenized and maintained for two hours at 150 °C. The vials were brought to ambient temperature and COD concentration levels were evaluated using a spectrophotometer at 620 nm. The concentration of COD was determined by comparing the absorbance difference between the digested and blank samples. The NH_3-N removal evaluation was conducted utilising USEPA Nessler method No. 8038 (Ghafari *et al*., 2009). The experiment was conducted using the DR6000 (HACH) device, the nitrogen-ammonia reagent set, 25 ml of deionized water, a 1 mL sterilized pipette, a 25 mL measuring cylinder, a glass stopper, as well as two sample cells. One of the graduated cylinders was filled with deionized water to the 25 mL mark, and the other graduated cylinder was filled with the sample solution to the 25 mL mark. Each cylinder received three drops of the mineral stabiliser. After placing the stopper on the cylinders, they were repeatedly inverted to ensure complete mixing. Before each cylinder is sealed, three equal droplets of a polyvinyl alcohol dispersing agent are added. The cylinder was then vigorously shaken to achieve full mixing. 1 mL of Nessler reactant was pipetted into each mixing cylinder using a pipette, which was then sealed and repeatedly inverted. The reaction time for both the sample and blank solutions was 1 minute. For the blank and sample solutions, sample cells were designated. Separate 10 mL volumes were placed from each cylinder into each sample cell, and the outer surface was wiped clean. The blank prepared sample was also used to zero out the DR6000, after which the remaining sample cell was inserted into the cuvette holder. On the display panel, the NH_3-N concentration was shown. The percentage of COD and NH_3-N removal was derived from the experimental results using Eqn. 1.

$$\%Removal = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \qquad (1)$$

Ci and *Cf* represent the initial and final COD (mg/L) or NH_3-N (mg/L) concentrations, respectively.

IV. MIXTURE DESIGN

The experimental mixture design was used to examine the influence of the four factor variables on the response variables COD and ammonia. The Design-Expert software (version 7, Stat-Ease Inc., Minneapolis, MN, USA) generated 16 runs, of which 10 were varied and 6 had been replicas. In accordance with the D-optimal methodology, the effect of the variables (factors) on COD as well as ammonia reduction was assessed, and the optimal adsorbent mixture was derived. As shown in Table 2, The optimal factor mix for optimisation was established based on the relative impact of each factor. Using the D- optimal criterion, a number of candidate points in the design were chosen. The codes, scales, and thresholds of the various independent variables are represented in Table 1. In D-optimal design, factor proportions Xj range between lower (Lj) and upper (Uj) constraints, the basic concept of D-optimal design parameters can be expressed as Eqn. 2.

$$Xj = 1 \; and \; Li \leq Xj \leq Uj \qquad (2)$$

Table 1: Independent variable codes, ranges, and levels for the design

Component,X_j	Code	Low,L_j	High,U_j
Feldspar (FE)	A	5	25
Zeolite (ZE)	B	5	25
AC	C	5	25
CS	D	5	25

Eqn. 3 represents the quadratic model equation for the mix component of the response Y derived for predicting optimal conditions and identifying which variables or interactions do have significant impact on the response.

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i . x_i + \sum_{i=1}^{k} \beta_{ii} . x_i^2 + \sum_{t_i=j}^{k} \sum_{j}^{k} \beta_{ij} . x_i . x_j + .. + e \qquad (3)$$

For which Y represents the anticipated response, $\beta o$is the intercept coefficient, $\beta i$is a linear coefficient βii consist of the quadratic coefficient βij are the interaction terms and k is the various factors considered and optimised in the experiment and e is a random error [Ghafari *et al*., 2009].

Analysis of variance (ANOVA) was utilised to establish the statistical significance between the independent variables. Only the significant ($p < 0.05$) independent variables were included in the reduced model, while the non significant ($p > 0.05$) independent variables have been eliminated. R^2 should be at least 0.80 for the model to be well-fitting [Ghafari, *et al*, 2009].

V. RESULTS AND DISCUSSION

A. Contac tangle

According to the contact measurements depicted in Figures 2 and 3, the contact angles for zeolite and feldspar were 12.60° as well as 8.10°, respectively. Hydrophilic materials typically have contact angles lower than 30 degrees. The result shows that both media are hydrophilic. Similarly, the contact angles of activated carbon and cockle shells are 98.70° and 97.4°, respectively (Figures 4 and 5). The findings also indicate that the adsorbents are hydrophobic (Adeleke *et al.*, 2017).

