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Endosulfan as Potentiometric Sensor in Kinetic Model of Molecularly Imprinted Polymer (MIP)

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ABSTRACT

Indonesia is an agrarian country with abundant agricultural and plantation land, where farmers often face severe challenge of pests damaging crop yields. To address this challenge, chemical agents such as pesticides and herbicides are used for plant management and care. However, the inappropriate use of these chemical agents poses significant risks to the environment when the prevalence surpasses environmental and human tolerance limits. Pesticides and herbicides containing endosulfan components require proper management to prevent adverse effects on humans and the environment. Therefore, this research aimed to develop Molecularly Imprinted Polymer (MIP) endosulfan pollutant sensors to assess the kinetics of MIP adsorption to endosulfan analyte. Among the various models used for assessment, the Freundlich Isotherm showed optimal results, with an AT value of 1.79 × 10^7 L/mg, B (Constant related to heat of sorption) of 6 x 10^{-8} J/mol, and b (Freundlich Isotherm constant) of 4.13×10^{10}. Furthermore, the obtained distribution coefficient (R2) at 0.9768 was more effective compared to other models.

1. Introduction

Indonesia is an agrarian country with extensive agricultural and plantation land, where farmers often face numerous pests capable of reducing or damaging crop yields. To address this problem, pesticides and herbicides are predominantly used for plant management and care. Pesticides and herbicides are active chemical agents used to eradicate plant pests, which are contaminants for the environment and humans consuming agricultural products [1]. The use of these chemical agents has been projected to rise annually, due to the necessity perceived by farmers to increase crop yields [2]. Meanwhile, the inappropriate use of herbicides containing endosulfan is hazardous, posing a significant risk of contaminating the surrounding environment [3].

Endosulfan is a non-systemic pesticide with a broad spectrum through direct contact or the digestive tract. The effectiveness of endosulfan in controlling various pests has led to its widespread use in fruit and vegetable plantations, flower cultivation, ornamental plants, as well as rice fields.

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However, the use of endosulfan is limited and prohibited in several countries due to its high toxicity to fish and other aquatic biota. In Indonesia, endosulfan is limited to areas not connected to water and is prohibited for use in rice fields. This is because the inappropriate use of endosulfan can cause damage to the aquatic environment including fish poisoning in river basins and traditional shrimp ponds.

In this context, analysis of pesticide residues in food and the environment is required to determine the level of toxicity and risks. The methods that are commonly used to detect pesticide residues are gas chromatography (GC) or high-pressure liquid chromatography (HPLC) [4]. The limitations of both methods include the extraction and purification treatment in the laboratory, which requires solvents and a longer analysis time. To overcome this deficiency, a new method is currently being developed for the analysis of endosulfan pesticide residues using Molecular Imprinted Polymer (MIP) [5-7].

MIP is a synthetic polymer with cavities that are specific for target molecules. These cavities are obtained due to template removal to recognize molecules with the same size, structure, and physicochemical properties. The selectivity and affinity of the template will increase with high concentration values, as shown in the general principles of MIP in Figure 1 [8,9].

