

Kinetic and equilibrium isotherm studies for the removal of acid blue 113 dye by dried *corallina officinalis* alga as a novel eco-friendly adsorbent

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Abstract. Water pollution is an alarming problem in developing countries. Dried algae can be considered as potential and suitable bio-sorbents due to their fast and easy growth and high availability. The special surface properties of these algae allow them to adsorb different types of organic and inorganic pollutants from solutions. In this context, the removal of anionic acid blue 113 dye (AB113) from aqueous solutions by dried *Corallina officinalis* alga as low-cost bio-sorbent was chosen as a case study of a typical remediation process of water contaminants. The effect of various environmental and physicochemical parameters has been studied. The results show that the equilibrium adsorption was established within 120 min. The sorption phenomenon was investigated by determining the process kinetics at different concentrations and the adsorption isotherms at different temperatures. The kinetics results showed that the pseudo second-order kinetics model generates the best agreement with the experimental data. The modeling results showed that linear Langmuir and Freundlich models appear to fit the adsorption data better than Temkin model for the adsorption of AB113 onto dried *C. officinalis* alga. It can be concluded that *C. officinalis* alga can be successfully used as adsorbent.

1 Introduction

Water pollution that affects rivers, seas, groundwater and lakes is the result of the discharge of wastewater without treatment or with insufficient treatment: this causes degradation of the ecosystem. The problem is even more serious in the case of industrial effluents, which have a much more pronounced toxic character. Various industries such as textile, paper, leather tanning, plastic, food, polymer, and printing are considered major sources of dyes because these industries use dyes in their coloring processes. Two percent of the produced dyes are discharged in the effluent. In addition, 10 % of dyes are lost in the textile dyeing. The dye concentrations in wastewater are approximately 10–200 mg L⁻¹ [1]. Discharge of these industrial effluents, even at very low concentrations, into the receiving environment causes many important problems such as increased toxicity and chemical oxygen demand of the effluent, as well as reduced light penetration. Industrial effluents such as dyes are mutagenic, toxic, allergenic, carcinogenic, and non-degradable, which create serious problems [2]. In order to reduce the negative effects of wastewater contaminated with organic pollutants on humans and the environment, wastewater must be carefully treated before it is discharged into major watercourses. Currently, much attention has been paid to the removal of dyes from industrial wastewater. The removal of these industrial pollutants from liquid waste has been carried out by several physicochemical processes such as coagulation-flocculation, oxidation, membrane filtration and adsorption [3–5]. Conventional processes for wastewater treatment and removal pollutants from aqueous solutions are ineffective and sophisticated

processes are very expensive for developing countries like Morocco. Hence, the need to research new processes whose efficiency and cost would be interesting. The aim of this work was to develop local natural materials for wastewater treatment and particularly for the removal of industrial dyes by the adsorption process. Algae can be considered as potential and suitable adsorbents due to their fast and easy growth and high availability. The special surface properties of these algae allow them to adsorb different types of organic and inorganic pollutants from solutions. The cell wall of algae offers a multitude of functional groups, including amino, carboxyl, sulfate, and phosphate and imidazole groups combined with polysaccharides, alginic acid and proteins for binding various pollutants [6]. Macroalgal biomass is one of the most promising types of bio-adsorbents due to its rigid macrostructure, high uptake capacity and immediate abundance. In our previous works, we have investigated the adsorption of various pollutants including, nitrate, orthophosphate ions, and heavy metal ions such as copper, lead, cadmium and arsenate from aqueous solutions onto micro-particles of dry plants [3,7,8]. In this paper, we have tested the removal of acid blue 113 dye on dried alga *Corallina officinalis* as low cost adsorbent collected from the coast of Agadir region. In this regard, the adsorption kinetics, as well as the adsorption isotherms have been studied.

2 Material and Methods

2.1 Adsorbent preparation

The seaweeds used in the present study for the adsorption tests were collected from the coast of Agadir city. These samples belong to the large family of red

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algae known as *Corallina officinalis*, the species of alga previously mentioned were washed thoroughly with tap water to remove impurities and twice with distilled water. After washing, these samples were air dried for a week, crushed and sieved to the desired particles size (315 μm), then dried again in an oven at 40 ° C until constant weight, and stored in polyethylene bottles for later use. The materials obtained as a result of the preparation steps are used as adsorbent without any pretreatment or modification to avoid additional expenses.