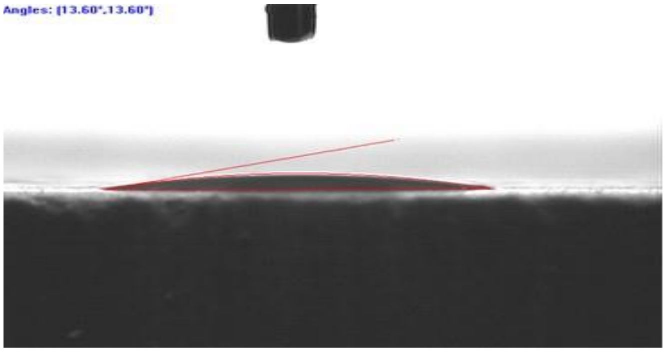

Figure 2: Zeolite contact angle

Figure 3: Feldspar contact angle

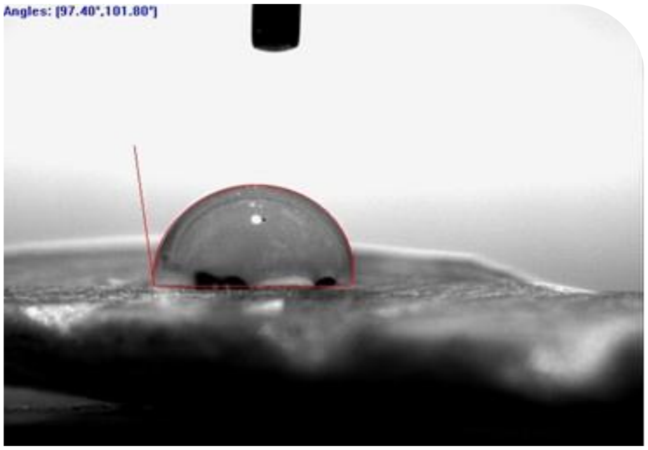

Figure 4: Cockle shells

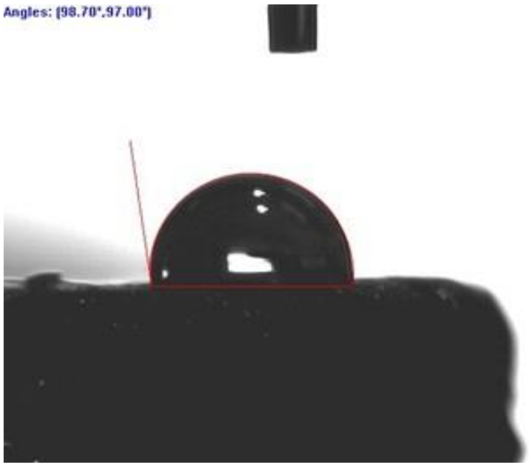

Figure 5: Activated carbon contact angle

B. Fourier transform infrared spectroscopy(FTIR)

Figure 6 depicts the FTIR of four mixed media in their pre-treatment and post-treatment states. The illustration depicts the incidence of hydroxyl's broad bending vibrations between 3000 as well as 3500 wave numbers. Additionally, their polarities exhibited partial opposite charges. Amides are associated with the presence of the stretch between 1500 and 2000 wave number. Given the treatment and the adsorption of various pollutants, the molecules appear to have transformed into an aromatic molecule with a 1473.80 wave number and an additional bending (Rafiee *et al*., 2012). These molecules, which are polar groups, may offer a charged surface for electrostatic interactions with the adsorbent. The spectra also display a Si-O-Si or O-Si-O bond vibration pattern between 1200 and 450 (Foo and Hameed, 2009).

C. Leachate

The characterisation of the raw leachate sample has shown that the COD and ammonia concentrations were 1763 and 573 mg/L, respectively; whereas the BOD5/COD ratio was 0.09, indicating that the leachate was stabilised (Daud *et al*., 2017).

