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Mathematical and Kinetic Modelling of the Adsorption of Crude Oil Spill Using Coconut Coir Activated Carbon

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Abstract: Crude oil spills have tremendous effects on our environment and poses severe pollution problems around the world as hazardous chemicals such as polycyclic aromatic hydrocarbons are released into the ecosystem. The clean-up of these spills using natural adsorbent is considered as an eco-friendly and cost effective method of handling the oil spills due to its high oil sorption capacity and biodegradability. Coconut coir predominantly found in the Niger Delta area of Nigeria was carbonized and chemically activated using Potassium Hydroxide (KOH) for the removal of crude oil spill. The kinetic data were fitted into various kinetic models with Pseudo-second order model showing best fit with a correlation coefficient R^2=0.999 and the Boyd model revealed that the adsorption was controlled by internal transport mechanism and film-diffusion was the major mode of adsorption. Thus, Coconut Coir Activated Carbon (CCAC) showed significant capability to be used as a low-cost, re-generable and eco-friendly adsorbent in oil spill clean-up. A mathematical model was also developed using multivariate numerical optimization method and was validated by fitting it into the experimental data which gave a correlation coefficient R^2=0.997. Hence, the empirical model developed using multivariate numerical optimization method can be used for the design of industrial treatment plant.

Keywords: Coconut Coir, Multivariate Numerical Optimization, Non-linear Regression, Crude Oil Removal, Batch Adsorption, Adsorbent

1. Introduction

The progressive increase in industrialization and the continuous reliance on petroleum hydrocarbons for energy generation has led to numerous cases of accidental crude oil spill due to the increase in production, exploration, transportation, distribution, storage and other related processes of crude oil. As a result, oil spills have become a worldwide concern due to its environmental and economic impact [1-3]. The release of hazardous chemicals such as Polycyclic Aromatic Hydrocarbons (PAHs), Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) from oil spills have adverse effect to aquatic and human lives and may require longer time before the effect can be reversed [4].

Apart from financial losses due to shut-down of production facilities as a result of pipeline vandalization [5], fire explosion leading to loss of lives and properties [6]; such incidents cause huge and sustained devastation in Earth's ecosystems and harm living organisms [7]. The Niger Delta landscape of Nigeria is criss-crossed with pipelines and punctuated with pumping stations that connect the over 600 oilfields with storage facilities and tanker loading ports. These installations and the spills are often in close proximity to villages which usually leads to oil spillage contaminating agricultural fields, fishing areas and drinking-water sources. The ecological effects have only been spot-wise investigated, but those few studies and the preponderance of oil on-land and water makes it obvious that the impact is massive [8]. These environmental disasters together with some local scale

incidents seriously endanger the environment; thus, it has become imperative in improving oil spill clean-up methods and developing new materials which can be applied for this purpose. A number of mechanical, biological, chemical and adsorption methods are currently used to remove oil spill from water [9]. Among these several chemical and physical methods, the adsorption onto activated carbon has been found to be superior to other techniques because of its capability for adsorbing a broad range of different types of adsorbate efficiently; and its simplicity of design [10, 3]. However, commercially available activated carbons are still considered expensive [11]. Consequent upon this, many researchers have resorted to studying cheaper substitutes, which are inexpensive, and are endowed with reasonable adsorptive capacity.

Adsorption technique has been proven to be an efficient and economical process for the treatment of oil spillage and are currently used to remove oil spills from water media and paved roads, remove volatile hydrocarbons [12] and Benzene, Toluene, Ethylbenzene and Xylene (BTEX) present in water soluble fraction (WSF) of crude oil [13-15]. The most popular method of adsorption technique involves the use of various kinds of adsorbent; especially during rescue operations on water bodies. A comprehensive rescue operation is aimed at efficient removal of oil spills from the water surface, coastal zones and at preventing further migration of these contaminants. The efficiency of the process lies in the choice of suitable/ideal adsorbent with the following characteristics: oleophilicity, buoyancy, biodegradable/renewable, high adsorption/retention capacity, environmentally-friendly, cheap and readily available [3]. In recent times, a number of agricultural waste products such as male flower of coconut tree [16], jute fibre [17], rubber wood sawdust [18], corncob [19], bamboo [20] and oil palm fibre [21] have been successfully utilized as renewable and cheaper precursors for the production of activated carbons for adsorption of oil-in-water.

