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Kinetic, Isotherm Studies of the Adsorption of the Congo Red Dye by *Posidonia Spheroids* Plants Sea Balls (PSPSB).

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ABSTRACT

Please This research investigates the kinetics and isotherms of Congo red dye adsorption using low-cost *Posidonia spherical plant sea Balls* (PSPSB), without any chemical or physical treatment. The study evaluated some physical properties such as moisture content, and solubility. Moreover, the effect parameters, including pH, adsorbent dose, contact time, and initial dye concentration, were examined for their effects on the adsorption process. The optimal pH for adsorption was found to be 3. The percent removal(%) of the dye increased with the increasing adsorbent doses and initial dye concentrations until reaching the equilibrium state. The contact time to equilibrium was 20 minutes, and the adsorption capacity maximum reached 49.96 mg/g. Kinetic reaction results indicated the adsorption process followed a pseudo-second-order reaction model more fit than a first-order model. Isotherm analyses showed the adsorption process fit with Freundlich isotherm, suggesting that the adsorption process is multi-layered and occurs on a heterogeneous surface. The findings confirm that PSPSB are adsorbents effective for removing various pollutants, including dyes and heavy metals, from aquatic environments.

دراسة حركية وازوثيرم امتزاز صبغة الكونجو الحمراء بواسطة نبات كرات البحر (*Posidonia Spheroids*)

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الكلمات المفتاحية:
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الكونجو الحمراء
الايزوثيرم
الحركية
نبات كرات البحر

الملخص

يبحث هذا البحث الحركية والإيزوثيرم لامتزاز الصبغة الحمراء في الكونغو باستخدام كرات البحر الكروية منخفضة التكلفة من *posidonia spherical* (PSPSB) ، دون أي معالجة كيميائية أو فيزيائية. قيمت الدراسة بعض الخصائص الفيزيائية مثل محتوى الرطوبة والقابلية للذوبان والرقم الهيدروجيني ومحتوى السليلوز والمحتوى الرمادي ومحتوى الرطوبة . علاوة على ذلك، تم دراسة العوامل المؤثرة على عملية الامتزاز ، بما في ذلك الرقم الهيدروجيني، وكمية المادة المازة، ووقت التلامس، وتركيز الصبغة الأولي، للتأكد من تأثيرها على عملية الامتزاز. حيث وجد أن الرقم الهيدروجيني الأمثل للامتزاز هو3. ولوحظ زيادة نسبة إزالة الصبغة (٪) مع زيادة كمية المادة المازة وتركيزات الصبغة الأولية حتى الوصول إلى حالة الاتزان . وكان وقت التلامس للتوازن 20 دقيقة، ووصلت سعة الامتزاز إلى 49.96 مجم/جم. وأشارت نتائج حركية التفاعل إلى أن عملية الامتزاز توافقت مع نموذج التفاعل من الدرجة الثانية الزائفة أكثر ملاءمة من نموذج الدرجة الأولى. وأظهرت نتائج Isotherm أن عملية الامتزاز تتناسب مع Freundlich isotherm، مما يشير إلى أن عملية الامتزاز متعددة الطبقات وتحدث على سطح غير متجانس. تؤكد النتائج أن (PSPSB) هي مواد امتزازيه فعالة لإزالة الملوثات المختلفة، مثل الأصباغ والمعادن الثقيلة، من بيئاتها المائية.

1. Introduction

Pollution refers to the introduction of harmful pollutants into various environmental domains such as water, air, and soil, leading to ecological disruption and damage. These pollutants may be either foreign substances to the environment or natural substances present

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in elevated concentrations. Among various types of pollution, water pollution is particularly significant due to the critical role water plays in the life of organisms. Water contamination manifests in several forms, including poisoning from organic waste, pesticides, detergents, nutrient pollution, thermal pollution, and contamination from petroleum products, all of which result from various industrial activities [1]. Environmental pollution is a serious problem facing humans in modern life. These problems have emerged as a result of human technological, industrial and civilized progress. Thus, the problem of aqueous solution pollution has received great attention from researchers [2]

pollution is becoming a big environmental problem and a serious concern for researchers. It is found in several forms such as water pollution, air pollution, soil pollution, Noise Pollution and Radioactive pollution etc, water pollution is mow a sensitive topic due to water is important for life [3].

