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Comprehensive analysis of reclamation of spent lubricating oil using green solvent: RSM and ANN approach

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Waste lubricating oil (WLO) is the most significant liquid hazardous waste, and indiscriminate disposal of waste lubricating oil creates a high risk to the environment and ecology. Present investigation emphasizes the re-refining of used automobile engine oil using the extraction-flocculation approach to reduce environmental hazards and convert the waste to energy. The extraction-flocculation process was modeled and optimized using response surface methodology (RSM), artificial neural network (ANN), and genetic algorithm (GA). The present study assessed parametric effects of refining time, refining temperature, solvent to waste oil ratio, and flocculant dosage. Experimental findings showed that the percentage of yield of recovered oil is to the tune of 86.13%. With the Central Composite Design approach, the maximum percentage of extracted oil is 85.95%, evaluated with 80 minutes of refining time, 50.17 °C refining temperature, 7:1 solvent to waste oil ratio and flocculant dosage of 3 g/kg of solvent and 86.71% with 79.97 minutes refining time, 55.53 °C refining temperature, 4.89:1 g/g solvent to waste oil ratio, 2.99 g/kg of flocculant concentration with Artificial Neural Network. A comparison shows that the ANN gives better results than the CCD approach. Physico-chemical properties of the recovered lube oil are comparable with the properties of fresh lubricating oil.

Keywords: modelling, optimization, extraction-flocculation, artificial neural network, genetic algorithm

1. INTRODUCTION

Lubricating oil plays a major role in achieving effective performance (Usman et al., 2021). Lubricating oil is a viscous liquid used to lubricate machine moving parts, reduce friction, protect against wear, and remove impurities from the engine. It also acts as a cleaning and corrosion-preventing agent (Abro et al., 2013; Armioni and Raţiu, 2020; Udonne, 2011). During long-term operation, lubricants are generally prone to degradation and contamination from various sources (Mortier et al., 2010). Their physical and chemical characteristics can be severely damaged by contamination during prolonged uses. The loss of essential characteristics critical to a system's useful service life can lead to inefficient system performance

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and accelerated degradation. With globalization on the upswing, the number of industries and vehicles are increasing day by day, churning out a large volume of waste lubricating oil (Kamal and Khan, 2009). The indiscriminate disposal of waste lubricating oil accelerates the environmental pollution problem (soil, air, and water) and human health risk (Pinheiro et al., 2018a; Speight and Exall, 2014). Regeneration/re-refining draws significant attention in light of mitigating a substantial antagonistic environmental burden of this hazardous waste (Pinheiro et al., 2018b). Over the past few decades, various researchers have investigated several reclamation techniques of used oil like acid-clay, vacuum distillation, hydro-treating, and combined technologies. Keeping all the limitations for regeneration of waste oil, solvent extraction with the integration of flocculation has emerged as a most promising eco-friendly technology in re-refining due to its numerous advantages such as (i) it is the most efficient process for separating the sludge particles from used oil, (ii) reduces oil losses from the sludge phase, (iii) higher yield of finished reclaimed oil, (iv) formation of appreciably less by-product sludge and (v) obtaining more oxidation resistance reclaimed oil (Mohammed et al., 2013; Osman et al., 2018). However, it is essential to optimize the operating parameters of extraction-flocculation technology to get the highest yield of standard quality recovered base oil. Various optimization techniques such as response surface methodology (RSM) and artificial neural network (ANN) played a significant role.

The limits of the response surface approach arise from the fact that there are only a few built-in models to which experimental data must be fitted. With the exception of cubic and quadratic functions, RSM techniques cannot handle vast amounts of data and non-linearity in functions. Whereas the artificial neural network can be effectively utilized to address the aforementioned flaw, it can make the optimization process more accurate and authentic to the actual experimental system (Shojaeimehr et al., 2014). In the current investigation, a comprehensive multi-regression analysis between Response Surface Methodology using CCD and Artificial Neural Network with the integration of Genetic Algorithm (GA) approach of optimization for maximizing the percentage recovery of re-refined waste lubricating oil using cleaner technology approach of extraction-flocculation has been attempted, which is not yet reported in the literature. The four parameters such as refining time (minutes), refining temperature (°C), solvent to waste oil ratio (wt./wt.), and flocculant dosage (g/kg of solvent) as independent variables were chosen which can have an influence on the percentage yield of recovered oil (dependent variable) in the extraction flocculation process. This study elaborates on the process of refining of waste lubricating oil by eco-friendly extraction flocculation method (using butan–1–ol as a solvent and potassium hydroxide as a flocculant and fuller's earth as an adsorbent) to maximize the percentage yield of regenerated oil with modeling and optimization using a comparative approach of two simulation techniques (RSM and ANN) to conserve our natural resources and increase the economy of the refined product from waste.

2. MATERIALS AND METHODS

2.1. Materials

Refining waste lubricating oil was done using butan–1–ol (C_4H_9OH) as the solvent, potassium hydroxide (KOH) as flocculant, and fuller's earth as an adsorbent. The solvent was provided by Loba Chemie, Mumbai, the flocculant and adsorbent were provided by EMPARTA, Mumbai. The waste lubricating oil was gathered from the automotive garage at NIT, Durgapur.

2.2. Experimental procedure

The physico-chemical properties of fresh and used lubricating oil like kinematic viscosity (ASTM D-445), pour point (ASTM D-97), specific gravity (ASTM D-1298), viscosity index (ASTM D2270), flash point (ASTM D-93), total acid number (ASTM D-664) and ash content (ASTM D-874) were determined. The waste oil is filtered before being heated in a graduated beaker on a hot plate magnetic stirrer to

a temperature range from 120 °C to 130 °C to remove light hydrocarbon and water, which are both unwanted components in the formulation of fresh base oil. Following the dehydration process, several combinations of pre-treated used lubricating oil with solvent and flocculating agent (1–butanol as solvent and KOH as a flocculant) are agitated at different process conditions, as indicated in Table 1. Ultra-centrifugation (7500 rpm) was used to separate the sludge (Sigma 3k30 lab centrifuge, USA). After sludge