2.2 Solution preparation

The stock solution of acid blue 113 dye used as adsorbate in this study was prepared by dissolving an amount of 500 mg in a volume of 1 liter of double distilled water. The aqueous solution was diluted each time to obtain the desired concentration. The anionic dye was purchased from Sigma-Aldrich and used without any purification. All the compounds used to prepare the reagent solutions were of analytical reagent grade and all experiments were performed with the use of double distilled water.

2.3 Instrumentation

A UV-Vis Spectrophotometer (Jasco, Model V-550, Japan) was used to measure the residual concentration of acid blue dye 113 in solution. The centrifuge HETTICH model EBA 21 was employed in order to separate the dried alga particles from the solution obtained at the end of the adsorption experiments.

2.4 Experimental procedure

2.4.1 Adsorption studies

Various adsorption experiments were performed in the batch system at room temperature, and the choice of this mode is due to its simplicity and reliability. An amount of dried *C. officinalis* alga was placed in a series of Erlenmeyer glass flasks of 100 ml containing 40 ml of dye solution of known concentration and pH. The solutions were stirred vigorously for a given time period to reach equilibrium. The stirring speed was kept constant for each run to ensure uniform mixing. After various contact times (T_c), the resulting solutions were centrifuged at 5000 rpm for 15 min, and the supernatant was filtered through a 0.45 μm membrane filter and the result solution was measured through UV-Vis Spectrophotometer at a wavelength of 566 nm. All the experiments were repeated three times and the results were recorded as the average (error: ± 1-2% for the removal percentage and ± 0.005-0.01 mg / g for the amount adsorbed). Adsorption equilibrium studies were conducted at an initial dye solution pH of ~6.3. The initial concentration of AB113 was varied from 20 mg/L to 300 mg/L at fixed pH and temperature. Equilibrium data were obtained by adding 0.5 g of dried alga into a series of 100 ml Erlenmeyer each filled with 40 ml of AB113 solution after 120 min of contact time.

2.4.2. Analysis of AB113 dye

The removed concentration of AB113 dye was determined by the difference between the initial concentration and the residual concentration at time t. whereas; the removal rate of that dye was calculated through the following equation:

$$\% \text{ Removal} = \frac{100(C_i - C_t)}{C_i} \quad (1)$$

The amount of AB113 dye adsorbed at time (t) per mass unit of alga *C. officinalis* used as adsorbent in this study was calculated from the next equation:

$$q_t = \frac{V(C_i - C_t)}{m} \quad (2)$$

$$q_e = \frac{V(C_i - C_e)}{m} \quad (3)$$

where, C_i (mg/L) is the initial dye in aqueous solutions at time "t"; q_t (mg/g) is the quantity removed per unit mass of *C. officinalis* bio-adsorbent at time "t"; C_e (mg/L) is the equilibrium concentration of the anionic dye in aqueous solutions; q_e (mg/g) is the quantity eliminated per unit mass of *C. officinalis* at equilibrium; m (g) is the amount of bio-adsorbent and V (L) is the volume of the working solution.

3 Results and discussion

3.1 Effect of contact time

The effect of contact time on the adsorption of Acid blue 113 dye was performed for two initial concentrations (20 and 100 mg/L). The impact of contact time on the adsorption of AB113 dye solution at room temperature (23 ± 2 °C) and initial pH value 6.3 is shown in Figure 1. It noted that the uptake adsorbed of AB113 dye retaining by *C. officinalis* surface increases with contact time. This adsorption is very fast in the first 90 min. Then, the adsorption equilibrium is reached after a contact time of about 120 min. The percentage removed of AB113 dye at equilibrium is about 70 %. This result could be due to the high availability of free active sites at the beginning of adsorption process [3,9,10]. This study revealed that the contact time is an important parameter for the adsorption of AB113 dye on *C.officinalis*. Therefore, taking into account these results, the contact time (T_c) was fixed to 120 min for the rest of the batch experiments.