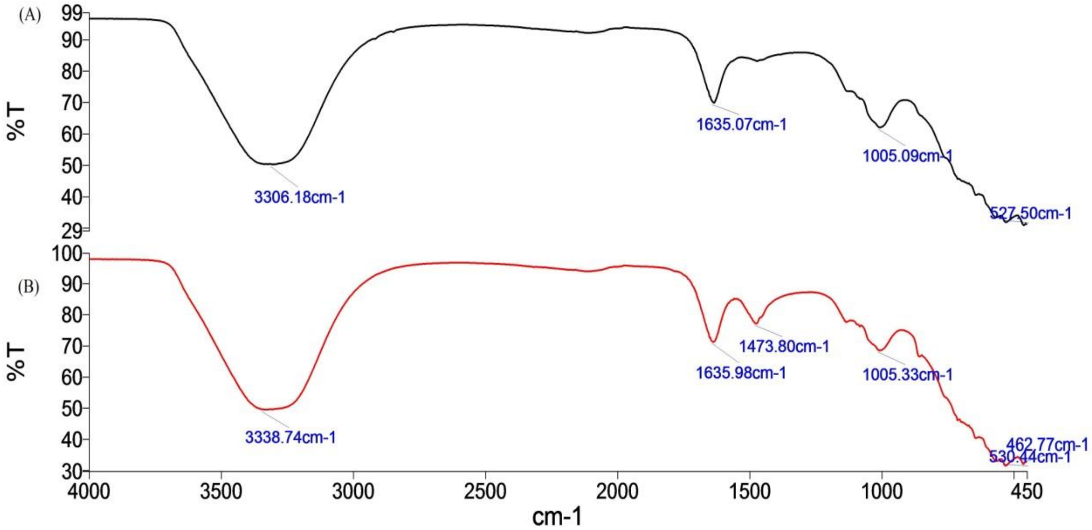

Figure 6: FTIR spectra (A) before treatment (B) after treatment

D. Statistical analysis

The relationship between the four variable media mixtures (FE, ZE, AC, and CS) and the two important process responses (COD and ammonia removal efficiencies) for the optimum mixing process was analyzed using D-optimal mixture design. As a result of each experimental design, the reduction percentage in the presented mixture was analyzed. The range of actual as well as observed NH_3-N reduction percentages was 49.21 to 70.95 percent based on Table 2's real components, and from 49.45 to 70.92 percent based on Table 2's actual components. Furthermore, for actual versus observed COD removal, the results were 58.87 percent to 82.06 percent and 58.56 percent to 82.26 percent, respectively. Using the technique of multi-regression analysis, the tool presented a linear model of the parameters, with models chosen based on polynomials of the highest order. According to Eqns. 4 and 5, the resultant model and regression coefficients for both the reductions of COD (YCOD) and NH_3-N (YNH_3N) were expressed in the form of real components:

$$YCOD = 12.68*A + 17.71*B+30.47*C+19.53*D+275.21*A*B+85.95*A*C+80.64*A*D+59.27*B*C+158.84*B*D+170.77*C*D \quad (4)$$

$$YNH3-N=12.01*A+72.47*B+52.95*C-11.02*D+164.19*A*B+58.29*A*C+137.97*A*D-163.03*B*C+95.27*B*D+255.56*C*D \quad (5)$$

The least square method was used to determine the model's regression coefficients and their interaction with the model's factors. With a P-value < 0.05 and a confidence interval of 95 percent, then each independent parameter was considered to have a significant effect. Table 3 displays the F-value of the COD model to be 165.33, while the F-value of the NH_3-N model was 278.07. Based on statistical significance, the small probability P-value (<0.0001) suggested that the derived models adequately represented the experimental data presented in Table 2. The model with the greater value of the determination coefficient, R^2 (0.9976 for COD and 0.9976 for NH_3-N) validates the derived models.

Table 2: Variables real mixture design matrix and their responses

Standard Order	A: FE	B: ZE	C:AC	D:CS	Response 1 NH_3-N (%)		Response 2 COD (%)	
					Actual	Predicted	Actual	Predicted
1	0.125	0.125	0.125	0.625	49.75	49.45	60.49	60.03
2	0.625	0.125	0.125	0.125	52.93	52.92	58.87	58.56
3	0.331	0.419	0.125	0.125	70.95	70.92	82.06	82.26
4	0.457	0.125	0.293	0.125	58.48	58.65	65.40	65.80
5	0.125	0.410	0.125	0.340	65.22	65.08	75.42	75.75
6	0.125	0.125	0.625	0.125	60.86	60.27	65.67	65.84
7	0.425	0.125	0.125	0.325	59.89	59.79	63.61	63.98
8	0.125	0.125	0.303	0.447	67.83	67.94	71.46	71.87
9	0.125	0.411	0.339	0.125	53.94	53.95	77.35	78.27
10	0.125	0.625	0.125	0.125	66.61	66.63	70.75	70.54
11	0.223	0.176	0.390	0.211	65.75	65.18	75.45	74.89
12	0.254	0.249	0.199	0.297	65.75	66.28	78.05	77.21
13	0.457	0.255	0.125	0.163	65.62	65.52	75.38	75.47
14	0.125	0.125	0.625	0.125	59.58	60.27	65.97	65.84
15	0.125	0.125	0.125	0.625	49.21	49.45	59.74	60.03
16	0.125	0.411	0.339	0.125	53.91	53.95	78.94	78.27

Table 3: ANOVA for D-optimal mixture Model of COD and NH_3-N removal by media.