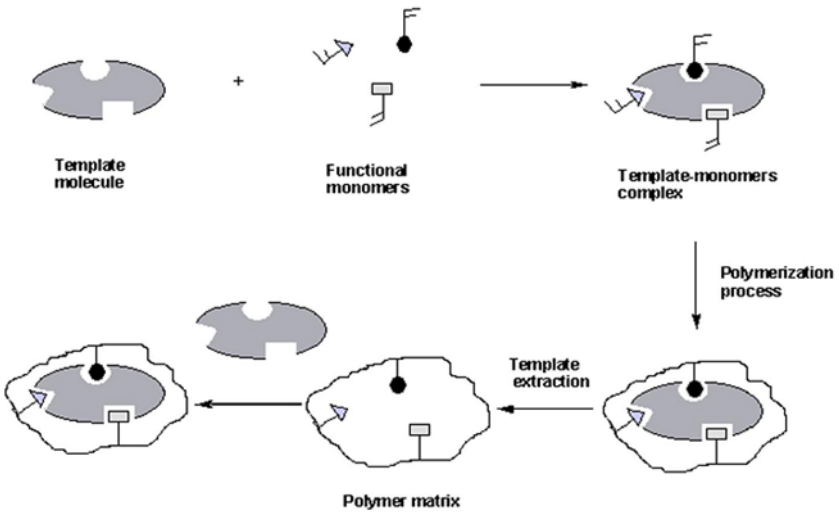

Fig. 1. General principles of MIP formation

MIP is a cross-linking method used to produce polymers with specific cavities, capable of recognizing molecules with the same size, shape, structure, and physico-chemical properties by mechanical interaction based on molecular conformity [10-14]. In MIP synthesis, several parameters must be considered to avoid alteration of morphology, characteristics, and usefulness of polymers. Furthermore, the selection of chemical reagents is important in producing efficient functional MIP.

Polymers that are produced using MIP method can be applied to the surface of the sensor material with high selectivity and effectiveness, speed of response, relatively low cost, and easy operation. Consequently, MIP becomes an analytical alternative as a detection and analyzing instrument. Another advantage is the ability to provide analysis results for pollutants quickly, easily, and reliably in small amounts [15-17].

MIP method is used to make polymer materials that can be applied as sensors to recognize "target" foreign objects, including chemical and biological elements such as those found in medicines and food [18-20]. This method is developed to produce cavities from special molecules that resemble receptor binding in place. After growth, the template is removed and the control polymer is able to recognize the presence of template molecules with a high degree of capability [21]. Due to the

sensing properties, MIP has significant potential for application as sensor materials across various fields.

Sensing properties are part of MIP-based polymers, which depend on the characteristics of the cavities produced. During template removal process, the cavities produced serve as quality indication when polymers have formed as a solid. Subsequently, polymers with cavities that have the same physicochemical properties and spatial shape as the template will be able to recognize the target [12]. Positive results from testing the sensing properties of the MIP particles show that the polymers have the potential to be applied as potentiometric sensors [22,23].

The advantages of this potentiometric method include lower cost compared to other modern scientific instruments, and ease of use across various target molecules. This method is also non-destructive, indicating that inserting the sensor does not change the composition of the test solution. However, potentiometric method is not suitable for cells with high internal resistances, including glass sensors, which function by measuring voltage based on concentration changes in the test solution, namely endosulfan [24].

Templates direct functional groups that depend on functional monomers in all molecular imprinting processes. Although the majority of MIP uses small organic molecules as templates, several larger imprinting structures are still a major challenge in facilitating the removal of binding cavities properly during the printing process. These cavities result from the washing process of the polymers formed using a solvent that dissolves only the analyte molecules. Therefore, MIP polymers serve as active sensor materials with high sensing properties for the analyte or other molecules that have similar physicochemical properties and spatial shapes [12].

The MIP manufacturing process consists of three stages, namely, the polymerization, template removal, and the sensing test. Potentiometric sensors in the form of ion-selective electrodes (ESI) are membrane electrodes that respond selectively to the activity of certain ions [25]. In this research, MIP endosulfan is used as the membrane in the potentiometric sensors to measure the electrode potential of galvanic cells, which depends on the activity of various species included in cell reactions. The relationship is expressed by the Nernst equation, where the characteristics of potentiometric sensors are indicated by several parameters, including immersion time, Nernst factor, concentration range, detection limit, selectivity, response time, and service life. These parameters show the quality of the potentiometric sensor for use as a measurement tool [26].

In this research, a wire electrode consisting of aluminum metal coated with MIP membrane was developed as a sensing agent. Subsequently, aluminum metal was used as a comparison electrode and the notation for potentiometric cell is expressed using equation (1).

Al | analyte solution| |Al (1)

When the left Al functions as an anode, the electrochemical reaction at the left Al electrode is as shown in equations (2) and (3).