Table 1. Design of experiment with actual and predicted responses

Std	Run	Refining time (min)	Refining temperature (°C)	Solvent: waste oil (g/g)	Flocculant dosage (g/kg of solvent)	Actual response (Yield %)	Predicted by RSM (%)	Predicted by ANN (%)
28	1	55	40	4	2	86.00	80.16	80.52
18	2	105	40	4	2	84.62	84.37	84.62
14	3	80	20	7	3	79.50	80.31	80.33
19	4	55	20	4	2	66.20	65.62	66.20
9	5	30	20	1	3	80.00	80.19	80.00
15	6	30	60	7	3	81.72	81.84	81.72
5	7	30	20	7	1	72.68	72.96	72.68
23	8	55	40	4	0	67.78	67.79	67.78
20	9	55	80	4	2	73.28	73.62	73.28
26	10	55	40	4	2	79.15	80.16	80.52
21	11	55	40	2	2	79.49	80.37	79.49
11	12	30	60	1	3	85.78	85.75	85.78
2	13	80	20	1	1	71.07	71.26	71.07
6	14	80	20	7	1	77.52	77.48	77.52
24	15	55	40	4	4	81.37	81.13	81.37
8	16	80	60	7	1	79.80	79.92	79.80
17	17	5	40	4	2	81.86	81.87	81.86
12	18	80	60	1	3	83.70	83.73	83.70
4	19	80	60	1	1	71.11	71.08	71.54
13	20	30	20	7	3	73.69	73.65	73.69
22	21	55	40	10	2	87.01	86.68	87.01
29	23	55	40	4	2	79.15	80.16	80.52
27	24	55	40	4	2	79.15	80.16	80.52
10	25	80	20	1	3	81.60	81.47	81.60
25	26	55	40	4	2	79.15	80.16	80.52
16	27	80	60	7	3	85.41	85.20	85.41
30	28	55	40	4	2	79.15	80.16	80.52
3	29	30	60	1	1	75.73	75.23	75.00
7	30	30	60	7	1	78.64	78.70	78.64

separation, the solvent-oil mixture was distilled in an ASTM distillation setup (Petroleum Instruments Private Limited, India) to recover the solvent. The oil that has been recovered has been weighed. Due to its dark tint, distilled oil did not match the color specifications before adsorption. 35 wt% adsorbent was then added to the recovered oil followed by continuous heating with an increase in temperature from 70 °C to 100 °C, as shown in Fig. 1. Oil containing adsorbent was also stirred (370–470 rpm) continuously throughout the adsorption process. The adsorption time ranged from 60 to 150 minutes. After mixing, centrifugation was done to segregate the recovered oil from the spent adsorbent. The percentage recovery of lubricating oil can be determined by Eq. (1). The physico-chemical characteristics of the virgin oil, waste lubricating oil, and refined lubricating oil are shown in Table 2.

$$\text{Percentage yield of recovered oil} = \frac{\text{weight of recovered oil}}{\text{weight of used oil}} \cdot 100 \tag{1}$$

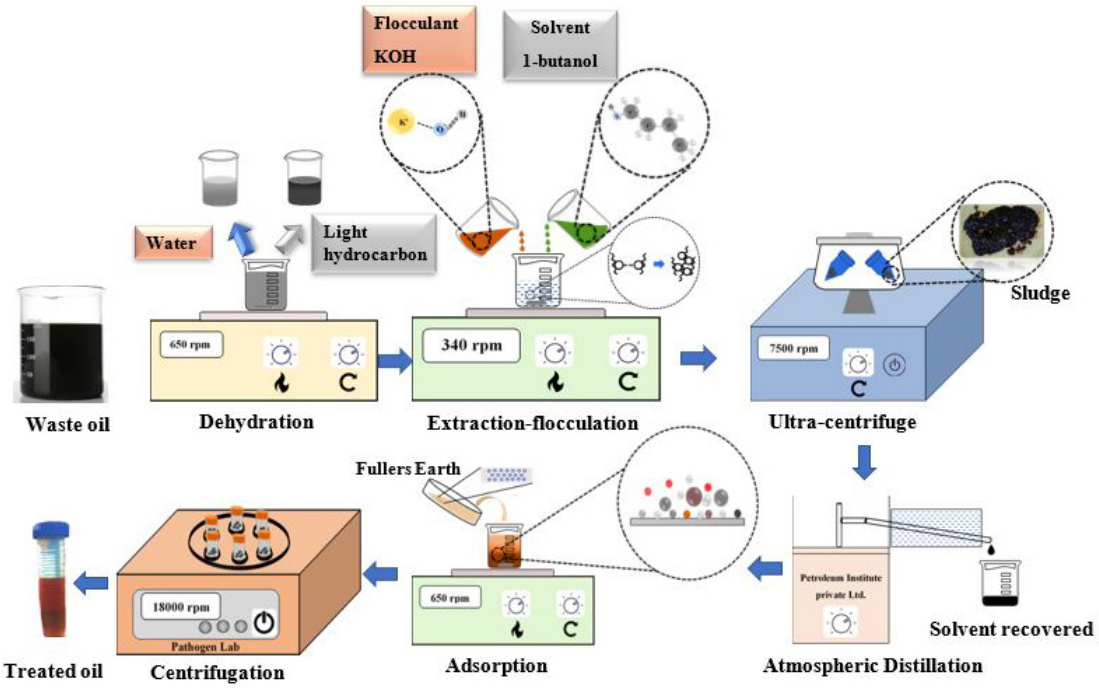

Fig. 1. Process flow diagram of extraction-flocculation process

Table 2. Properties of the fresh, used and recovered oil

Properties	Virgin oil	Waste oil	Refined lubricating oil
Appearance	Light pink	Black opaque	Reddish Brown
Kinematic Viscosity, @ 40 °C	164.67	115.38	141
Kinematic Viscosity, @ 100 °C	18.75	14.30	17.75
Viscosity index	183.60	118.10	184
Sp.gr	0.85	0.887	0.85
Flashpoint (°C)	240	180	230
Pour Point (°C)	–35	–27	–25
TAN (mg KOH/g)	–	2	0.11
Ash Content	0.3	0.95	0.30

2.3. Selection of solvent and flocculant

Various criteria were considered when choosing a solvent. Contaminants should dissolve more quickly in the heavier solvent, according to Hildebrand's solubility theory (Yang et al., 2013). Heavy solvent solubility characteristics are similar to impurity particle solubility parameters. Impurities are not removed from the solution by using stronger solvents. Moreover, in Burrell's solvent classification, alcohol has a high capacity to form hydrogen bonds and is a better solvent. In this case, the solvents used were alcohol with a high capacity to form a hydrogen bond. The solvent selected should have carbon atoms between 3 to 5 in their molecule because alcohol and ketones with lower molecular weight (less than 3 carbon atoms) cannot dissolve base oil, and those with a longer chain (more than 5 carbon atoms) may prevent aggregation of waste oil impurities. In the current investigation, the carbon atom of the solvent is in the range between 3 to 5 (Rincón et al., 2003, 2005). Polarizability can be measured by the dipole moment of the solvent. The dipole moment of 1–butanol is 1.60D (McClellan, 1963; Pinheiro et al., 2018a) which is similar to that of the lubricating oil (1.23–1.64D) that is essential for the support of the solvent to extract base oil from waste lubricating oil. The solubility parameter of mineral, synthetic, and semi-synthetic base oil is determined by (Voelkel and Fall, 2014). The values varied from 16.2 to 19.7 $MPa^{1/2}$. The lower the solubility parameter difference between base oil and solvent, the higher will be oil miscibility. In this particular investigation, the value of the solubility parameter difference was on the lower side $(5.9\ J/cm^3)^{0.5}$ and that is why in the present study 1–butanol has been taken as the solvent.

The addition of an alkaline substance to the solvent, such as potassium hydroxide, improves flocculation and boosts impurity removal from waste oil. Since the quick ionization, potassium hydroxide is the most excellent flocculating agent because it forms a stronger nucleophile, OH^- ion that destabilizes the particle (Diphare and Muzenda, 2013).