Dyes are organic compounds used to impart color to textiles, leather, paper, and other materials. The compounds used for dyeing typically contain conjugated systems of double bonds, with the color-producing group known as the chromophore [4]. Congo red is an azo dye that is particularly hazardous, as exposure to it can lead to cancer among other health issues [5]. In the adsorption process, the atoms or molecules of a substance (sorbate) adhere to the surface of another material (adsorbent), forming a multi-layered film. Adsorption is a key method for removing pollutants from water [6]. Various marine plants and shells, such as coconut shells, palm kernels, and olive residues, have been utilized to mitigate water pollution by adsorbing industrial pollutants, including dyes and heavy metals, through physical and chemical methods [7]. This research aims to investigate the use of the marine plant *(PSPSB)*.to remove Congo red dye from aqueous solutions, providing a sustainable and cost-effective method for environmental protection.

2. Materials and Methods

2.1 Chemicals

Hydrochloric acid (HCl), Sodium hydroxide (Na OH) from ChiMiE Plus Laboratories, Congo red dye from T-Baker Chemicals.

2.2 Instruments

Memmert laboratory oven (Model L 600, Germany), Adam electronic balance (AAA 250L), Moulinex Mill electric grinder, Retch equipment, Germany, ASTM standards Sieve 0.5mm) , Uv-Visible spectrophotometer (Jenway 6305, UK) were used. Altay Filter papers (12.5 cm), Thermo electronic pH/conductivity meter, Electronic vibrator. (Electron Corporation, USA).

2.3 Preparation of Adsorbent PSPSB

2.3.1 Materials Preparation;

Posidonia spheroids plant sea balls (PSPSB) were collected from various coastal locations along the region extending from 30 kilometres west of Sirte to Sawawh (village east of Sirte city) city, east of Sirte city. The collected samples were thoroughly washed with tap water followed by multiple washes with distilled water. Subsequently, the samples were treated with diluted nitric acid to activation, dried, and ground and sieved to obtain a particle size range of 0.125-0.063 mm. To ensure the removal of any residual contaminants, the samples were washed again with distilled water and acid. The pH was adjusted to 7 using a pinch suppression method.

2.3.2 Preparation of Adsorbate:

A solution of Congo red dye was prepared by dissolving 1 gram of the dye in distilled water within a 1 litre volumetric flask. The solution was then diluted to the mark with additional distilled water to achieve a concentration of 1000 ppm. as a base solution. The following solutions were prepared (1,3,5,7,10 pm) and absorption was measured by the ultraviolet device at 450-500nm wavelength and plot the relationship between absorption and concentration.

2.4 Characterization and Analysis of Some Physical Properties of Adsorbent:

2.4.1 Measurement Procedures

Humidity levels were measured, and the pH of the adsorbent was determined using established methods. The solubility of the adsorbent was assessed according to standard protocols, while the ash content was measured as per the methodology outlined by A. W. Verla. The cellulose content was also measured following the procedures specified in the literature [8].

2.4.2. Point of zero charge (pHpzc)

The point of zero charge for (PSPSB) was determined by using 0.1 N NaCl solution. 50 ml of 0.1 N NaCl solution was added into a series of flasks of 250 ml. Initial pH values of 0.1N NaCl solutions were adjusted from 2 to 10 by the addition of 0.1 M NaOH or 0.1 M HNO3 solutions. 0.5g of (PSPSB) was introduced into each flask and these flasks were allowed to equilibrate for 48 hrs in a shaker at room temperature. The pH was measured again and the difference between the initial pH (pH_i) and final pH (pH_f) values was plotted against the pH_i [9].