$Al \rightarrow Al3+ + 3e \quad (E_{left})$ (2)

Al | analyte solution| |Al (3)

When the right Al functions as a cathode, the electrochemical reaction at the right Al electrode is shown in equations (4) and (5).

$Al3+ + 3e \rightleftharpoons Al \quad (E_{right})$ (4)

$$E_{cell} = E_{left} + E_{right} + EM \quad (5)$$

with the provisions: EM = membrane potential
since: $E_{left} = - E_{right}$
then: $E_{cell} = E_{membrane}$

MIP evaluation was carried out using several mathematical models that estimate adsorption interactions, namely the Langmuir Isotherm, Freundlich Isotherm, Temkin Isotherm, and Dubinin-Radushkevich (DRK) Isotherm models. In batch systems, the Freundlich Isotherm and Langmuir Isotherm models are most often applied.

Adsorption kinetics explains the rate at which adsorbate molecules bind to MIP surface, using reaction order. The Langmuir isotherm model describes monolayer adsorption, assuming that all adsorption sites have an equal template affinity, without affecting each other. Meanwhile, the Freundlich isotherm model assumes that the adsorption process occurs on a heterogeneous surface, with capacity based on adsorbate concentration. When the adsorbate concentration increases, the adsorption capacity will also increase. The Temkin isotherm model incorporates adsorbent-adsorbate interactions by ignoring the concentration value (low or high), assuming that the heat of adsorption (a function of temperature) of all molecules in the layer decreases linearly. The DRK isotherm is generally applied to express the adsorption mechanism with Gaussian energy distribution onto heterogeneous surfaces. This model is usually applied to differentiate physical and chemical adsorption on metal ions with the average free energy per adsorbate molecule to remove a molecule from its location in the adsorption space to infinity.

2. Methodology

2.1 Materials and Equipment

The material used in this research included a pre-polymer solution which was a mixture of endosulfan, methacrylic acid (MAA) from Sigma-Aldrich, ethylene glycol methacrylic acid (EDMA), and benzoyl peroxide (BPO) from Merck, functioning as template, monomer, cross-linker, and initiator, respectively. BPO was selected due to its cost-effectiveness and stable free radicals, facilitating reactive interaction with monomer molecules [1]. Previous research has established that the selection of the right cross-linker and solvent will affect the resulting polymer [1]. Furthermore, the tools used are an Ag/AgCl reference sensor, voltmeter, and potentiometer.

2.2 Measurement Stages

This research aimed to develop endosulfan MIP for application as a sensing layer in a potentiometric sensor. The developmental phase included several stages, namely making of NIP (Non-Imprinted Polymer), MIP, templates, and MIP-based sensor bodies, as well as the process of placing MIP on the sensor surface, and measurements using MIP sensor through potentiometric method. The measurement stages using potentiometric method included preparing a standard endosulfan solution with the lowest to highest concentrations, from 0.1×10^{-3} ppm to 1.0×10^{-3} ppm. This was followed by measurements for each solution on the first day until potential changes occurred, including on days 20, 45, and 90. Moreover, the length of potential stability is required to determine the lifetime of the sensor. Table 1 shows the operating condition during the measurement process, while the equipment used for potential measurements is presented in Figure 2.

Table 1
Operating conditions during measurement with assumptions

Parameter	Value
Ambient Temperature	22-30°C
Pressure	760 mmHg
Relative Humidity	58-60%
Current	Range 20 mA/0,01 mA DC and Range ~500 mA/0,01 mA AC