2.4. Modelling using response surface methodology (RSM) and artificial neural network (ANN)

Response Surface Methodology is a performance modeling technique used in experimental design, new process development, and product design and formulation enhancement. RSM is especially important when many variables influence the system's characteristics (Myers et al., 2002). The Response Surface Methodology is investigated using the Central Composite Design technique, which comprises a simulation of the interaction between quantitative and process variables. The inclusive research findings are mainly subjected to figures of parameters to be investigated, and their relation with axial, factorial, and replicated experiments is reflected in Eq. (2) (Chen et al., 2013; Gottipati and Mishra, 2010).

$$N = 2^n + 2n + n_c = 2^4 + 2 \cdot 4 + 6 = 30 \tag{2}$$

where, n represents the number of independent factors, and n_c depicts the number of replicates. The total number of runs (N) can be calculated using Eq. (2) for four independent factors. In the present investigation, the central composite design method is employed to model the reclamation of spent engine oil by eco-friendly environmentally sustainable extraction flocculation approach implicating the process constraints viz. Refining time (A), Refining temperature (B), solvent to waste oil ratio (C), and flocculant concentration (D). The developed experimental matrix by Design Expert 11 software (State-Ease, Inc., Minneapolis, USA) includes 30 trial runs consisting of sixteen factorial points, eight axial points, and six replicate points to maximize the percentage of yield recovered oil which have been exemplified in Table 1. In the CCD method, factorial points are coded as –1 (low) and +1 (high). Response surface methodology can be used to create an empirical model equation in lieu of the relationship between the process response and individual independent process variables. Central Composite Design works only with the coded value for actual variables, and the transformations of these coded values can be accepted, as shown in Eq. (3).

$$X_a = \frac{X_{ac} - X_{avg}}{(X_h - X_l)/2} \tag{3}$$

where, X_{ac} represents the actual value of the i-th factor in actual units, X_{avg} represents the average of the low and high values for the i-th factors. X_h and X_l interpret the high and low values for the i-th factors. An empirical quadratic equation was modeled to show the functional association describing the relationship between the independent variables and the response as shown in Eq. (4) consisting of linear, quadratic, and cross-product terms.

$$\eta = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j + e_i \tag{4}$$

where, η is the response, β_0 is the constant coefficient, β_i is a linear coefficient, β_{ii} is a quadratic coefficient, β_{ij} is an interaction coefficient of second-order term, x_i and x_j represent coded values of independent variables, and e_i is an error. Artificial neural network (ANN) is one of the frequently used data-driven modeling techniques used in different fields of science and engineering. It uses Multi-Layer Perceptron (MLP), a feed-forward neural network in which neurons are often arranged into three subdomains, i.e., one input and output layer and one extra hidden layer. Each layer consists of neuron(s), e.g., an input layer, the input variables (here refining time, refining temperature, solvent to waste oil ratio, flocculant dosage) are neurons, the output layer consists of the output variable (yield %), and the hidden layer is in the middle of two consisting of hidden neurons, the number of which the user fixes. The input and hidden layer and the hidden layer and output layer are connected with two types of parameters called weights and biases, which pass through a pre-defined function called the transfer function. By iterative process, the values of weights and biases are calculated and the process is called training. Several training algorithms are available in the literature. Details of ANN can be found in several published articles (Al-Shathr et al., 2021; Khoshroo et al., 2018; Sevinc and Hazar, 2020). In this study, by trial-and-error approach with the objective of maximizing correlation coefficient (R^2) and minimizing root-mean-square error (RMSE), Levenberg-Marquardt backpropagation (trainlm) training algorithm was chosen, the optimum number of neurons was selected to be 10 (Fig. 2), and again by the same method, a log-sigmoid function was

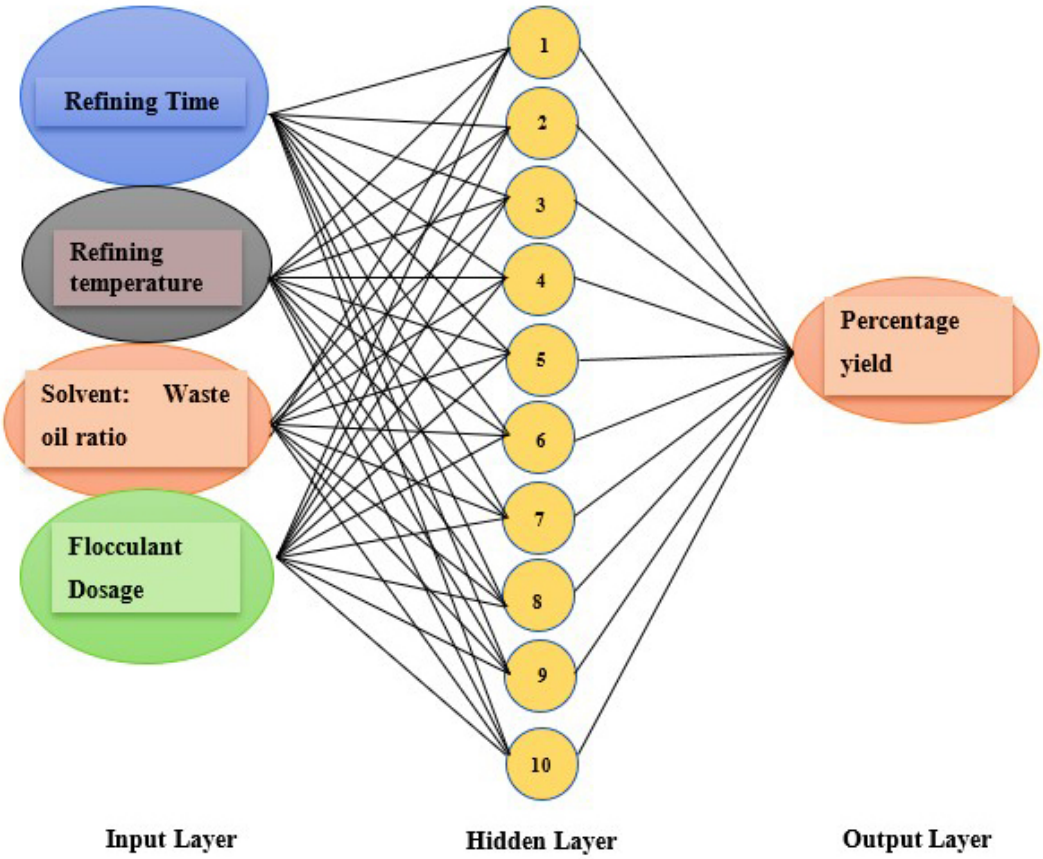

Fig. 2. ANN architecture

considered to be the transfer function for making the connection between the input layer and hidden layer. One of the issues of any data-driven modelling is overfitting. If the model complexity increases, the model tends to overfit and becomes invalid on unseen dataset. In this study, to avoid overfitting early stopping criteria were involved. Three errors viz. training error, test error and validation error are simultaneously evaluated. In the iterative process, increasing model complexity decreases the training error and test error but up to a certain point, the validation error starts increasing and at that point the iteration is stopped where validation error is minimum. After building up the model with the help of an artificial neural network, it is imperative to optimize the process parameters to maximize the percentage recovery of lubricating oil. In light of the global optimization approach, the well adept technique is the optimization through genetic algorithm. MATLAB 2019a software was used for this purpose. The parameters related to GA selected for this study are fitness function: polynomial fit, population 700, crossover 0.667, scattered mutation, generation 200, and iteration 200.