2.4.3 Ash Content.

Ash content is determined according to the reference [7], in which, 1.0 g of dried PSPSB was placed in a ceramic crucible and transferred to a muffled oven at 1000 °C for 1 h. Ash content was calculated using the following formula:

$$\text{Ash}\,\% = \frac{W_{\text{ash}}}{W_{\circ}} \times 100 \quad \text{-----------(1)}$$

2.4.4. Solubility in aqueous solutions.

To determine the solubility of natural samples (PSPSB).in aqueous solutions, 0.50 grams of (PSPSB).was placed in an Erlenmayer 'beaker with a ground plastic plug containing 100 ml of distilled water, Shake the mixture for 1 hour at 60 ° C. The mixture was filtered and 5 ml of the filter solution was in a glass plate of known weight and dried at 105 ° C in the oven until a steady weight was reached. The following formula 2 was used:

$$\text{Solubility}\,\% = \frac{\text{weight difference}\times 100}{0.5\times 5} \times 100 \qquad (2)$$

2.5 Batch adsorption experiments.

The batch method was employed to investigate the adsorption process using *(*PSPSB*)* as the adsorbent material for the removal of Congo red dye from aqueous solutions. Each experiment was conducted under uniform conditions. Specifically, 0.1 g of the adsorbent was added to 50 mL of dye solution with an initial concentration (C_0) of 100 ppm. The mixture was agitated at a constant speed of 150 rpm for 90 minutes to reach equilibrium. The effect of pH on the adsorption process was evaluated by preparing Congo red dye solutions at various pH levels (3, 5, 7, 10, and 12).

Furthermore, the impact of different dye concentrations (30, 50, 100, 200, and 300 ppm) was studied under optimal pH conditions, adsorbent dosage, and contact time. The adsorbent dosage was varied (0.1, 0.3, 0.5, and 1 g) under the same conditions. Following the adsorption process, the solutions were filtered to obtain clear solutions. The residual dye concentration was measured using a dual-beam UV-Vis spectrophotometer at a wavelength of 499 nm. The adsorption capacity (q_e) and percentage removal ratio (%) were calculated using the following

$$q_e = \frac{C_o - C_e}{M} \times V \quad \text{…………..(3)} \quad \text{adsorption capacity}$$

$$\%\,R = \frac{C_o - C_e}{C_o} \times 100 \quad \text{………..(4)} \quad \text{Percentage removal}$$

3. Results and discussion.

3.1 Results of Physical Properties of PSPSB

Several physical properties of PSPSB were identified, including pH, moisture content, ash content, cellulose content, and solubility. The results are summarized in Table 1. The pH value of the *(PSPSB)*was found to be acidic (3.01), The solubility of (PSPSB) was lower. This is favorable in aqueous solutions as shown in the literature [10]. The cellulose content, which is crucial for the chemical composition of plant fibres provides strength and stability. According to the results in Table 1, the cellulose content was 6.5%, indicating that the physical properties of *(PSPSB)* are conducive to use as an adsorbent[11]

Table 1: Physical Properties The *Posidonia spheroids* (PSPSB).

Properties	results
pH	3.7
Particles size	0.125-0.063mm
Solubility	5.3 g/l
Cellulose	6.5%
Ash content	0.948%
Moisture	5.35%

The high moisture content suggests persistent mechanical properties High value of moisture content results in instability and poor mechanical properties for plants. Chemical treatment can reduce the moisture content, and this results in better mechanical properties [12], which can be improved through chemical treatment and processing. The ash content was very low (0.948%), indicating minimal metal pollutants [13]. The granule size ranged from 0.125 to 5 mm, and the experiments were conducted in relatively dark conditions to prevent light.