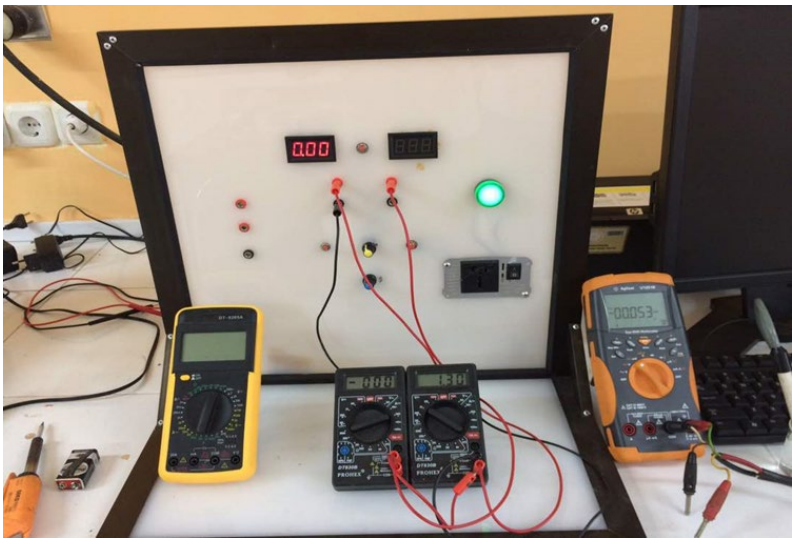

Fig. 2. Potential measurement equipment

3. Results and Discussions

3.1 Determination of Steady State Measurement Conditions with Endosulfan MIP Sensor

Steady and non-steady state profiles were determined to evaluate the constant current value at the time of measurement, which was used as measurement area. This profile was determined by measuring several concentrations of standard endosulfan solutions at a fixed working potential of 0.6V, using variations in endosulfan concentrations of 0.05×10^{-3} ppm, 0.2×10^{-3} ppm, 0.4×10^{-3} ppm, 0.6×10^{-3} ppm, 0.8×10^{-3} ppm, and 1.0×10^{-3} ppm. The current measurement at each working potential value was carried out three times and the results were recorded at an interval of 2 seconds starting from 0 seconds until a stable current value (steady state).

Based on the measurement profile curve, a working potential of 0.6 V produced steady and non-steady state areas. This curve is shown in Figure 3, indicating that non-steady state condition ranges from 0 to 40 seconds. During the process, simazine degradation occurs rapidly as shown by the change in reduction current at 0 - 40 seconds with a current of 2.3 µA to 0.5 µA. This phenomenon suggests that in the initial state, only endosulfan equilibrium occurs in the electrode-electrolyte solution interface area.

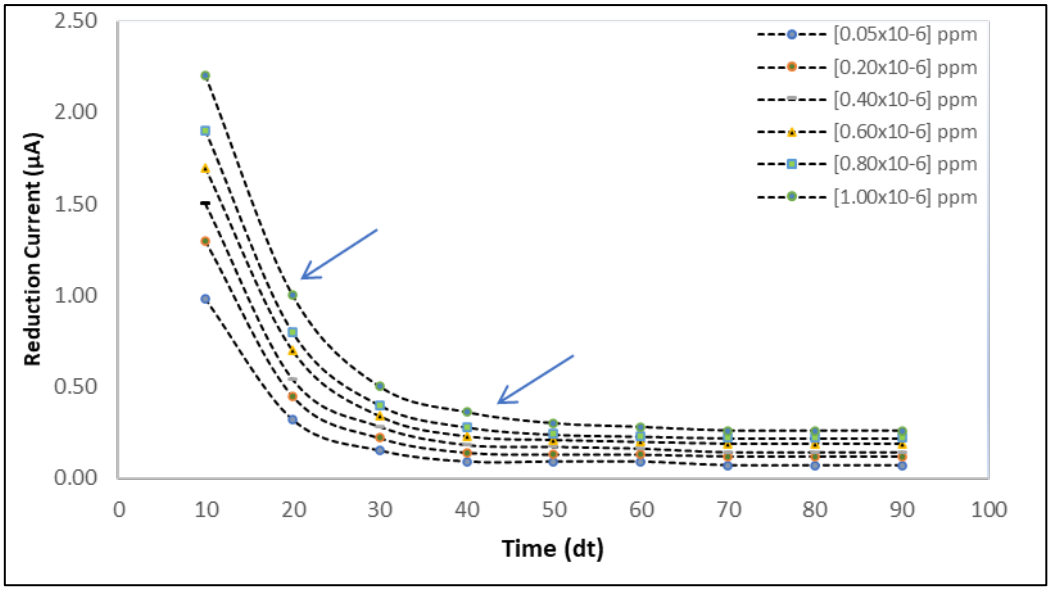

Fig. 3. Steady and non-steady state profile curves for reduced current versus time with a working potential of 0.6V

3.2 Adsorption Kinetics of Aluminum-Carbon (Al-C) Sensors with MIP Endosulfan

This research aims to obtain endosulfan MIP for application as a layer in potentiometric sensors.