2.5. Characterization

2.5.1. Fourier transform Infrared Spectrophotometry

The molecular fingerprint of the fresh, used, and recovered lubricating oil was determined using Fourier transform infrared spectroscopy. The functional groups and their structure in fresh oil, used oil, and recovered lubricating oil were determined using a Spectrum Two, Perkin Elmer Infrared spectrophotometer (Perkin Elmer, USA) with a resolution of 0.5 cm^{-1} and a data interval of 1 cm^{-1}. A small quantity of 1 ml of each sample, i.e., fresh, used, and recovered base oil, was deposited in a liquid sample holder using a Tarson 1000L micropipette (Tarson, Kolkata) for FTIR characterization. All of the spectra were acquired using Perkin Elmer spectrum 10 software and were recorded in the 4000 cm^{-1} to 500 cm^{-1} region.

3. RESULTS AND DISCUSSIONS

3.1. Parametric effect on the percentage of yield

3.1.1. Influence of refining time, refining temperature, solvent to waste oil ratio and flocculant dosage on percentage yield

The influence of refining time for enhancing the percentage yield of regenerated base oil was found out by varying refining time in the range of 30 minutes to 80 minutes when other parameters such as refining temperature (50 °C), solvent to waste oil ratio (5:1), and flocculant dosage (2.99 g/kg of solvent) were kept constant. Initially, when the refining time is 30 minutes, the percentage recovery of regenerated oil is 79.28%, as illustrated by Fig. 3(a1). With an increment of refining time, the percentage yield of regenerated oil increases to 86%. Further increase in refining time leads to attaining equilibrium, and after that, yield percentage will not increase anymore. An increase in percentage yield with an increase in refining time may be attributed to the fact that it should be long enough to allow the solvent to dissolve the base oil contained in the waste oil, as well as it will allow the additives and impurities to be rejected from the solution by allowing their aggregation to particle sizes large enough to separate from the liquid phase via sedimentation (Diphare and Muzenda, 2013). The effect of refining temperature on yield% of refined lubricating oil has been illustrated in Fig. 3(a2). Temperature plays a significant role in affecting the solubility of both base oil and the waste oil contaminants in organic solvents (Diphare and Muzenda, 2013). It is understood that when extraction temperature increased from 30 °C to 50 °C, there was an increase in percentage yield of recovered oil from 79.25% to 86.12%, which is due to two factors: (i) on the one hand with refining

temperature increases the viscosity of organic solvent mixture reduced which increased the amount of oil dissolved in 1–butanol, (ii) on the other hand when the temperature was higher the solubility of the base oil component in the extraction solvent increased further (Rincón et al., 2005). For further increment of refining temperature from 50 °C to 70 °C, there was a very marginal increase in percentage yield of recovered oil.

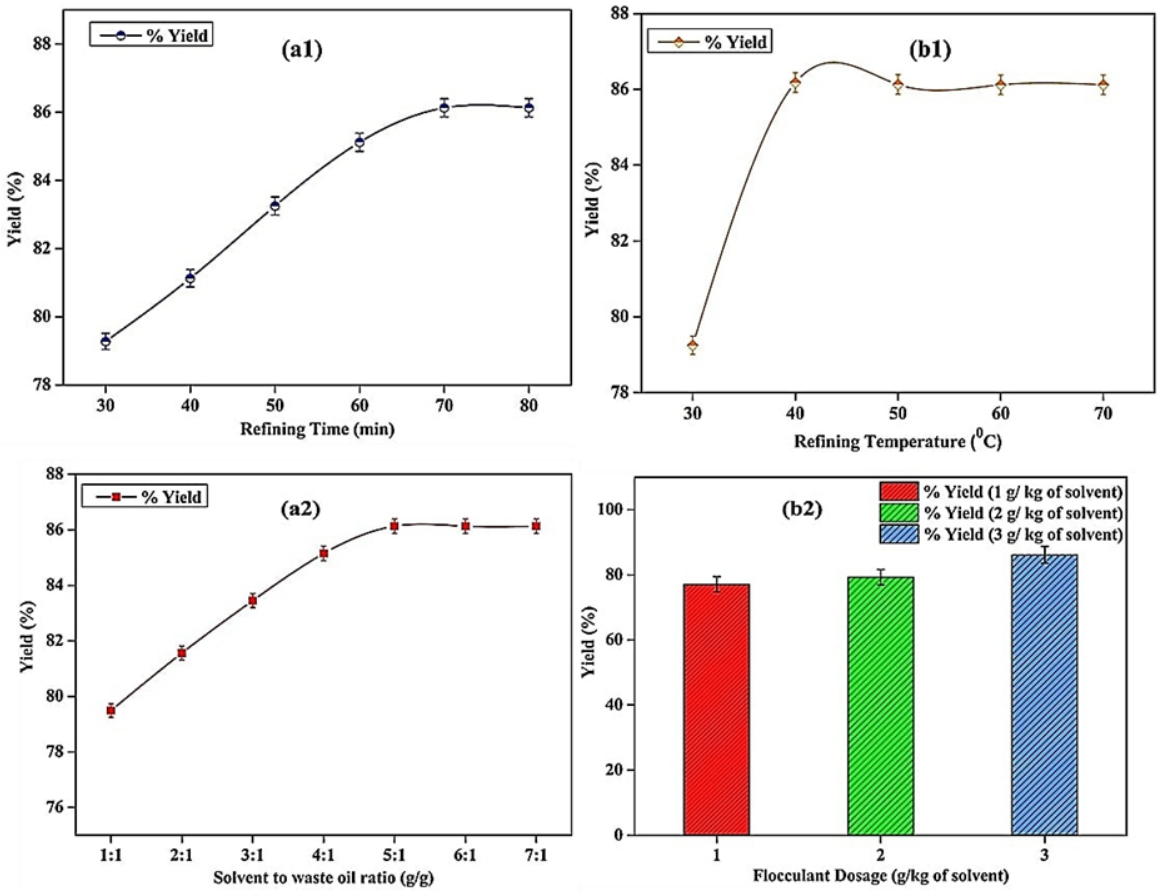

Fig. 3. Effect of (a1) refining time (b1) refining temperature on percentage yield of recovered oil (a2) solvent to waste oil ratio (b2) flocculant dosage on yield% of recovered oil

Overall, the optimal temperature should result in maximum sludge removal with minimized oil loss. As a result, the optimum reaction temperature was determined to be around 50 °C. Solvent to waste oil ratio is one of the main driving forces acting in re-refining used lubricating oil. In the current investigation, solvent to used oil ratio was varied from 1:1 to 7:1, keeping other parameters such as flocculant dosage, refining temperature, and refining time constant. Fig. 3(a2) reveals that refining yields shoot up with increasing solvent to waste oil ratio up to a point where it reaches the equilibrium. After that, further increase in solvent to used oil ratio, the yield of regenerated oil will not proliferate anymore. The reason behind the increase in percentage recovery is because of the combined influence of two factors: (i) at a lower solvent to waste oil ratio, the solvent saturates and does not dissolve all the base oil contained in waste oil; (ii) as the ratio of solvent to spent oil increased, dissolution of base oil in the solvent increased (Yang et al., 2013). The influence of flocculant dosage on the percentage yield of regenerated oil was investigated by varying flocculant concentration from 1 g/kg of solvent to 3 g/kg of solvent Fig. 3(b2). A steep increase of yield percentage has been noticed, and the highest level of the yield of recovered oil to the tune of 86.13 % is obtained when the flocculant concentration reaches a level of 3 g/kg of solvent. An increase in yield percentage of regenerated lubricating oil with increasing flocculant dosage may be because of an alkaline agent (KOH), which enhances the flocculation process due to fast ionization, forming stronger nucleophile OH^- to destabilize the particles (Diphare and Muzenda, 2013).