3.2 Determine of pH at zero charge of PSPSB

The Zero point pHpzc (pH at zero charge) is used to understand the adsorption mechanism and the types of active places to the surface and inactive places where we find that the charge is equal to any negative concentrations and positive on the surface the pH (between 7-8), and when PH < PHz the surface charge is positive and when PH > PHz the surface charge is negative and therefore the surface is suitable for dyes adsorption or any positive pollutants (Figure 1).

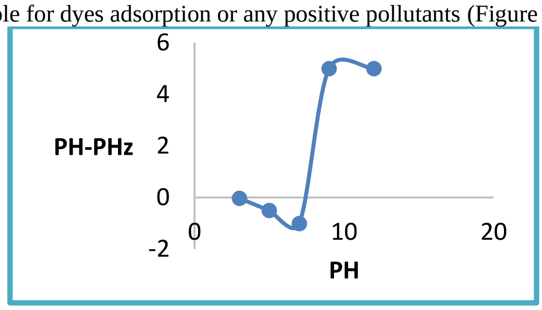

Fig. 1: The degree of pH equivalent of PSPSB.

3.3 Study of the Factors Affecting on Adsorption Process:

3.3.1 Effect of the pH

From Figure 2, the results showed the pH function had a different effect on the adsorption dye as evidenced by Figure 2 "a" & "b" the amount of adsorption of the Congo's red dye increased when the solution was acidic PH 3 while decreased when the solution is more alkali). This can be explained by the fact that the surface used has negative charges and the dye in the acidic medium carries a positive charge.

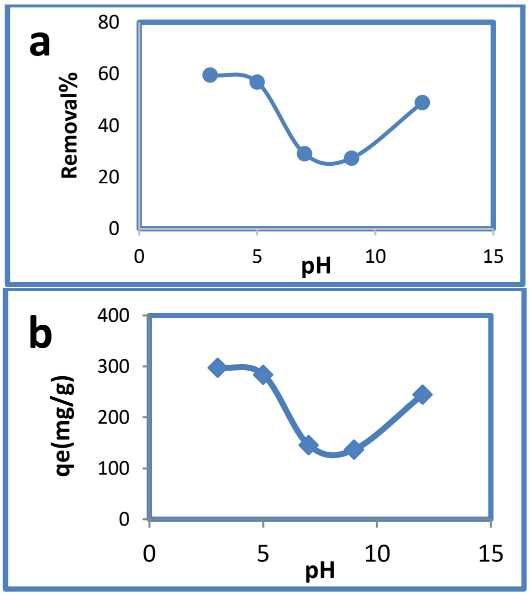

Fig. 2: The effect of pH on the adsorption of Congo's red dye

2.3..2 Effect of Adsorbent Dose.

Figures 3 "a" & "b" Show the removal percent (%) and adsorption capacity q_e (m/mg) under the effect of the adsorbent dose of the (PSPSB) by Congo red dye, Adsorption capacity at different doses were experimented with (0.1, 0.3, 0.5, 1g), It has been observed that the adsorption capacity of the dye is affected by increase the dose, at the dose (0.3g) recorded the highest adsorption capacity of the dye while at the dose (1g) was lowest, the percent removal (%) was had been opposite with results of adsorption capacity This may be due to the availability of more surface area with the higher dose (PSPSB) in solution.[14]