3.2.1 Langmuir isotherm

The Langmuir Isotherm absorption capacity presented in Figure 4 showed that decreasing the concentration at each time, using the Langmuir adsorption equation obtained straight line equation y = 13.559x + 4x 106, with R^2 = 0.8982. From this straight-line equation, the Langmuir constant can be calculated, as 2.95 × 10^5 (L/mg), with a maximum adsorption capacity of 2.5 × 10^{-7} (mg/g).

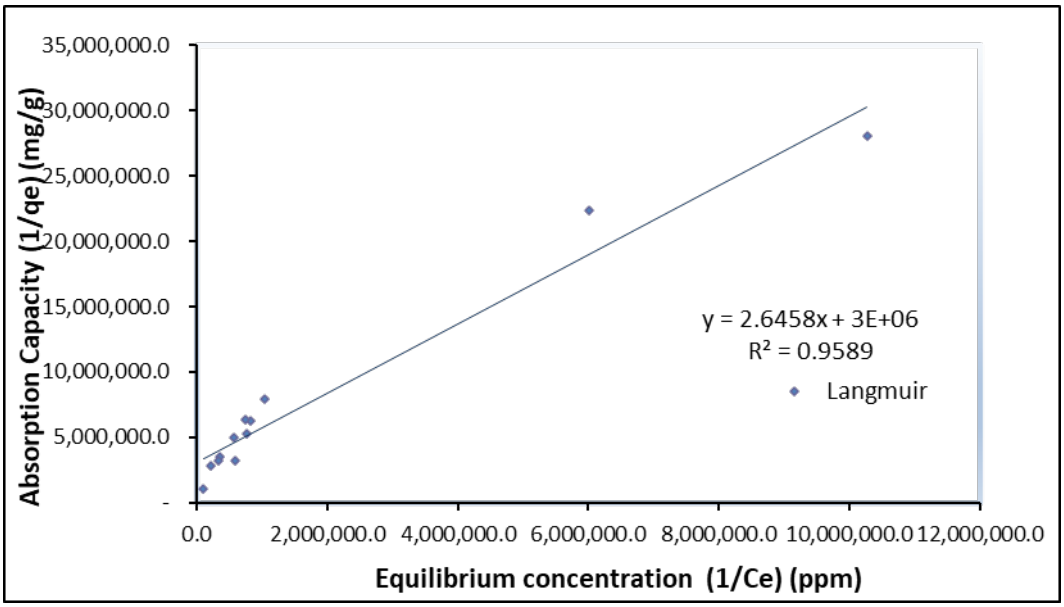

Fig. 4. Langmuir Isotherm for Endosulfan

3.2.2 Freundlich isotherm

The Freundlich isotherm for MIP endosulfan in Figure 5 showed that the R^2 was obtained at 0.9588. Based on these results, the Langmuir isotherm regression value tended to be better compared to the Freundlich isotherm. From the straight line equation y = 2.6458x – 3.3935, the Freundlich constant was calculated as Kf = 4.04×10^{-3} (mg/g), with n = 1.2338. This Freundlich isotherm model has the largest distribution coefficient value compared to other models. Consequently, the kinetic model that is suitable for MIP endosulfan is the Freundlich Isotherm.