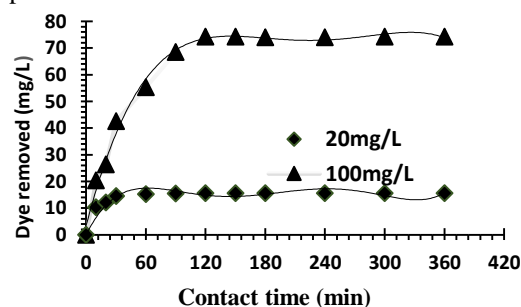


Fig. 1. Effect of contact time on the removal of AB113 dye onto *C. officinalis* alga: $m/V = 12.5$ g/L, $pH_i=6.3$ and $T = 23 \pm 2^\circ C$.

3.2 Effect of initial dye concentration

The initial concentration of AB113 was varied from 20 mg/l to 300 mg/l at fixed pH and temperature. The results are illustrated in Figure 2. The increase in the adsorption capacity is probably due to greater interaction between the adsorbate and adsorbent. At equilibrium (after 120 min of contact time) the adsorption capacity of *C. officinalis* alga increased with the initial AB113 dye concentration in the solution which may be due to more availability of acid dye molecules and the active of the adsorbent have not reached saturation even at initial dye concentrations more than 300 mg/L. Similar results were reported by other researches [11]. The higher amount of dye adsorption at higher concentrations is probably due to increased diffusion and decreased resistance to dye uptake [12]. These results indicate a great potential application of *C. officinalis* alga particles, as a bio-adsorbent to the treatment of industrial wastewaters.

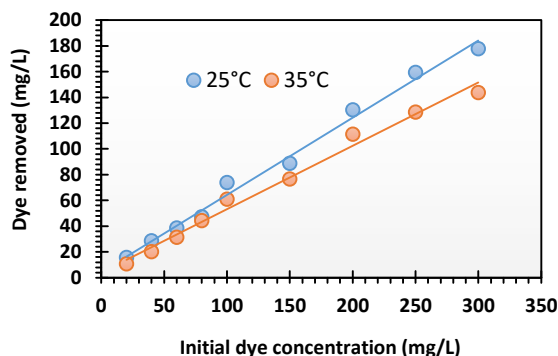


Fig. 2. Effect of initial dye concentration on the removal of AB113 dye: Ratio m/V=12.5 g/L, pH=6.3, T_c=120 min.

3.3 Adsorption kinetics

Designing adsorption treatment systems requires knowledge of kinetic processes due to the many different chemical systems, the nature of the different adsorbents and the different designs of contact systems. These models are mainly used to analyze the adsorption kinetic experimental data. Moreover, the kinetic study allowed the monitoring of the adsorption rate of pollutants, thus clearly controlling the residence time of adsorbate at the solid-liquid interface. Adsorption on dried *C. officinalis* alga was evaluated using kinetic models as expressed below. In this study, two liquid-phase adsorption kinetic models, pseudo-first-order model, and pseudo-second-order model were highlighted.

3.3.1 Pseudo-first order kinetics model

The simplest one which expresses on the proportionality between the anionic dye adsorption and the number of vacant adsorption sites on the surface of biosorbents is Lagergren model (pseudo-first-order). The nonlinear and linear forms of the model are represented in Eqs. (4) and (5), respectively [13,14]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (4)$$

$$q_t = q_e (1 - e^{-k_1 t}) \quad (5)$$

Where, q_t and q_e (mg/g), are the adsorption capacity at any time (t) and at equilibrium respectively. k_1 (min⁻¹) is the pseudo-first-order rate constant. The plot of $\ln(q_e - q_t)$ versus contact time t for the dried *C. officinalis* alga gives a straight line of slope $-k_1$ and intercepts $\ln(q_e)$ (Figure 3). The values of the theoretical adsorption capacity (q_e , cal), the rate constant for the pseudo-first order kinetics model (k_1) and the correlation coefficient (R^2) were presented in Table 1. From the data of Figure 3 and Table 1 it can be observed that the calculated adsorbed amount in case of pseudo-first order kinetics model, are lower than those found experimentally. As well as, the correlation coefficient (R^2) value for both 20mg/L and 100 mg/L used as initial concentration of dye confirm that the pseudo-first order model is not suitable to describe the kinetics of AB113 dye from aqueous solution on the dried alga used as adsorbent.