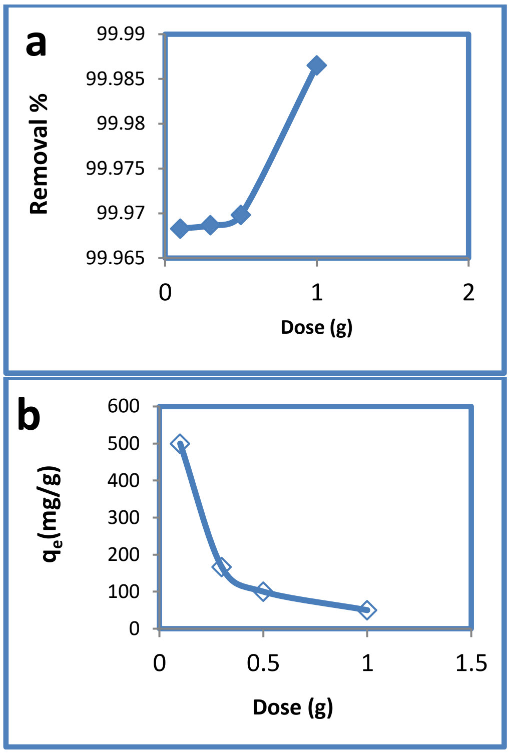

Fig. 3: Effect of adsorbent dose on the adsorption of Congo's red.

3.3.3 Effect of the Contact. Time

From Figure 4 "a" & "b" percent removal (%) and adsorption capacity q_e (m /mg) the absorbability of dye on the surface of the (PSPSB) up to reach equilibrium and it was observed that the time for equilibrium to occur is (20 minutes). The mechanical reaction is explained by the migration and movement of dye particles from the solution to the adsorbent surface by the effect of distribution and dispersion forces until they reach the state of equilibrium**.**

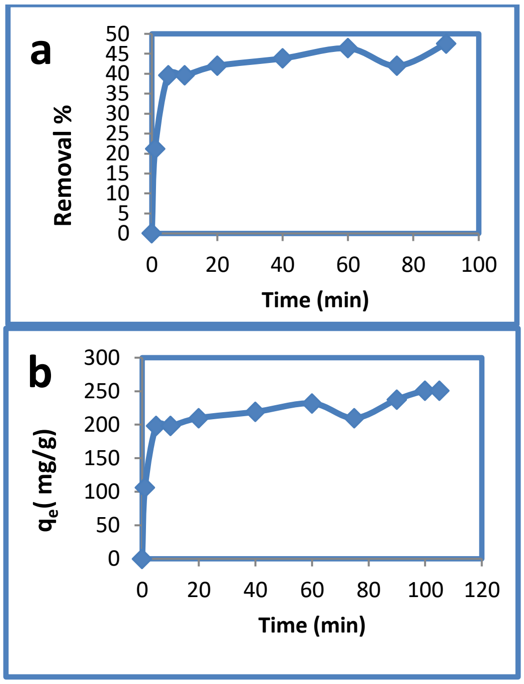

Fig. 4: Effect of contact time on the adsorption of Congo's red.

3.3.4 Effect of the Initial Concentration

Figure 5 "a" & "b" Show removal percentage (%) and adsorption capacity q_e(m/mg) under the effect of initial concentration on the adsorption process by different concentrations of dye while stabilizing the rest of the conditions of the dose of the adsorbent, pH, temperature, and speed of the shake, respectively (0.1 g, PH = 7, 25, 150 r.p.m at room temperature 25 °C) It was observed that the adsorption capacity increases with the increase of initial concentration then equilibrium, while the percentage of removal (%) decreased with increase the initial concentration up to the saturation.

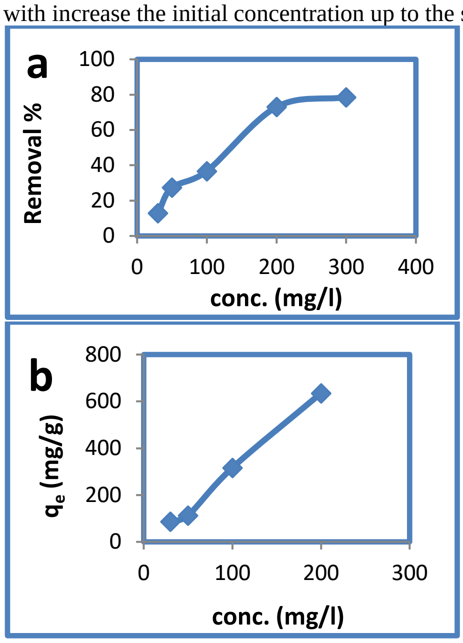

Fig. 5: Effect of initial concentration on the adsorption of Congo red.