	Sum of Squares		Mean Square		F - Value		P-value	
Source	**NH_3-N**	**COD**	**NH_3-N**	**COD**	**NH_3-N**	**COD**	**NH_3-N**	**COD**
Model	694.25	846.73	77.14	94.08	278.07	165.33	< 0.0001	< 0.0001
Linear Mixture	115.32	391.84	38.44	130.61	138.57	229.53	< 0.0001	< 0.0001
AB	89.35	251.01	89.35	251.01	322.08	441.09	< 0.0001	< 0.0001
AC	8.70	18.91	8.70	18.91	31.36	33.23	0.0014	0.0012
AD	54.97	18.78	54.97	18.78	198.14	33.00	< 0.0001	0.0012
BC	112.62	107.48	112.62	107.48	405.96	188.88	< 0.0001	< 0.0001
BD	27.14	75.45	27.14	75.45	97.84	132.58	< 0.0001	< 0.0001
CD	189.62	84.66	189.62	84.66	683.55	148.78	< 0.0001	< 0.0001
Residual	1.66	3.41	0.28	0.57				
Lack of Fit	0.70	1.82	0.23	0.61	0.72	1.15	0.6015	0.4565
Pure Error	0.97	1.59	0.32	0.53	77.14	165.33	< 0.0001	< 0.0001

Table 4: ANOVA for RSM using mixed media

	NH_3-N	COD
Std. Dev.	0.53	0.75
Mean	60.39	70.29
C.V. %	0.87	1.07
R-Squared	0.9976	0.9960
Adj R-Squared	0.9940	0.9900
Pred R-Squared	0.9839	0.8972
Adeq Precision	51.560	39.742

The model's root-mean-square deviation and variation coefficient were considerably smaller and acceptable (see Table 4). The high adjusted R^2 values of 0.9980 for COD and 0.9940 for NH_3-N indicated that the models are indeed adequate for predicting the removal under various operational parameters. The "Lack of Fit F-value" of 0.4565 (COD removal) and 0.6015 (NH_3-N removal) demonstrated the validity of the models, indicating that the Lack of Fit was non - significant and the models reliably predicted the removal. FE, ZE, AC, and CS were found to have a positive and positive and significant linear effects on the decrease of COD.

The FE, ZE, and AC constituents contribute significantly to the NH_3-N removal. The interaction BC between activated carbon and zeolite has a negative impact. Consequently, the adsorption decreases as the amount of activated carbon relative to zeolite increases, depending on the surface nature of the adsorbent. Moreover, significant model terms AB, AC, AD, BC, BD, and CD were also obtained, given the factor component interactions. Table 3 indicates that all constituent terms are significant. It is detectable when P-values are less than 0.05, indicating a significant factor relationship with a 95 percent level of confidence. Additionally, significant terms have a higher F-value. The linear CD term has the strongest influence on NH_3-N removal (F-value = 683.55), accompanied by the linear BC term (F-value = 405.96), then linear AB term (F-value = 322.08), and linear AD term (F-value = 198.14), the BD term (F-value = 97.84), as well as the linear AC term (F-value = 31.36). The term with the highest significance for COD is AB (F-value = 441.09), accompanied by BC, CD, BD, AC, and AD with F-values of 188.88, 148.78, 132.58, 33.23, and 33.00, respectively.

The interaction between the independent variable factors is visualized using D-optimal surface or contour plots. Figures 7 and 8 depict the 3-D response surface graphs depicting the reduction of COD as well as NH_3-N parameters, as determined by the RSM, as a function of mixture components. Clearly, the highest values for all parameters are located at the surface. The process removed more COD than NH_3-N, according to both figures.