3.2. FTIR analysis of fresh, used, and recovered oil

The FTIR analysis of the fresh oil, waste lubricating oil, and regenerated oil is shown in Fig. 4. From Figure 4, we can understand that in the fresh oil, various bands are represented by the peaks of 2951 cm^{-1}, 2920 cm^{-1} and 2850 cm^{-1} (Kupareva et al., 2013) that depict symmetric stretching of the C–H group. The peak at 1463 cm^{-1} indicated bending vibration of C–H bond, which belongs to CH_2 group, and asymmetric vibration of C–H bond with a peak at 1373 cm^{-1} is attributed to CH_3 group (Khalaf et al., 2021; Sejkorová et al., 2020). The waste lubricating oil contained various contaminants identified by the functional groups like 1175 cm^{-1} which indicated the presence of carboxylic acid (Abu-Elella et al., 2015). The spectra consist of the band at 1700 cm^{-1} related to the carbonyl compounds with symmetric stretching of the C=O from esters, ketones, or acids (Kupareva et al., 2013). Stretching vibration of H–C=O: C–H (aldehydes) appears at 2730 cm^{-1} (Abu-Elella et al., 2015). In the waste oil, the spectrum around 820 cm^{-1} is assigned to aromatic content, indicating waste oil content fuels (Abu-Elella et al., 2015). The aforementioned oxidized products are also formed in the waste oil via a chemically rooted oxidation process (Dabai and Bello, 2019). After the process of regeneration of waste oil by 1–butanol, we could observe that the quality of the oil was similar to that of the fresh oil. After the process of regeneration using 1–butanol and potassium hydroxide, aromatics were removed because there is no functional group at 820 cm^{-1}, indicating the removal of aromatic compounds from the oil. Flashpoint improvement was observed in the regenerated lubricating oil because of the elimination of aromatics in the regenerated oil (Daham et al., 2017).

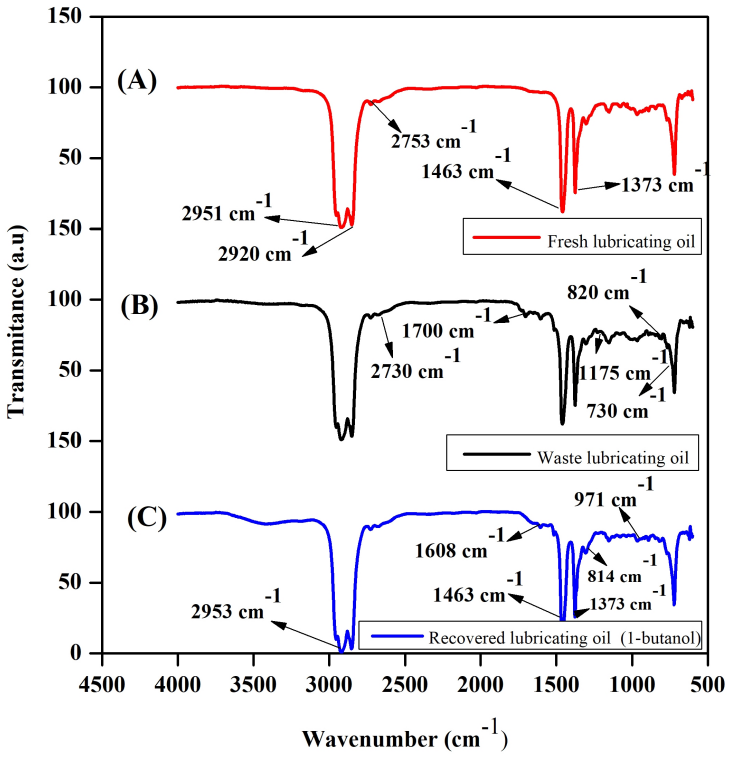

Fig. 4. FTIR analysis of fresh, used and recovered lubricating oil

3.3. Development of regression model equation for maximization of yield

The response surface methodology technique has established a mathematical relationship between independent variables and their responses, depicted by Eq. (4). Moreover, the coded variables are dimensionless, and it can be demonstrated by Eq. (5) as shown below.

$$x_i = \frac{X_i - \overline{X}_i}{\Delta X} \tag{5}$$

Here, X_i denotes the value of actual uncoded process variables, $\overline{X_i}$ represents an uncoded value of process variables at a center point, which can be obtained by considering the average values of "high" (+1) and "low" (–1), and ΔX refers to the step change, or it is the half of the deviation of "high" and "low" variables. The obtained quadratic equations for the response (percentage yield of recovered oil) can be expressed by Eq. (6)

$$Y_b = 80.16 + 0.62A + 2B + 0.58C + 3.33D - 0.82AB + 1.35AC + 0.54AD + 0.66BC + 0.61BD - 1.84CD + 0.74A^2 - 2.63B^2 + 1.34C^2 - 1.43D^2 \quad (6)$$

Model equations including actual factors have been illustrated in Eq. (7)

$$\%\ \text{Yield} = 59.04717 - 0.154068A + 0.612285B - 1.19606C + 9.09144D - 0.001646AB + 0.021425AD + 0.010969BC + 0.030656BD - 0.614375CD + 0.001184A^2 - 0.006587B^2 + 0.148935C^2 - 1.426D^2 \quad (7)$$

From Eq. (6), it can be presumed that A (refining time), B (refining temperature), C (solvent/waste oil ratio), and D (flocculant dosage) are the independent variables (in Table 1). They have a positive impact on Y_b (the percentage yield of recovered oil) in the extraction technique. When the reaction temperature changes, positive interaction between solvent to waste oil ratio and refining temperature occurs. D (flocculant dosage) also has a positive interaction due to the formation of a bridge between the impurities present in the waste oil and flocculant particle, which repulses the electrostatic charge to enhance the yield of recovered lubricating oil.