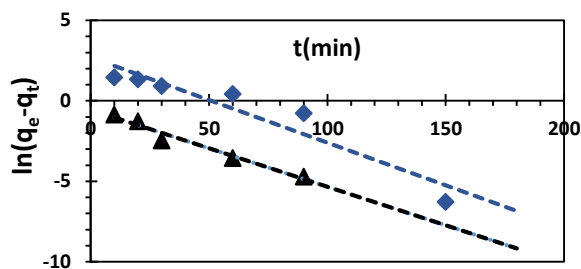


Fig. 3. Pseudo-first order adsorption kinetics of AB113 onto *C. officinalis* alga at different dye concentrations.

3.3.2. Pseudo-second order kinetics model

The pseudo-second order is a kinetic model that represents the correlation between the adsorption of dye and the square of the vacant active adsorption sites on the surface of the adsorbents [15]. This model can be represented with its linear form, and its non-linear form expressed as follows:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \quad (6)$$

$$q_e = \frac{q_e^2 (k_2 t)}{(1 + (k_2 q_e t))} \quad (7)$$

where, q_e and q_t (mg/g), are the adsorption capacity at equilibrium and time (t) respectively. While k_2 is the pseudo-second order rate constant (g/mg min). The plotting of the previous equations curves of the equations allows determining all the parameters of the adsorption kinetics.

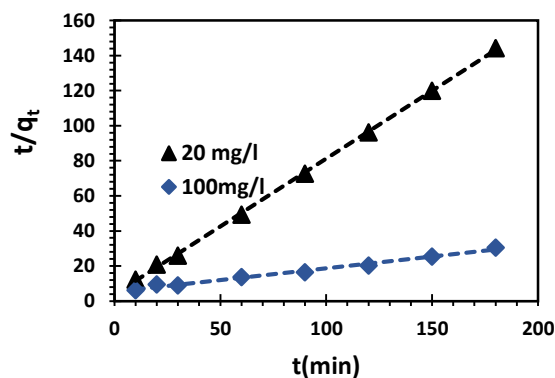


Fig. 4. Pseudo-second order adsorption kinetics of AB113 dye onto *C. officinalis* alga at different dye concentrations.

Table 1. Parameters of kinetic models for AB113 dye adsorption onto dried *C. officinalis* alga at different initial dye concentrations.

Kinetic models	Parameters	A AB113 dye (mg/L)	
		20	100
Pseudo-first order	k_1 (min ⁻¹)	0.048	0.053
	$q_{e,cal}$ (mg/g)	0.57	14.90
	R^2	1.24	5.93
Pseudo-second order	k_2 (g.mg ⁻¹ min ⁻¹)	0.162	0.003.42
	$q_{e,cal}$ (mg/g)	1.29	7.46
	R^2	0,999	0,988
	$q_{e,exp}$ (mg/g)	1.24	5.93

The pseudo-second order plots for AB113- adsorbent system at different initial concentrations are shown in Figure 4 and the kinetic parameters are given in Table 1. The value of R^2 for the pseudo-second-order adsorption model for both initial concentrations is relatively high than 0.99 and the adsorption capacities calculated by this model are also close to those experimentally determined. Therefore, it has been concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption of AB113 dye onto dried *C. officinalis* alga.

3.4 Adsorption isotherms

The maximum adsorption capacity illustrates the relationship between the adsorbed amount and the residual concentration at equilibrium. Today, different theoretical, empirical and sometimes developed models are implemented for this purpose, namely; (i) Langmuir's model, (ii) Freundlich's model, and (iii) Temkin's model. The best model that fits with the experimental data are selected based on the correlation coefficient value (R^2). The first three isotherms remain the most commonly used. The data obtained in this study were then fitted to these latest models.