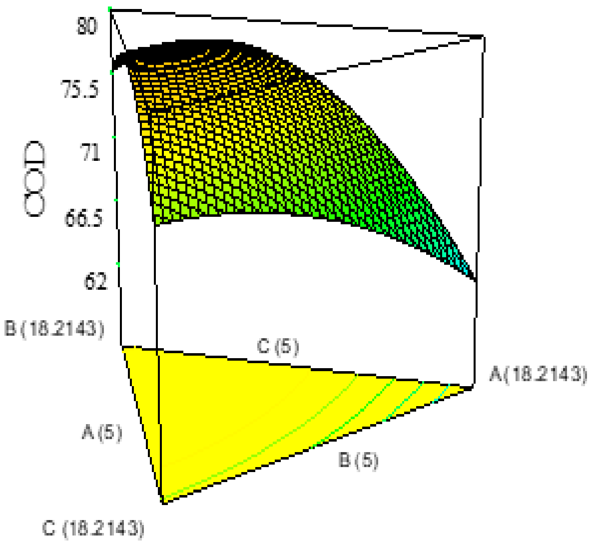

Figure 7: Response surface diagram for COD reduction with mixed constituent media

Figures 9 and 10 depict the graph of the observed (predicted) and actual COD and ammonia removal values, respectively. The predicted results were being evenly dispersed. By analyzing the interactive effects between independent variables inside of optimisation boundaries, optimal mixture components have been investigated. Consequently, the proportions recommended for the mixture are AC (6 mg/L), CS (12.0 mg/L), FE (12.5 mg/L), and ZE (9.72 mg/L) (see Figure 11).

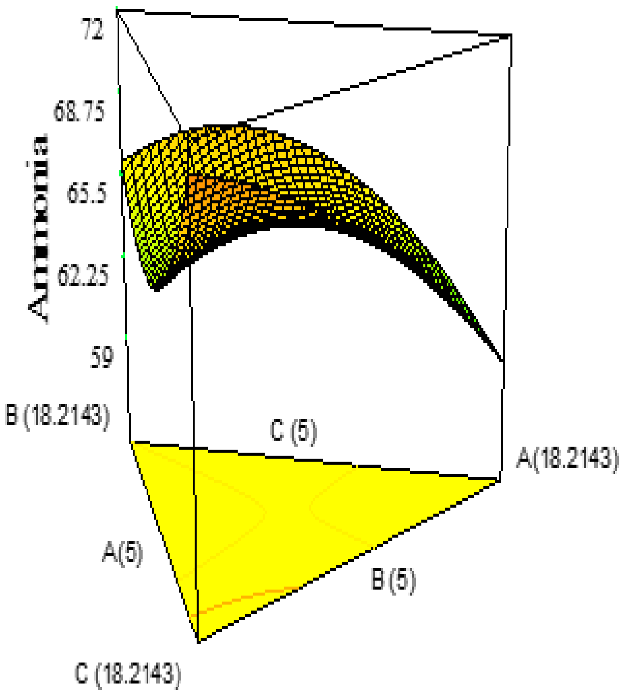

Figure 8: Response surface chart for NH_3-N reduction utilizing mixed constituent media.

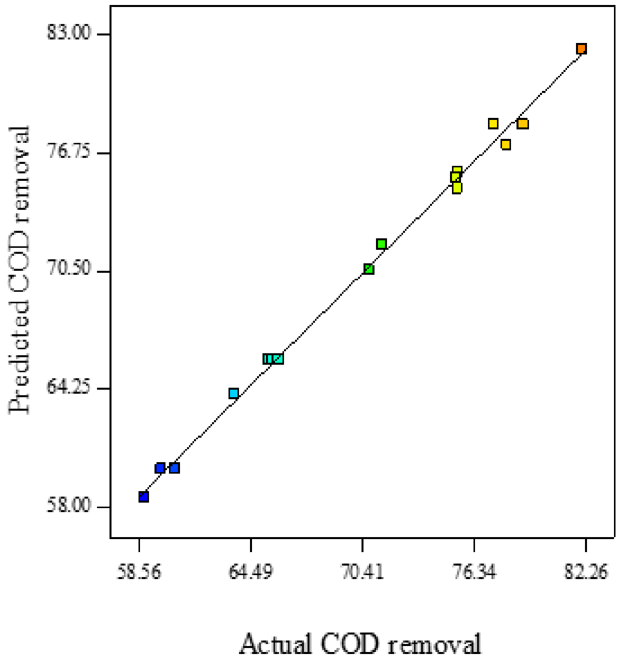

Figure 9: Plot of predicted versus experimental COD removal by mixed media.