3.4. Optimization of process conditions for maximizing % yield of recovered oil

3.4.1. Effect of refining time, refining temperature, solvent to waste oil ratio and flocculant dosage on percentage yield

Fig. 5 illustrates the effect of refining time and refining temperature on percentage yield when solvent to waste oil ratio and flocculant concentration are constant. It is seen from the 3D plot of CCD (Fig. 5(a1)) that, keeping refining time constant, if we increase refining temperature, the % yield of recovered oil increases. From the 3D plot of CCD, when the refining temperature is in the range of 20 °C to 25 °C, the % yield is 76%, and the color indicated within the region is light green. In contrast, with the same condition, the 3D plot obtained from ANN (Fig. 5(b1)) gives a variation of yield percentage from 66% to 68%, and the color in this region is light blue. This is due to the fact that at the initial temperature, the viscosity of oil was higher and did not dissolve all the base oil. Furthermore, when refining temperature increases, due to reduction of viscosity of the organic solvent mixture, there is an increased amount of oil dissolved in both the solvent as a result of which the percentage yield of recovered oil increases from 68% to 74% and from 74% to 82% in ANN, whereas from 76% it increases to 80% in case of CCD. However, maximum yield % can be achieved with 80 minutes of refining time, 50.17 °C refining temperature, and 79.97 minutes reaction time, 55.53 °C refining temperature for CCD and ANN, where the percentage recovery is found to be 85.95% and 86.71%, respectively. Fig. 5(a2) depicts the effect of refining time and solvent to waste oil on the percentage yield of recovered oil. It is observed from the 3D response plot of the CCD (Fig. 5(a2)) approach that keeping refining time constant, with an increase in solvent to waste oil ratio, initially there is an increase in the percentage of yield, indicated by yellow color within the range of 1 to 1.5 g/g of solvent. Furthermore, the highest percentage yield can be achieved to the tune of 84%, and in that region, the color is red when the refining time reaches 80 min refining at a solvent to oil ratio of 7:1. Compared with ANN (Fig. 5(b2)), the highest yield percentage can be obtained to the tune of 86.71%, and the color changes from deep blue to sea green. The best condition for getting maximum recovery of treated oil is 79.97 minutes refining time with solvent to waste oil ratio of 4.89:1. It is evident from Fig. 5(a3) that the highest

flocculant concentration of 3 g/kg of solvent and refining time is 80 minutes. The gradual change in color from green to yellow and then red indicated in the 3D plot describes the change in percentage yield from 80 to 83%. In contrast, from the 3D plot of ANN (Fig. 5(b3)), it is found that initially, at low flocculant dosage, the yield is 65%, denoted by dark blue color. Subsequently, with an increase in flocculant doses, yield% is enhanced to 75%, and the color switches from light blue to green. Moreover, at a flocculant dosage of 2.99 g/kg of solvent, the highest percentage yield of 86 % can be achieved. The color is changed from green to yellow in that region.

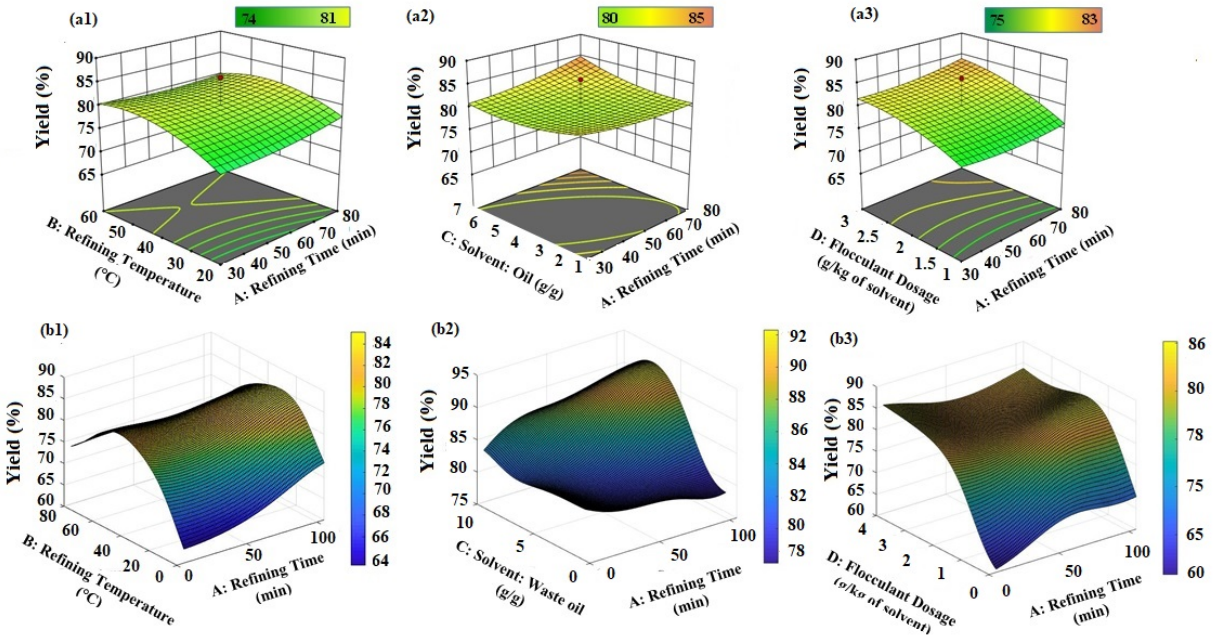

Fig. 5. The combined effect of refining time and refining temperature with (a1) CCD model (b1) ANN model; combined effect of refining time and solvent to oil ratio with (a2) CCD model and (b2) ANN model; combined effect of refining time and flocculant dosage with (a3) CCD model and (b3) ANN Model

It is evident from the 3D plot of CCD (Fig. 6(a1)) that with an increase in refining temperature and solvent to waste oil ratio, the percentage yield of recovered oil increases. Initially, when the solvent to waste oil ratio is constant, an increase of refining temperature of 20 °C, the yield percentage is found to be 76%, and the color is indicated by green in that region.

With the exact condition of refining temperature and solvent to waste oil ratio stated above, from the 3D plot of ANN (Fig. 6(b1)), the percentage yield of re-refined oil is 70%. The color is depicted as light blue. With an increase in refining temperature from 40 °C to 60 °C, the percentage yield increases from 86% to 89%, and in this region, the color is indicated by yellow. According to the 3D plot of CCD (Fig. 6(a2)), the % yield of recovered oil increases with increased flocculant concentration and refining temperature. Initially, when refining temperature is low, the percentage recovery of reclaimed oil is 66%, but when refining temperature and flocculant doses increase, the percentage yield also increases as observed from the 3D plot, it is evident that, for maximum refining temperature of 50 °C, percentage yield is maximum to the tune of 82% as indicated in the yellow color region. With the same condition for the 3D plot obtained from ANN (Fig. 6(b2)), the percentage yield of re-refined oil is higher (86%), and the color is also denoted by yellow. According to the 3D plot, the percentage of oil yield is enhanced with an increase in flocculant concentration and solvent to waste oil ratio. In the case of the CCD approach (Fig. 6(a3)), initially, when the flocculant dosage is 1.3 g/ kg of solvent, the percentage yield of reclaimed oil is 76%, and the color is indicated by light-blue in the plot. Increase in flocculation concentration from 1.7 g/kg of solvent to 2.5g/kg of solvent, the yield of recovered oil varies from 78% to 84%, and the color changes from green to red. Compared with ANN (Fig. 6(b3)), it is found that, the increase in flocculant dosages, the color changes