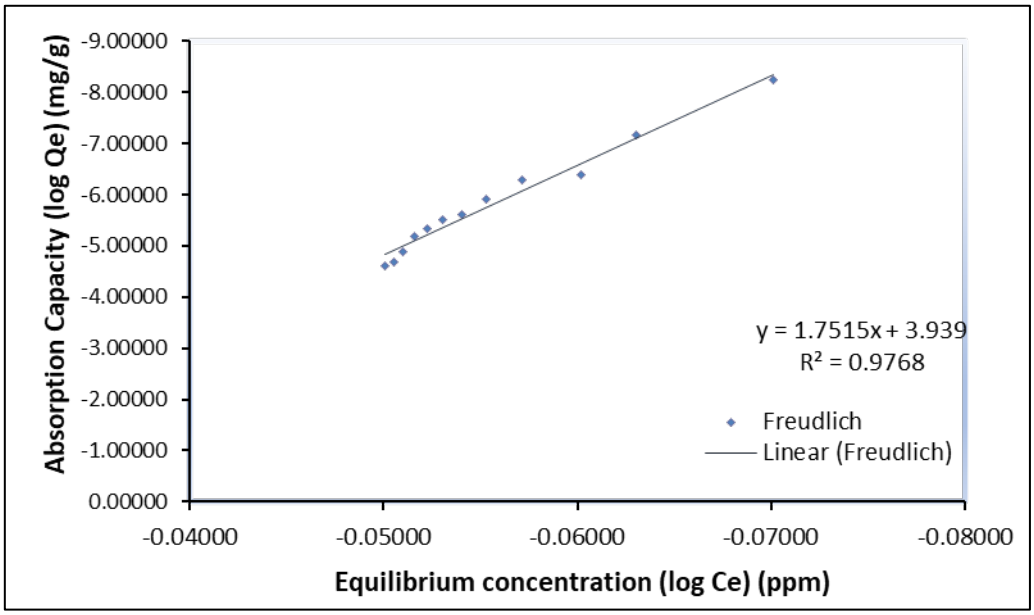

Fig. 5. Freundlich Isotherm for Endosulfan

3.2.3 Temkin isotherm

The Temkin isotherm shows the distribution of bond energy that occurs during the adsorption process. As shown in the equation, the derivation is characterized by a uniform binding energy distribution to certain maximum binding energy. This derivation is carried out by modifying the equation of the absorbed quantity (qe) regarding ln Ce, with constants determined from the slope and intercept.

From Figure 6, the equation shows an AT value of 1.79×10^{7} L/mg, with a B (Constant related to the heat of sorption) of 6×10^{-8} J/mol and b (Freundlich isotherm constant) of 4.13×10^{10}. Furthermore, the distribution coefficient obtained (R^2) at 0.9186 was greater compared to other models.