As shown in Figure 11, the ideal criterion for COD and NH_3-N removal is indicated by a desirability attribute of 0.886. The optimal COD and as well as ammonia removal values, according to the optimal mixture components, were also 79.65 and 66.13 percent, respectively.

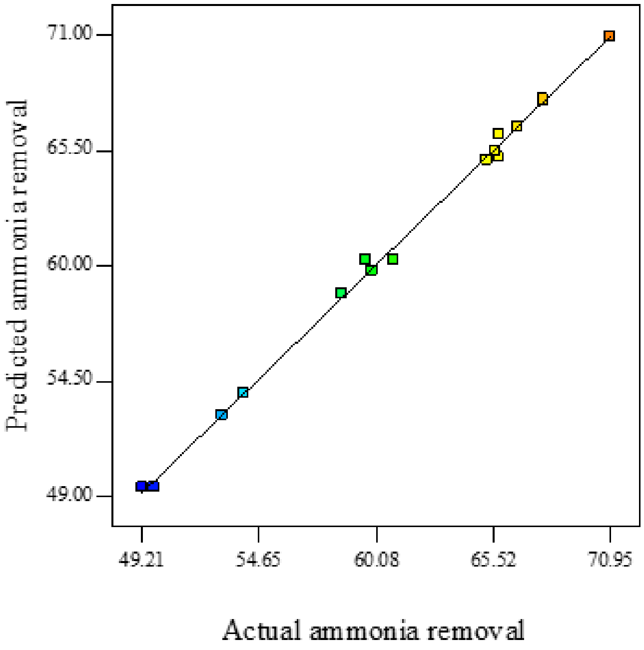

Figure 10: Graph of predicted versus measured NH_3-N removal by mixed media.

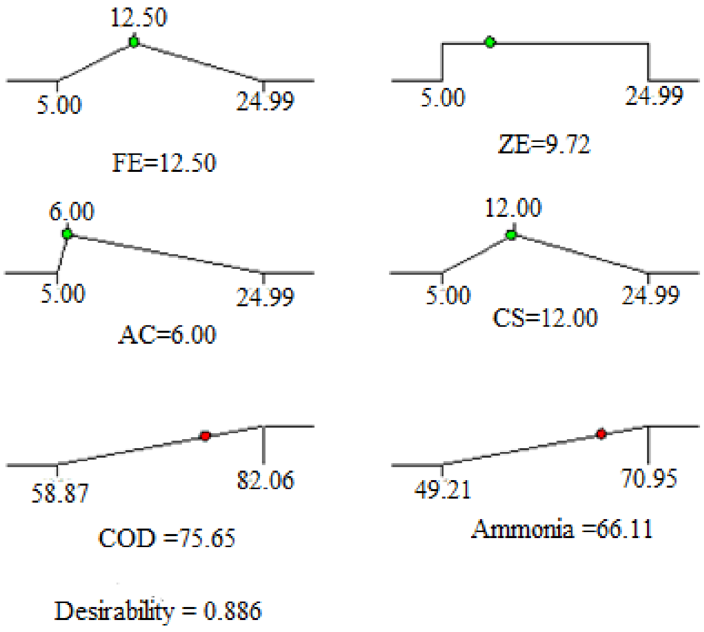

Figure 11: Solution based on numerical optimisation for COD and NH_3-N removal using mixed media.

VI. CONCLUSION

The present study revealed the effectiveness of the D-optimal mixture experimental design as an approach for carrying out the optimisation of media mixture components by combining the independent variables such as feldspar, zeolite, activated carbon, and cockle shells. The optimum linear mixture of the components was established. According to the data obtained from the analysis, mixture amounts of 12.5, 9.72, 6, and 11.79 mg/L for FE, ZE, AC, and CS, respectively, are suggested to be the optimum mixture combinations to achieve

COD (79.65%) and NH_3-N (66.13%) removal. The accuracy of the model is indicated by high F-values of 278.07 and 165.33 for NH_3-N and COD, respectively. Moreover, a low P-value (<0.0001) for NH_3-N and COD indicates the model significance. The predicted R-squared is in close agreement with the adjusted R-squared. The D-optimal design has simultaneously facilitated an investigation into multiple variables and an analysis of the effects of their interactions.

AUTHOR CONTRIBUTIONS

M. H. Abubakar: Performed the experiments as well as drafted the manuscript. **Z. Daud and H. Abba:** Conceptualization, Writing, Reviewing, and Editing.

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