3.4.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm has traditionally been used to quantify, and contrast the performance of different biosorbents, it was originally developed to describe the gas–solid phase adsorption of activated carbon [16]. Langmuir isotherm is based on certain initial hypotheses that are as follows: the solid adsorbent has a limited adsorption capacity (q_L), all the active sites are identical and they can complex only a single solute molecule (monolayer adsorption) and the absence of interactions between the adsorbed molecules [17]. The module can also be expressed by the non-linear equation (Eq 8) and its linear form expressed in Eq 9.

$$q_e = \frac{q_L * K_L * C_e}{1 + K_L * C_e} \quad (8)$$

$$\frac{1}{q_e} = \frac{1}{q_L * K_L * C_e} + \frac{1}{q_L} \quad (9)$$

where q_e and q_L are both expressed in mg.g⁻¹ and C_e is expressed in mg.L⁻¹, the Langmuir adsorption constant

K_L is expressed in L.mg⁻¹ and related to the free energy of adsorption [7]. The plot of $1/q_e$ versus $1/C_e$ for dried *C. officinalis* alga gives a straight line of slope $1/q_L K_L$ and intercepts $1/q_L$ (Figure 5), the various parameters that characterize the Langmuir isotherm namely, K_L , and R^2 are shown in Table 2. The value of the coefficient of determination for the dried alga was 97 and 98% obtained at a temperature of 25 and 35 ° C respectively, indicating the good fit of Langmuir model to the experimental data related to the adsorption of AB113 dye on *C. officinalis* alga.

Table 2. Isotherm constants for AB113 dye adsorption onto *C. officinalis* alga.

Isotherm of adsorption	Parameters	Temperature	
		25°C	35°C
Langmuir model	q_L (mg/g)	11.79	16.72
	K_L (L/mg)	0.013	$7*10^{-3}$
	R^2	0.971	0.980
Freundlich model	n	1.382	1.057
	K_F (mg/g)	0.398	0.126
	R^2	0.914	0.965
Temkin model	K_T (L.mg ⁻¹)	0.224	0.113
	b_T (J.mol ⁻¹)	8546	774.8
	R^2	0.756	0.770

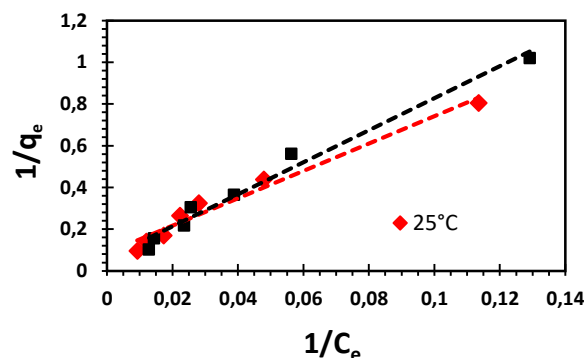


Fig. 5. Langmuir adsorption isotherm for AB113 dye on *C. officinalis* alga at 25 and 35°C.

The adsorption capacity of the adsorbent increased with increasing in the temperature, the highest value of 16.72 mg/g related to the adsorption of dye was obtained at 35°C. While, at 25°C the calculated adsorbent amount was about 11.79 mg/g (Table 2). Additional to the important characteristics of the Langmuir isotherm, another parameter can be explained separation factor R_L also called equilibrium parameter, which is calculated by the equation expressed below [18].

$$R_L = \frac{1}{1 + K_L * C_i} \quad (10)$$

where, C_i (mg/L) is the initial dye concentration and K_L (L/mg) is the Langmuir constant related to the energy of adsorption. The value of this parameter assumes the nature and the feasibility of adsorption process (Table 3). All values of R_L at both temperatures (25 and 35°C) studied range from 0.793 to 0.877 for *C. officinalis* alga used as sorbent of AB113 dye. Therefore, the adsorption is favorable.

Table 3. Nature of adsorption process.

R_L	Adsorption process
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable
$R_L = 1$	Linear
$R_L > 1$	Unfavorable

3.4.2. Freundlich adsorption isotherm

Freundlich isotherm has also been employed to quantify equilibrium biosorption systems like the Langmuir isotherm. While the Langmuir model is used in the case of monolayer adsorption and no interactions between adsorbed molecules, this model is considered applicable in many cases, particularly in the case of the adsorption multilayer with possible interactions between the adsorbed molecules. The Freundlich equation is purely empirical based on adsorption on heterogeneous surface. This isotherm is represented by the linear formula as it can be expressed under a nonlinear form as presented in Eqs below: where K_F and n are constants related to adsorption capacity and intensity, respectively. The Freundlich constants values and correlation coefficients (R^2) for the *C. officinalis* adsorbent investigated in this study are shown in Table 2. In addition, the numerical value of n at 25°C and 35°C lies between 1,382 and 1,057 and is greater than unity, indicating that AB113 dye are favorably adsorbed by dried alga at all the temperatures studied.