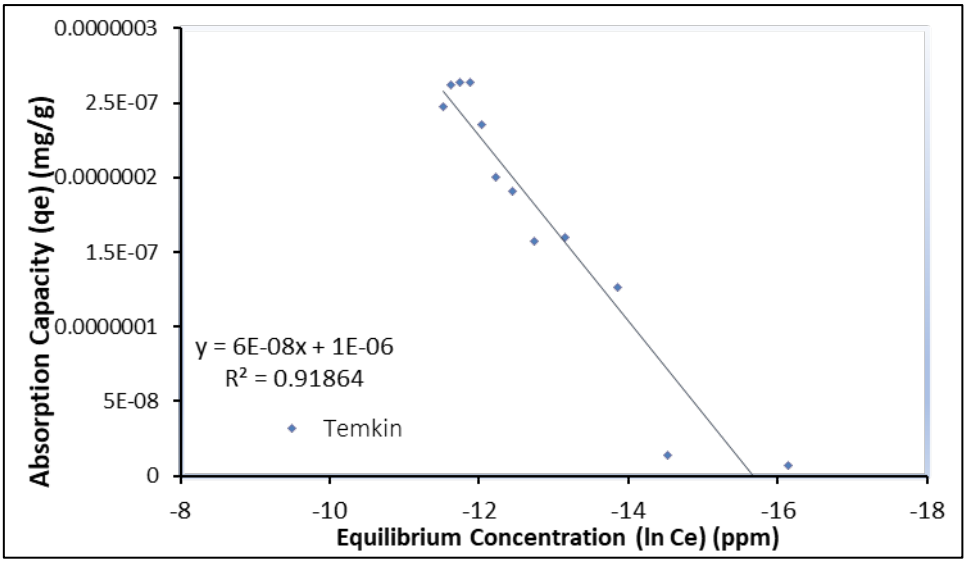

Fig. 6. Temkin Isotherm for Endosulfan

3.2.4 Dubinin–Radushkevich isotherm

The Dubinin-Radushkevich (DRK) isotherm is an adsorption mechanism with Gaussian energy distribution onto heterogeneous surfaces. By plotting the data ln qe versus $(\ln(1+1/Ce))^2$, a slope $K_{ad}/(R^2T^2)$ of 0.0298 was obtained, while sorption energy coefficient of 182,923,218 mol^2/J^2 was achieved by entering R of 8.314 J/mol.K and T of 298 K. The intercept obtained was qs = 1.76×10^{-5} mg/g with E (free energy) 1.6533×10^{-6} kJ/mol, which was indicated as a physical adsorption process. Although the R^2 was 0.8909 lower when compared to Temkin and Langmuir adsorption, the value was higher than Freundlich isotherm. (see Figure 7)

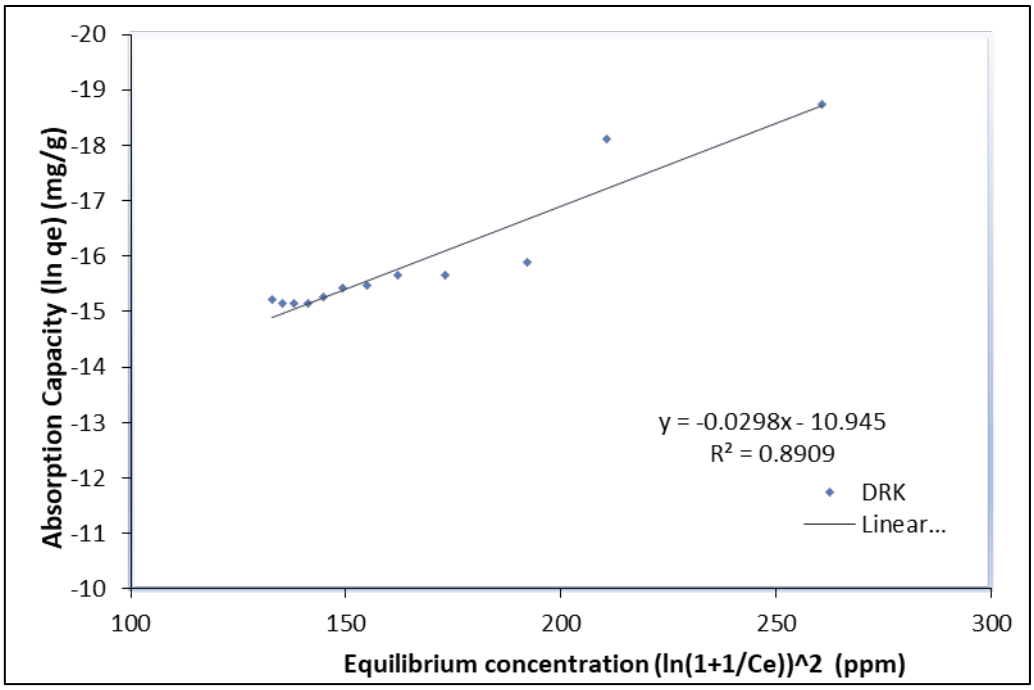

Fig. 7. DRK Isotherm for Endosulfan

4. Conclusion

In conclusion, this research showed that the most suitable adsorption kinetics model for endosulfan was the Freundlich Isotherm. This model had an AT value of 1.79×10^{7} L/mg, with a B (Constant related to heat of sorption) of 6×10^{-8} J/mol and b (Freundlich Isotherm constant) 4.13×10^{10}. Furthermore, the distribution coefficient (R) obtained (R^2) at 0.9768 was greater compared to other models.

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