Adsorption kinetics describes the rate of retention or release of a solute from an aqueous environment to solid-phase interface at a given adsorbents dose, temperature, flow rate and pH. During adsorption two main processes are involved; physical (physisorption) or chemical (chemisorption). Physical adsorption is as a result of weak forces of attraction (van der Waals), while chemisorption involves the formation of a strong bond between the solute and the adsorbent that involves the transfer of electrons. The kinetic equations of the chemical reaction show the dependence of the reaction rate on the concentrations of the reactants which is determined from data obtained experimentally. The study of adsorption kinetics is important because it provides valuable information and describes the mechanism of the reaction and also helps to determine the overall rate of the adsorption process [22].

In recent times, linear regression analysis has been among the most pronounced and viable tools frequently applied for analysis of experimental data obtained from adsorption process. It has been used to define the best fitting relationship that quantify the distribution of adsorbates, verification of the consistency of adsorption models and the theoretical assumptions of adsorption models [23, 24]. Several mathematically rigorous error functions have been used to drastically address the inherent biasness in the error structure of experimental data resulting from the transformation of adsorption isotherms into their linearized forms [25, 26]. It is against this backdrop that non-linear regression analysis becomes inevitable, since it provides a mathematically rigorous method for determining adsorption parameters using original form of isotherm equations [27, 28]. Unlike linear regression, nonlinear regression usually involved the minimization or maximization of error distribution between the experimental data and the predicted isotherm based on its convergence criteria [29].

In the aspect of engineering and science, modelling can be referred to the process of identifying objective, variables and constraints for a given problem. Formulation of an appropriate model that describes the problem (process) is the first and most important step in the optimization process. Once the model is formulated, an optimization algorithm can be used to find its solution.

Generally, models and algorithms are complicated; hence computer simulation is required to implement the optimization process. Multivariate numerical optimization means optimization of a scalar function of several variables. Mathematically, optimization is simply the minimization or maximization of an objective function, constraints on its variables. Sometimes, it is usually the user's responsibility to choose an algorithm that is most appropriate for the specific problem [30]. This is important as it determines whether the problem is solved rapidly or slowly and indeed the solution is found at all.

In numerical optimization, the fastest algorithm seeks only a local solution; which is referred to as local optimal. Basically, this is the point at which the objective function is smaller than all other feasible point in its vicinity. Global solution (global optimal) is simply referred to as the best of all the minima of the objective function [30, 31].

Most numerical optimization algorithms are iterative and simply begin with an initial guess to be optimal values of the variables and a sequence of improved estimates is generated until a final solution is reached. The strategy used to move from one iterate to the next distinguishes the algorithm from another and most strategies make use of the values of the objective function and constraints with possibly the first and second derivatives of these functions [30]. Some algorithms accumulate information gathered at previous iteration while others use only local information from current point. Regardless of these specifics, algorithms should be robust, efficient and accurate [32]. There are several developed optimization approaches in the literature to perform this iterative estimation namely Gauss-Newton, Steepest Descent, Marquardt-Levenberg, Nelder-Mead, General Reduced Gradient (GRG) protocol, among others [33, 30, 31].

Mathematical modelling and computer simulation of adsorption offers an extremely powerful tool for a number of

tasks on different levels. It is essential for process design and optimization where the equilibrium and dynamic test information comes together representing a multivariable system which cannot be effectively handled without appropriate modelling and computer-based techniques. When reaction kinetics is combined with mass transfer that is, in turn, dependent on the particle and fluid flow properties only a rather sophisticated apparatus can make sense out of the web of variables. Hence, the purpose of this research is to develop an empirical model using multivariate numerical optimization method to predict the adsorption process performance under different conditions where computer simulations can then replace numerous tedious and costly experiments.