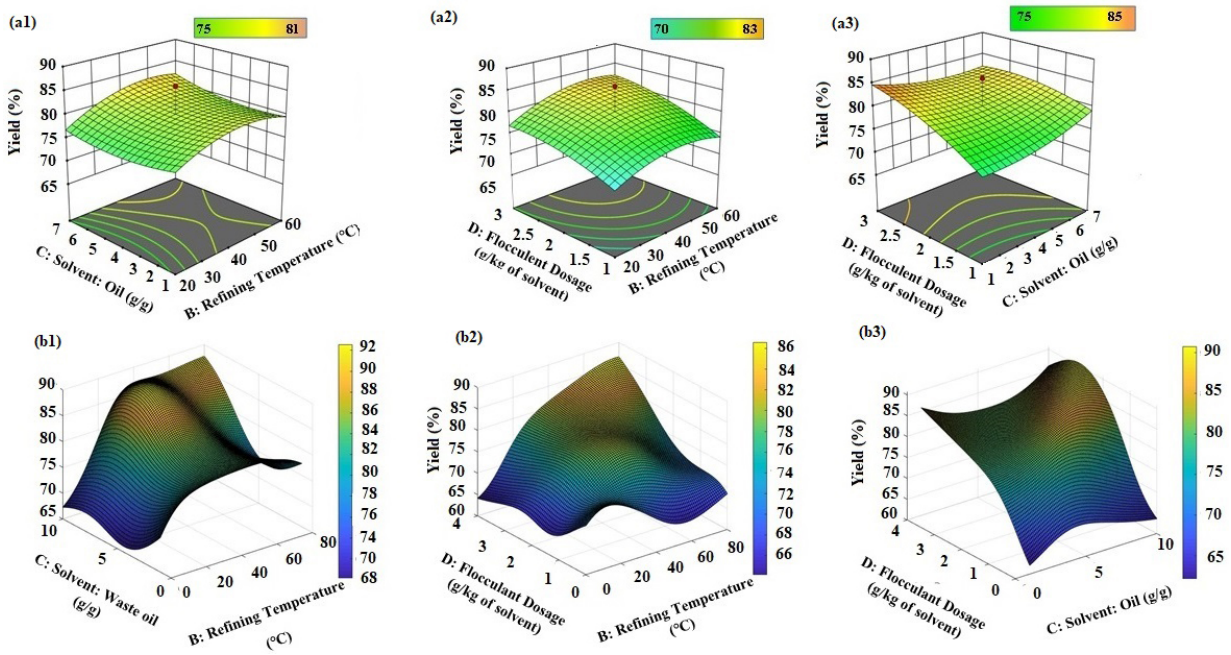

Fig. 6. The combined effect of refining temperature and solvent to waste oil ratio with (a1) CCD model (b1) ANN model; combined effect of refining temperature and flocculant dosage with (a2) CCD model (b2) ANN model; combined effect of solvent to waste oil ratio and flocculant dosage with (a3) CCD model (b3) ANN model

from dark blue to yellow, showing a variation of % oil yield from 65% at a solvent to waste oil ratio of 2:1, flocculant concentration of 0.5 g/kg of solvent to 86.71% when solvent to waste oil ratio is 4.89:1 and flocculant dosage of 3 g/kg of solvent.

3.5. Analysis of variance (ANOVA) for maximizing the yield of recovered oil

To evaluate the significance of the chosen model, statistical analysis in terms of ANOVA was carried out. The statistical parameter for the percentage yield of recovered oil acquired from analysis of variance have been demonstrated in Table 3.

The model significance and model terms can be concluded based on some parameters related to this statistical analysis, such as the sum of squares (SS), F-value (Fisher's test), and p-value. Higher the sum of squares, F-value, and lower the p-value signifies that the model is significant. From Table 3, the results show that the sum of squares value is relatively high, and the F-value supports the models' significance. However, the p-value of 0.0001 indicates that there is $a < 0.01\%$ probability of the F-value appearing that high due to noise. In ANOVA analysis, p-value < 0.05 denominates the term to be significant. The p-value in the case of percentage recovery of recovered lubricating oil B, D, AC, CD, A^2 , B^2, C^2, D^2 is a significant model term. Additionally, the sum of squares value can be used to determine the magnitude of the effect of each model terms on the response. From Table 3, it can be seen that the term D (flocculant dosage) has the highest sum of squares value followed by term B (refining temperature). Hence term D has the most significant influence on the maximum percentage of recovered lubricating oil, followed by term B. The details of Model Fit Statistics are given in Table 4. It is evident from Table 4 that the coefficient of determination (R^2) value was 95.09% for 1–butanol as a solvent in the process. There was suitable conformity with an adjusted coefficient of determination. The predicted R^2 value of 92.10% is reasonably agreed to the adjusted R^2 of 90.51%, as the difference is less than 0.2 only. The adequate precision value of the model, which denotes the ratio between signal and noise, was found to be 17.8283. The value is considered desirable if it goes above 4, which is highly beneficial in the current analysis (Chowdhury et

Table 3. ANOVA analysis for percentage yield of recovered oil

Source	Sum of squares	DF	Mean square	F-value	p-value	Comments
Model	810.70	14	57.91	20.76	< 0.0001	significant
Refining time, A	9.36	1	9.36	3.36	0.0868	
Refining temperature, B	95.96	1	95.96	34.41	< 0.0001	
Solvent/oil, C	5.90	1	5.90	2.12	0.1665	
flocculant concentration, D	266.87	1	266.87	95.69	< 0.0001	
AB	10.84	1	10.84	3.89	0.0674	
AC	28.97	1	28.97	10.39	0.0057	
AD	4.59	1	4.59	1.65	0.2190	
BC	6.93	1	6.93	2.48	0.1358	
BD	6.01	1	6.01	2.16	0.1626	
CD	54.35	1	54.35	19.49	0.0005	
A^2	15.30	1	15.30	5.48	0.0334	
B^2	193.76	1	193.76	69.48	< 0.0001	
C^2	28.75	1	28.75	10.31	0.0058	
D^2	56.76	1	56.76	20.35	0.0004	
Residual	41.83	15	2.79			
Lack of fit	2.73	10	0.2732	0.0349	1.0000	not significant
Pure error	39.10	5	7.82			
Cor total	852.54	29				

Table 4. Model Fit Statistics

Source	Standard deviation	R^2	Adjusted R^2	Predicted R^2	PRESS	Comments
Linear	4.25	0.4708	0.3862	0.2020	680.298	
2FI	4.23	0.6019	0.3923	0.3628	543.211	
Quadratic	1.67	0.9509	0.9051	0.9210	67.389	suggested
Cubic	2.56	0.9540	0.7775	–	–	aliased

al., 2019). The high value of the coefficient of determination (R^2), a slight difference between the adjusted determination of coefficient (R^2_{adj}), and predicted determination of coefficient (R^2_{pred}), and non-significant lack of fit test suggest that the quadratic model is the best-fitted model for maximization of percentage yield of recovered oil (Table 4). Aside from R^2, R^2_{adj}, and R^2_{pred}, other statistical measures such as standard deviation (SD), coefficient of variation (CV percent), and adequate precision can be used to characterize the magnitude of fitting experimental data into the chosen model (AP). The standard deviation depicts

whether the predicted value agrees with the experimental value. From Table 5, the standard deviation value is 1.67, which signifies the conformity between predicted and experimental values. The coefficient of variation (CV) is a parameter that expresses a developed model's reproducibility. The lower value of CV (2.13 %) justifies the model (Chakraborty et al., 2014). The model's fitness can also be shown in the predicted vs. actual plot (Fig. 7), where the points in the case of the model based on the percentage yield of recovered oil are on the diagonal line. Therefore, it can be inferred from the graph that the predictability of the model is higher for the percentage recovery of lubricating oil. In the present study, the high value of performance coefficient (R) for training, validation, and test signifies the justification of the above model. The overall R-value can be conferred model based on the percentage yield of extracted oil with ANN, which gives better predictability.