3.5. Adsorption Kinetic

3.5.1 Pseudo First Order

Pseudo First rate reaction adsorption of Congo dye by *(PSPSB).*

Table 2: The first-rate reaction of the Lagergren constant.

First order	R^2	K_1	$(q_e)_{cal}$	$(q_e)_{exp}$
	0.5537	0.0169	689	316
Second order	R^2	K_2	$(q_e)_{cal}$	$(q_e)_{exp}$
	0.991	0.041	49	316

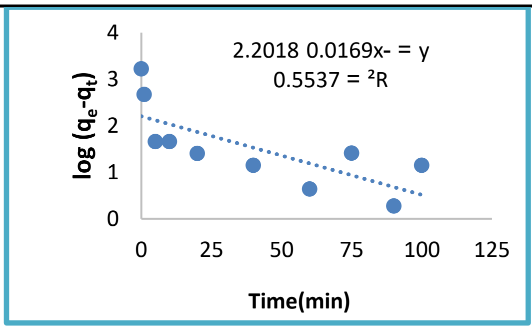

Fig. 6: Pseudo first-order reaction model Lagergren of conge red.

An adsorption kinetic study is considered important and gives a clear picture of the prediction of the adsorption rate. It is given important information to visualize the design and model of the adsorption process. It involves the first-order interaction and the second-order interaction that we use to evaluate the adsorption mechanism of the dye on the sea ball [15].

The first-order equation was derived by the World Lagergren for a liquid/steel system and depends on the adsorption capacity of the solid state.

$$\text{Log}\ (q_e - q_t) = \log q_e - (k1/2.303)\ t$$

Where q_e, q_t represents the adsorption capacity at equilibrium and time respectively and the tendency and intersection resulting from the Log (q_e- q_t) against t(time adsorption process) at different concentrations. The plots of Congo red dyes showed Figure 6 to be used to determine k_1 and $q_{e\ Cal}$ (calculation adsorption) [16], and K_1 (first-rate reaction factors) were shown in Table 2.

3.5.2 pseudo-second order

Pseudo-second order reaction(Ho:s model) adsorption of Congo dye by *(PSPSB)* model.

The second-order reaction was hypothesized by the high HO and MCkay where it depends on the adsorption capacity of the solid state and the equation was as follows: -

$$t/q_t = 1/k_2 q_e \quad +1/q_e \quad t$$

where the K_2 is (constant second rate reaction),qe (equilibrium adsorption), and t (time adsorption).

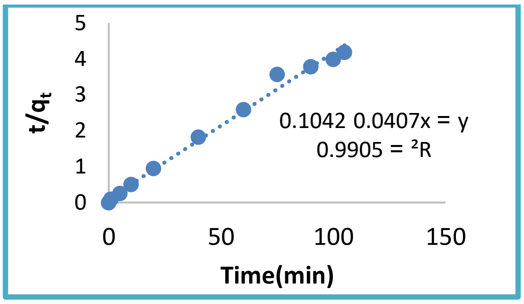

Fig. 7: Pseudo-second order reaction model for coarse red dye.

The linear relationship between t/q_t against t The plots of Congo red dyes showed Figure 7, is used to designate q_e and k_2 from inclination and intersection [11] Through the R^2 values shown in Table 3, we note that R_2 for the second reaction is higher than R^2 for the first reaction. We also note the value of X^2 in the second reaction is less than the first order. s model) exemplifies the methylene dye adsorption process by (PSPSB) that the main second order is more fit, [17].

3.6 adsorption Isotherm

Table 3: Values of Langmuir and Frendlich isotherm.