2. Experimental Methods

2.1. Preparation of Adsorbent

The procedure for preparing coconut coir activated carbon (CCAC) is explicitly expatiated in Ukpong et al. (2020) [3]. The coconut coir was obtained from Etinan main market in Etinan LGA, Akwa Ibom State, Nigeria and were washed with distilled water; thereafter dried to constant weight at 105°C for 24 h in a laboratory drying oven (DHG-9101 model) to remove excess water content and some volatile components. The dried sample was then crushed and sieved into smaller size particle (1-2mm) and stored at room temperature. The crushed coconut coir sample was carbonized in a muffle furnace at a temperature of 600°C for 2 h in the absence of oxygen and the carbonized sample was activated with KOH pellets at an Impregnation Ratio (I. R) of 1:2. The mixture was then dried in a laboratory drying oven at 105°C for 12 h to remove moisture and was further heated in a muffle furnace at a temperature of 800 °C for 1 h to complete the activation process. The coconut coir activated carbon (CCAC) produced was cooled to room temperature and washed with 0.1 M HCl solution to remove any residual ash content and with distilled water until the pH of washing solution reached 6-7. The prepared CCAC was then oven dried at temperature of 105°C for 2 h and further crushed and sieved into 63-500μm particle sizes and then stored in a desiccator until needed for the adsorption experiment.

2.2. Batch Adsorption Kinetics Studies

The batch adsorption kinetics study as reported by Ukpong et al. (2020) was carried out by measuring 250 mL of the simulated oil spill of 19440 mg/L initial concentration into a 500 mL beaker for each experimental run and 1.0 g of $CCAC_{KOH}$ was measured into the simulated oil spill while being agitated in an orbital shaker (Rotamax 120, Reidolph) at 20 rpm and at a temperature of 25°C for varying contact time of (15, 30, 45, 60, 75, 90, 105 and 120 min) [3, 34].

2.3. Development of Mathematical Model

Aryafar et al. (2019) applied non-linear multivariate regression analysis to develop mathematical equations for the adsorption kinetics which relate the adsorption process with many factors such as the contact time, pH, solution concentration, and adsorbent mass [35].

The mathematical model for the batch adsorption is potentially affected by the external film resistance and the surface mass transfer resistance. The batch surface diffusion model was based on the following assumptions:

The porous adsorbent particles are perfectly spherical containing reacting sites that are homogeneously distributed within them [36].

The reaction of the adsorbent particles is governed by a chemisorption mechanism [37].

The system is perfectly mixed, so the external mass transfer process occurs solely in a thin boundary layer surrounding the particles.

The aqueous phase is an isothermal process and having fast intrinsic adsorption kinetics [38].

The equilibrium process is described by the Langmuir adsorption isotherm [37].

The diffusion coefficient is constant during the adsorption process.

The pH of the external phase is constant with time.

For the development of the correlation in this study, the Adsorption capacity (A. C) depends directly proportional to both contact time and initial concentration as shown in Eqs. (1) and (2) and also indirectly proportional to the adsorbent mass as shown in Eq. (3). Based on this assertion, the relationship of A. C with the adsorption parameters are presented in Eqs. (1) to (3).

$$A.C \propto t \qquad (1)$$

$$A.C \propto C_o \qquad (2)$$

$$A.C \propto \frac{1}{M} \qquad (3)$$

The Adsorption capacity (A. C) can also be expressed as a function of the aforementioned parameters in Eq. (4).

$$A.C = f(t, C_o, M) \qquad (4)$$

However, Eqs. (1) to (3) can be expanded in the basic form of non-linear multivariate algebraic expression as given in Eq. (5).

$$A.C = \beta_o(t^{\beta_1} \times C_o^{\beta_2} \times M^{-\beta_3}) \qquad (5)$$

Alternatively, Eq. (5) can also be expressed as Eq. (6).

$$A.C = \beta_o \left[\frac{t^{\beta_1} \times C_o^{\beta_2}}{M^{\beta_3}} \right] \qquad (6)$$

By applying the logarithmic transformation to linearize Eq. (6), we obtain Eq. (7).

$$LOG(A.C) = LOG(\beta_o) + \left[(\beta_1 LOG(t) + \beta_2 LOG(C_o)) - \beta_3 LOG(M) \right] \quad (7)$$

where β_o is the adsorption coefficient while β_1, β_2 and β_3 are exponential constants of the adsorption parameters.