Table 5. Model Fit Summary

Properties	Value	Properties	Value
Std. Dev.	1.67	R^2	0.9509
Mean	78.44	adjusted R^2	0.9051
CV (%)	2.13	predicted R^2	0.9210
PRESS	67.39	adequate precision	17.8283

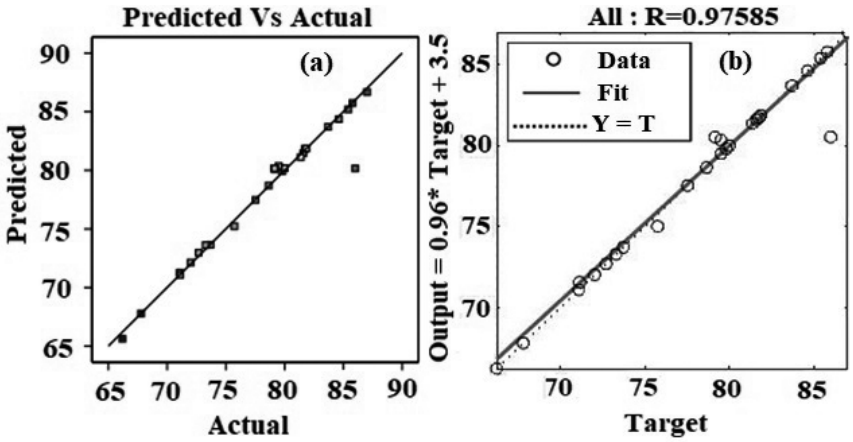

Fig. 7. Actual vs. Predicted plot for (a) RSM model based on percentage recovery, (b) ANN model based on percentage recovery of lubricating oil

3.6. Analysis of variance (ANOVA) for maximizing the yield of recovered oil

The prediction with RSM and ANN models was statistically compared using parameters such as (i) root mean squared error (RMSE), (ii) absolute average deviation (AAD), and (iii) mean absolute error (MAE), which are calculated using Eq. (8)–Eq. (11) (Al-Shathr et al., 2021; Azad et al., 2016).

$$R^2 = 1 - \sum_{i=1}^{n} \left(\frac{\left(y_{\text{pred},i} - y_{\text{exp},i}\right)^2}{\left(y_{\text{pred},i} - y_m\right)^2} \right) \tag{8}$$

$$\text{MAE} = \frac{\sum_{i=1}^{n} \left| y_{\text{pred},i} - y_{\text{exp}.i} \right|}{n} \tag{9}$$

$$\text{AAD\%} = \left(\frac{1}{n} \sum_{i=1}^{n} \left| \frac{y_{\text{pred},i} - y_{\text{exp},i}}{y_{\text{pred},i}} \right| \right) \times 100 \tag{10}$$

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} \left(y_{\mathrm{pred},i} - y_{\mathrm{exp},i}\right)^2}{n}} \tag{11}$$

where, $y_{\mathrm{pred},i}$ is the predicted response obtained from the model and $y_{\mathrm{exp},i}$ is the actual response obtained from the experiment, n denotes the total number of runs and y_m is the average of actual responses. It can be seen from Table 6 that proficiency of the ANN model is far better in comparison to the RSM model as in the case of ANN coefficient of performance (R^2) value was found to be higher, MAE, AAD% and RMSE values were found lower. Fig. 7 portrays the higher predictability of ANN over RSM. RSM and ANN models have some advantages and limitations. The response surface methodology, an essential non-linear optimization technique, exhibits parametric and inter-parametric interactive effects on responses. Still, it is limited by the fact that it only assumes non-linear quadratic correlation. Conversely, an artificial neural network cannot show the contour plot of each parameter and their combined effect on responses but can accumulate a massive range of non-linear behavior of parameters (Shojaeimehr et al., 2014), which results in better predictability. In addition to the number, the defect sizes were also taken into account.

Table 6. Optimization result

Sr. no.	Refining time (min)	Refining temp. (°C)	Solvent/ waste oil (g/g)	Flocculant dosage (g/kg of solvent)	Yield obtained from optimization	Yield obtained from the experiment
1	79.98	55.5	5:1	3	86.71	86.29
2	79.98	55.5	5:1	3	86.71	86
3	79.98	55.5	5:1	3	86.71	86.12

4. CONCLUSIONS

In the present investigation, an effort has been made by employing greener technology of extraction-flocculation to recover the waste lubricating oil and make it ready for reuse. The impact of four independent variables viz. refining time (30 min to 80 min), refining temperature (20 °C to 60 °C), solvent to waste oil ratio (2:1 to 7:1 g/g), and flocculant concentration (1 g/kg of solvent to 3 g/kg of solvent) on the maximization of yield percentage was studied. The main objective of the current investigation was to maximize the percentage yield by modeling and optimization. Two modeling techniques viz. RSM with CCD approach and ANN have been employed, out of which ANN gave better predictability. The value of R2 for the ANN model was found to be 0.975, and the root mean square error (RMSE), absolute average deviation (AAD%), and mean absolute error (MAE) were obtained as 1.36, 0.59, and 0.47, respectively. Overall, the effect of process parameters on the percentage yield was well understood, as reflected by the 3D surface plots. Genetic Algorithm study using ANN model proved to be a better fit as the optimized yield obtained was found to be 86.71%, which is closer to the experimental value of 86.29% because ANN utilizes a vast amount of data making the optimization process much more accurate than the experiment. Various inorganic flocculants have already been used in the extraction flocculation process of regeneration of waste oil. However, there is an immense need for the development of bio-polymeric flocculants such as chitosan, sodium alginate, starch, and their derivatives for effective removal of sludge in the waste oil, which will in turn benefit commercial application and recycling of waste oil. Besides this, the use of other types of ANN such as multi-hidden-layer, convolutional, LSTM, recurrent will be required for proper data assessment and to come up with reliable techniques for maximization of percentage sludge removal and minimization of percentage oil loss in the extraction-flocculation process. Thus, the obtained

optimized condition helps to generate the maximum yield of recovered oil from waste oil, leading to the commercialization of the obtained product.

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