Langmuir isotherm	R^2	R_L	b	q_m	T
	0.897	0.970	0.0003	53.4	25ºC
Freundlich isotherm	N	R^2	1/n	K_f	T
	1.8	0,979	0.551	4419	ºC25

3.6.1-Langmuir Isotherm

Langmuir isotherm assumes that the molecules adsorb on a fixed number of well-known vacuoles on the surface of the adsorbent material. These cavities are energetically equivalent and each vacuole can carry only one adsorbent molecule. The molecules adsorbed on the surface do not interfere with each other or with other molecules present in the solutions, and thus one layer of the adsorbed molecules will form on the surface of the adsorbent material [18].

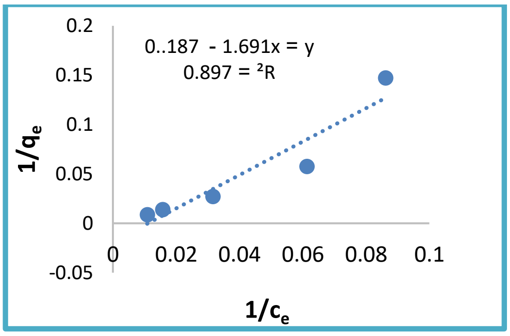

Fig. 8: Langmuir adsorption isotherms of conge red.

Equation of the Langmuir: -

$$1/qe = 1/q_m.b\ Ce + 1/q_m$$

Where b is constant for Langmuir and q_m (maximum adsorption capacity) and E (concentration of equilibrium)

By observing the isotherm in Table 3, and The Langmuir isotherm shown in Figure 8 for Congo red it is highly experiment-compatible and thus homogeneous adsorption. Given the RL value we find less than 1, adsorption is acceptable and confirms that adsorption is one of the most powerful on the surface.

3.6.2 Frendlich Isotherm.

Frendlich is an experimental model and applies to heterogeneous, layered surfaces and different energetic places.

Frendlich Equation:

$$\text{Log}\ q_e = \log K_f + 1/n\ \text{Log}\ C_e \quad \text{----------------1}$$

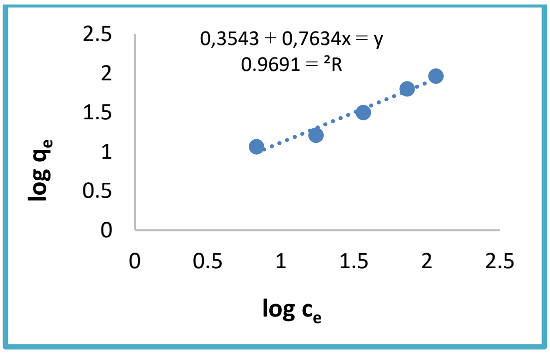

Fig. 9: Frendlich adsorption isotherm of Congo dye.

The k_f constant balance and 1/n coefficient of heterogeneity are related to the severity of adsorption on the surface of the adsorbed and through the data in Table 3 of the isotherm dye Congo red and showed in Figure 9 for dye the value of 1/n according to Table 3 is less than one indicates that the adsorption mechanism is relatively strong between the dye and the surface of the adsorbing material, The n value is higher than one indicating that adsorption conditions are acceptable.

4. Conclusion

In conclusion, this study demonstrates that the bio-adsorbent derived from (PSPSB), commonly known as sea balls and considered low-cost agricultural waste, effectively removes Congo red dye from aqueous solutions. The optimal pH for maximum dye adsorption was determined to be 10. Additionally, the particle size of the bio-adsorbent influenced the adsorption efficiency(, dried, ground and sieved to obtain a particle size range of 0.125-0.063 mm).

Equilibrium in the adsorption process was achieved in approximately 20 minutes. The adsorption isotherm data were best described by the Freundlich model, indicating that the adsorption mechanism was predominantly physisorption. Furthermore, the kinetics of the adsorption process followed the pseudo-second-order kinetic model, according to Ho's model, suggesting that this model most accurately describes the rate kinetics of the process. The findings indicate the ability of *PSPSB* as a promising material for the removal of pollutants, such as Congo red dye, from water environments.

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