The variables β_o, β_1, β_2 and β_3 can be determined iteratively using multivariate numerical optimization method. To perform this iterative estimation, several approaches can be employed to determine these variables such as Gauss-Newton, Nelder-Mead, Marquardt-Levenberg, steepest descent and General Reduced Gradient (GRG) protocol and the adsorption parameters (contact time, initial concentration and adsorbent mass) are also obtained experimentally [33, 30, 31].

The unknown adsorption coefficient (β_o) and the exponential constants (β_1, β_2 and β_3) are solved iteratively using GRG protocol in the Microsoft Excel SOLVER [33]. To validate this correlation, the predicted data obtained are compared with the experimental data and other established models. Also, the goodness of fit of the predicted data to that of the experimental data is established using coefficient of determination (R^2) and other error functions.

2.4. Adsorption Kinetics Models

Some of the kinetic models that were selected for fitting to the experimental data under study are as shown in Table 1. The parameters were determined using non-linear regression method.

Table 1. Kinetic models for the Adsorption process.

S/N	Kinetic Model	Model Equation	References
1.	Pseudo First Order Model	$q_t = q_e \left(1 - e^{-k_1 t} \right)$	[39]
2.	Pseudo Second Order Model	$q_t = \dfrac{k_s q_e^2 t}{1 + k_s q_e t}$	[40, 41]
3.	Intra-particle Diffusion Model	$q_t = K_p \sqrt{t} + C$	[42-44]
4.	Boyd Diffusivity Model	$0.86 \leq F \leq 1 : B_t = -0.4977 - \ln(1-F)$ $F = \dfrac{q_t}{q_\infty}$	[45, 46]

K_1, K_s and K_p are model constants.

2.5. Statistical Analysis

Nonlinear regression of kinetic models usually contains error between the experimental data and the predicted model. Therefore, several mathematically rigorous error functions were investigated as shown in Table 2.

Table 2. Statistical measures used in determining the goodness of fit for the Kinetic models.

S/N	Error Function	Equation	References
1.	The Sum Square of Errors (ERRSQ)	$ERRSQ = \sum_{i=1}^{n} \left(q_{e,exp} - q_{e,cal} \right)^2$	[47, 48]
2.	Hybrid Fractional Error Function (HYBRID)	$HYBRID = \dfrac{100}{n-p} \sum_{i=1}^{n} \left[\dfrac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right]$	[49, 50]
3.	Average Relative Error (ARE)	$ARE = \dfrac{100}{n} \sum_{i=1}^{n} \left| \dfrac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right|$	[49, 50]
4.	Marquardt's Percent Standard Deviation (MPSD)	$MPSD = 100 \sqrt{\dfrac{1}{n-p} \sum_{i=1}^{p} \left(\dfrac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right)_i^2}$	[49]
5.	Sum of Absolute Errors (EABS)	$EABS = \sum_{i=1}^{p} \left| q_{e,exp} - q_{e,cal} \right|$	[51]
6.	Coefficient of Determination (R^2)	$R^2 = \dfrac{\sum \left(q_{e,exp} - \overline{q_{e,cal}} \right)^2}{\sum \left[\left(q_{e,exp} - \overline{q_{e,cal}} \right)^2 + \left(q_{e,exp} - q_{e,cal} \right)^2 \right]}$	[52, 53]
7.	Nonlinear Chi-Square Test (χ^2)	$\chi^2 = \sum_{i=1}^{n} \dfrac{\left(q_{e,exp} - q_{e,cal} \right)^2}{q_{e,exp}}$	[54, 55]

Where, $q_{e,cal}$ is the theoretical concentration of adsorbate on the adsorbent, which have been calculated from one of the isotherm models, $q_{e,exp}$ is the experimentally measured adsorbed solid phase concentration of the adsorbate adsorbed

on the adsorbent. (n) is the number of data points, (p) is the number of parameters in the equation.