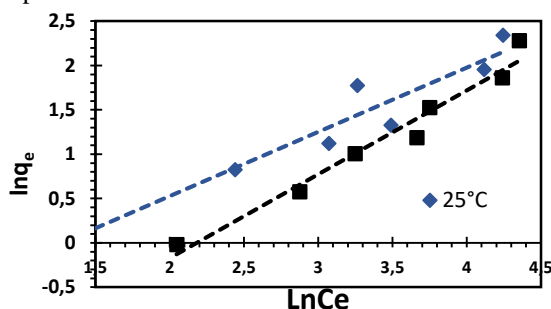


Fig. 6. Freundlich adsorption isotherm for AB113 dye on *C. officinalis* alga at 25 and 35°C.

Overall, the Langmuir and Freundlich models had a good agreement with the experimental data, as indicated by the high values of R^2 (all greater than 0.97) (Table 2). These results confirm the effectiveness of using *C. officinalis* alga as adsorbent to remove AB113 dye from aqueous solution.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (11)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (12)$$

3.4.3. Temkin adsorption isotherm

Temkin's isothermal adsorption model is based on the heat of adsorption of ions, which is due to the adsorbate and adsorbent interactions taken [19]. A linear form of

Temkin isotherm, as well as, various characteristic parameters can be expressed as follows:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (13)$$

where,

$$RT/b = \beta \quad (14)$$

$$q_e = \beta \ln(K_T) + \beta \ln(C_e) \quad (15)$$

where, T is absolute temperature in Kelvin and R the universal gaz constant, $8.314 \text{ J mol}^{-1}\text{K}^{-1}$. While, b is Temkin isotherm constant and constant β is related to the heat of adsorption, and K_T (L/mg) is the equilibrium binding constant, corresponding to the maximum binding energy [7]. The parameters of this model are incorporated in Table 2.

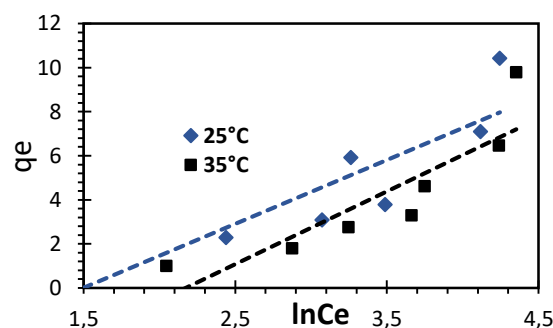


Fig. 7. Temkin adsorption isotherm for AB113 dye on *C. officinalis* alga at 25 and 35°C.

4 Conclusion

In course of this work, we conducted a comprehensive study of the adsorption of AB113 dye on *Corallina Officinalis* alga. Adsorption isotherms and equilibrium adsorption capacities were determined by fitting the experimental data to the three well-known isotherm models namely, Langmuir, Freundlich, and Temkin. The results showed that the Langmuir and Freundlich models appear to fit the adsorption better than Temkin model for the adsorption of AB113 onto dried *C. officinalis* alga. The good correlation obtained with Langmuir isotherm can be explained by the presence of several constituents inside biomaterial responsible of AB113 dye adsorption. While, the agreement of experimental data with Freundlich isotherms indicates that the surface of the biosorbent was heterogeneous, for the kinetics studies, it appeared that the pseudo-second-order kinetic model agrees very well with the kinetic behavior in case of the adsorption of AB113 on dried *C. officinalis* alga at both 20 and 100 mg/L values of initial dye concentrations. This study indicated that dried *C. officinalis* alga is a suitable candidate for the adsorption of anionic dye such as AB113 dye, considering that these adsorbents are naturally abundant and relatively low-cost materials.

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