3. Results and Discussion

3.1. Batch Adsorption Kinetics

Several kinetic models such as the pseudo-first order, pseudo-second order, intra-particle diffusion and Boyd models were used to study the kinetic behaviour and mechanism for the crude oil adsorption process. The adsorption kinetic model constants for the removal of crude oil are shown in Table 3 and the results showed that the coefficient of determination for the pseudo-second order kinetic model for $CCAC_{KOH}$ (R^2=0.999) was much higher and closer to unity than that of pseudo-first order kinetic model and intra-particle diffusion, thus; the adsorption behaviour of crude oil on $CCAC_{KOH}$ predominantly followed pseudo-second order kinetic model.

Table 3. Adsorption kinetic model constants for the removal of crude oil using $CCAC_{KOH}$.

Adsorbent	$q_{e,exp}$ (mg/g)	Pseudo-first order			Pseudo-second order		
		K_f (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2	K_s (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2
$CCAC_{KOH}$	4859.25	0.430698	4858.092	0.846	0.00659	4857.138	0.999
Adsorbent	$q_{e,exp}$ (mg/g)	Intra-particle Diffusion					
		K_{ip} (mg/g.min$^{1/2}$)		C (mg/g)	$q_{e,cal}$ (mg/g)	R^2	
$CCAC_{KOH}$	4859.25	1.107923676		4848.39	4859.747	0.8499	

Source: Ukpong *et al*. (2020).

According to Ukpong *et al*. (2020), this validated the fact that "the rates of surface reaction, chemical reaction (chemisorption) and transport of crude oil from liquid to adsorbent phase was faster due to the high hydrophobic nature of the modified adsorbents" [3, 56, 57].
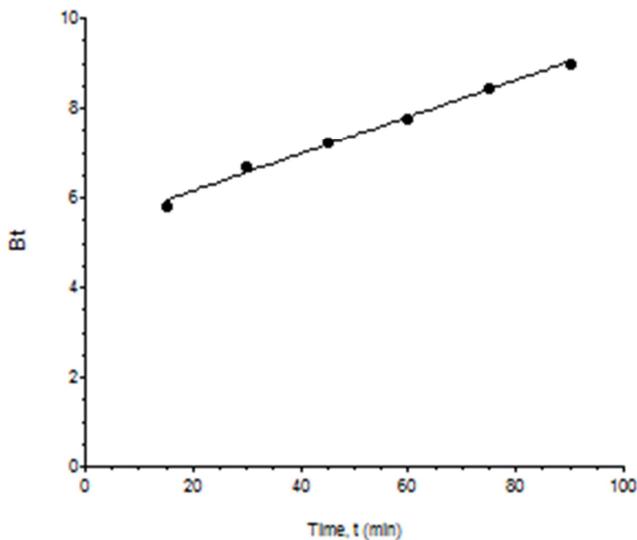
Source: Ukpong *et al*. (2020).

Figure 1. Boyd plot for the adsorption of crude oil onto $CCAC_{KOH}$.

For intra-particle diffusion model, the larger the intercept (boundary layer effect; C), the greater the contribution of the surface sorption in the rate-controlling step [58]. As elucidated by Ukpong *et al*. (2020), this implied that "the coefficient of determination and thickness of the boundary layer for $CCAC_{KOH}$ (R^2=0.8499; C=4848.39 mg/g) validated the presence of certain degree of boundary layer control over the adsorption process which also indicated that the intra-particle diffusion was not the only rate-limiting step, but other processes might as well have controlled the rate of adsorption" [3, 59].

Bulut and Zeki (2007) stated that "the Boyd model which is widely used for studying the mechanism of adsorption was also used to determine whether the main resistance to mass transfer was in the thin film (boundary layer) surrounding the adsorbent particle or in the resistance to diffusion inside the pores" [3, 60]. The linearity test of the plot of B_t against time was used to distinguish between the film and particle-diffusion controlled adsorption mechanism as shown in Figure 1. A straight line plot passing through the origin indicates that the adsorption rate is governed by the particle diffusion; otherwise it is governed by the film diffusion [60]. This deviation may be due to the difference in mass transfer rate in the initial and final stages of adsorption [61]. Figure 1 showed the Boyd plot for the crude oil adsorption onto $CCAC_{KOH}$ to be a linear graph which does not pass through the origin, thus confirming that the adsorption mechanism was film-diffusion controlled [3].

3.2. Developed Model

Three parameters were used to develop a mathematical model that relates Adsorption capacity (A. C) to contact time (t), initial concentration (C_o) and adsorbent mass (M) for the adsorption of crude oil to which this research work has been able to establish. For crude oil adsorption using $CCAC_{KOH}$, the developed adsorption coefficient (β_o=4124.887) and exponential constants (β_1=0.040975, β_2=0.002538 and β_3=0.043401) were obtained using Microsoft Excel Solver (after the iteration with the GRG protocol) as shown in Table 4.

The empirical model developed is given as Eq. (8).

$$A.C = 4124.887 \left[\frac{t^{0.04098} * C_o^{0.00254}}{M^{0.04340}} \right] \quad (8)$$

Table 4. *Statistical values of the developed model for CCAC*$_{KOH}$.

Developed model	β_0	β_1	β_2	β_3	(O. F)
MPSD	4126.19000	0.04078	0.00255	0.04232	6.53655×10^{-07}
HYBRID	4124.85100	0.04098	0.00254	0.04340	3.87513×10^{-16}
ARE	4126.19000	0.04078	0.00255	0.04232	1.30633×10^{-07}
EABS	4126.19000	0.04078	0.00255	0.04232	0.00016
SSE	4124.85100	0.04098	0.00254	0.04340	9.40871×10^{-14}
χ^2	4124.85100	0.04098	0.00254	0.04340	3.87494×10^{-18}
RMSE	4126.19000	0.04078	0.00255	0.04232	7.93529×10^{-05}
R^2	4124.88700	0.04098	0.00254	0.04340	0.99722

(O. F)-Objective function for the minimum error distribution between experimental and predicted data.

The characteristics of the developed model have been evaluated using the different statistical criteria as shown in Table 4. Table 4 showed that the value of R^2 is 0.997217 and the other error functions are MPSD: 6.53655×10^{-07}, HYBRID: 3.87513×10^{-16}, ARE: 1.30633×10^{-07}, EABS: 0.000159, SSE: 9.40871×10^{-14}, χ^2: 3.87494×10^{-18} and RMSE: 7.93529×10^{-05}. The values of R^2 and other statistical criteria of the developed model showed a better result compared to other models used in analysing the experimental data as shown in Table 5.

3.3. Prediction of Parameters for the Adsorption Kinetics using Error Functions

The calculated adsorption kinetics parameters and the corresponding error functions for the minimum error distribution between the experimental data and predicted data for crude oil removal using CCAC$_{KOH}$ is given in Table 5.

Table 5. *Predicted kinetics by minimizing the error distribution using six different error functions for CCAC*$_{KOH}$.

Pseudo-first order	K_f (g/mg.min)	$q_{e,cal}$ (mg/g)	(O. F)
MPSD	0.478049	4857.60800	3.44564×10^{-08}
HYBRID	0.430700	4858.09200	5.74776×10^{-20}
ARE	0.430929	4858.08900	1.70548×10^{-09}
EABS	0.473558	4857.64000	0.00055
ERRSQ	0.457800	4857.77400	1.14961×10^{-17}
χ^2	0.490944	4857.52600	1.93604×10^{-14}
RMSE	0.497367	4857.49000	1.04420×10^{-07}
R^2	0.430698	4858.09200	0.84647

Pseudo-second order	K_s (g/mg.min)	$q_{e,cal}$ (mg/g)	(O. F)
MPSD	0.47805	4857.18800	2.52653×10^{-06}
HYBRID	0.43170	4857.19300	4.07298×10^{-10}
ARE	0.43093	4857.19200	4.94635×10^{-07}
EABS	0.44895	4857.19100	0.00025
ERRSQ	0.45780	4857.19000	2.11758×10^{-22}
χ^2	0.49094	4857.18700	1.36242×10^{-27}
RMSE	0.53048	4857.18300	5.11672×10^{-07}
R^2	0.00659	4860.57200	0.99946

Intra-particle Diffusion	K_{ip} (mg/g.min$^{1/2}$)	C (mg/g)	$q_{e,cal}$ (mg/g)	(O. F)
MPSD	1.12815	4848.23500	4857.14100	1.78557×10^{-05}
HYBRID	1.15798	4847.99900	4857.14100	0
ARE	1.13827	4848.15500	4857.14100	1.35813×10^{-07}
EABS	1.12507	4848.25700	4857.13900	0.01489
ERRSQ	1.11833	4848.31200	4857.14100	0
χ^2	1.25800	4847.21000	4857.14100	1.36242×10^{-27}
RMSE	1.12816	4848.23400	4857.13400	0.00252
R^2	1.10792	4848.39400	4857.14000	0.84998

Developed model	β_0	β_1	β_2	β_3	(O. F)
MPSD	4126.19000	0.04078	0.00255	0.04232	6.53655×10^{-07}
HYBRID	4124.85100	0.04097	0.00254	0.04340	3.87513×10^{-16}
ARE	4126.19000	0.04078	0.00255	0.04232	1.30633×10^{-07}
EABS	4126.19000	0.04078	0.00255	0.04232	0.00016
SSE	4124.85100	0.04098	0.00254	0.04340	9.40871×10^{-14}
χ^2	4124.85100	0.04098	0.00254	0.04340	3.87494×10^{-18}
RMSE	4126.19000	0.04078	0.00254	0.04232	7.93529×10^{-05}
R^2	4124.88700	0.04098	0.00254	0.04340	0.99722

(O. F)-Objective function for the minimum error distribution between experimental and predicted data.

From Table 5, the error functions corresponding to the minimum deviations between the experimental kinetics data and calculated data for adsorption kinetics using CCAC$_{KOH}$ suggested that Pseudo-second order model was the best kinetics model with the highest R^2 value of 0.999464 and the least value for other error functions. Intra-particle diffusion model had R^2 value of 0.849982 and Pseudo-first order model had the least R^2 value of 0.846472.

These results emphasize the need for the use of statistical error function to better evaluate the adsorption models, as previously reported by [62, 63]. In addition, it was verified that the calculated q_e values found in the pseudo-second-order model for Table 3 was in conformity with the experimental q_e values which indicated that the pseudo-second-order kinetic model should be considered during the adsorption process of crude oil removal by CCAC$_{KOH}$. By analysing the values of the kinetic parameters as illustrated in Table 3, it should be noted that the k_s values strongly depend on the initial concentration, since its units is g/(mg.min).

4. Conclusions

The adsorption kinetic study showed that the adsorption of crude oil followed a pseudo-second order model for CAC$_{KOH}$ (R^2=0.999) compared to pseudo-first order kinetic model and intra-particle diffusion model and was controlled by film diffusion and governed by the internal transport mechanism. The developed mathematical model was validated by fitting it into the experimental data which gave a better result of correlation coefficient of 0.9972 for CCAC$_{KOH}$ when compared to pseudo first order model, pseudo second order model and intra-particle diffusion model. Hence, an empirical model developed using multivariate numerical optimization method can be used for design of industrial treatment plant.

Declarations of Competing Interest

The authors declare that they have no competing interests.

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