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Evaluation of the Marine Algae *Gracilaria* and its Activated Carbon for the Adsorption of Ni(II) from Wastewater

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Abstract: The batch removal of Ni^{2+} from aqueous solution and wastewater using marine dried (MD) red algae *Gracilaria* and its activated carbon (AC) was studied. For these experiments, adsorption of Ni^{2+} was used to form two biomasses of AC and MD. Both methods used different pH values, biomass and initial concentration of Ni^{2+}. Subsequently adsorption models and kinetic studies were carried out. The maximum efficiencies of Ni^{2+} removal were 83.55% and 99.04% for MD and AC respectively developed from it. The experimental adsorption data were fitted to the Langmuir adsorption model. The nickel(II) uptake by the biosorbents was best described by pseudo-second order rate model. The kinetic studies showed that the heavy metal uptake was observed more rapidly by the AC with compared to MD. AC method developed from MD biomass exhibited higher biosorption capacity. Adsorption capacity is related to the pH of solution, pH 5.0 is optimal for nickel. The maximum efficiencies of Ni^{2+} removal were for AC method. The capacity is related to the pH of solution, pH 5.0 is optimal for nickel. The equilibrium adsorption data are correlated by Langmuir isotherm equation. The adsorption kinetic data can be described by the second order kinetic models

Introduction

The presence of the toxic heavy metals in water resulting from rapid industrialization and technological advances is a worldwide environmental problem. Removal of these pollutants from aqueous effluents has conventionally been accomplished through abiotic processes[1-3].

However, these processes can be expensive and not fully effective. Recently, increasing interest in the application of materials of biological origin in heavy metals' removal from diluted, large volume solutions has been observed[4-5]. Biosorption, which uses the ability of biological materials to remove and accumulate heavy metals from aqueous solutions, has received considerable attention in recent years because of a few advantages compared to traditional methods[6].

Surface adsorption is found to be an important basis for the treatment of toxic Ni^{2+} contaminated water[7]. The presence of carboxylic and sulfate groups in algae cell wall polysaccharides can act as binding sites for metals. Alginate, which is composed of mannuronic and guluronic acids, is a major polysaccharide in brown algae and acts as the source of carboxylic groups[8]. The cost of decontamination of toxic metals from industrial effluents and wastewaters using ion exchange resins is exorbitant. Hence, the usage of indigenous biodegradable resources for treating hazardous waste being less expensive is relevant to regional emerging environmental biotechnology[9]. Activated carbon has unquestionably been the most popular and widely used adsorbent in wastewater treatment employments throughout the world. However, activated carbon remains a costly material since higher the quality of activated carbon, the greater its cost. Therefore, searching of a low cost activated carbon and other adsorbent materials for the wastewater treatment is of great importance[10-12]. The purpose of the present study is to evaluate the biosorption capacity of the MD red algae *Gracilaria* in comparison with an AC from red algae *Gracilaria* for the removal of Ni^{+2} from aqueous solution, natural sea water and synthetic sea water.

Experimental

Batch equilibrium adsorption experiments were carried out in Erlenmeyer flasks in a rotary shaker for AC and glass column for MD. These experiments were done from aqueous solutions of initial concentrations ranged from (30-70 mg L^{-1}) for AC and MD using pH 5.0.

Preparation of biomass

Gracilaria was collected from the Persian Gulf on Qeshm Island, Iran. Before use, it was washed several times with tap water to remove the sand particles and salts. It was then sun dried for 6 days. Dry biomass was chopped, milled (size fraction of 0.5-1 mm) and then used for adsorption experiments.

AC and MD preparation

AC preparation: The dried red algae *Gracilaria* 120 g were added in a small portion to 96 mL of 97% H_2SO_4. The resulting mixture was kept for 24 h at room temperature followed by refluxing in fume hood for 4 h. After cooling, reaction mixture was washed repeatedly with deionized water and soaked in 2% $NaHCO_3$ solution to remove any remaining acid and pH of the activated carbon reached 7, dried in an oven at 150 ^{o}C for 48 h and the activation temperature and activation time were selected based on the preliminary studies at different temperatures and activation time that gives maximum sorption capacity for methylene blue removal. The activated materials were then powdered using a domestic Sumeet mixie. The powdered materials were then used as adsorbents for the study. The powdered materials were then sieved and the particle size in the range of 0.3 mm to 1 mm was used and kept in a glass bottle until used. MD Preparation: The samples were then grounded to an average particle size of 0.5-1 mm[13]. The tests were carried out at the chemical laboratory of the Islamic Azad University, North Tehran Branch from April to May 2007.

Determination of the nickel contents

The concentration of nickel in the solution before and after the equilibrium was determined by atomic absorption spectrometry (AAS, GBC-932), using a Perkin -Elmer analyst 300 atomic absorption spectrometer equipped with deuterium as background corrector, an air-acetylene burner and controlled by IBM personal computer. The hollow cathode lamp was operated at 15 mA and the analytical wavelength was set at 324.8 nm.

Chemicals

The synthetics solutions were all prepared by using deionized water and analytical graded salts of $NiCl_2$ $6H_2O$ (Merck supplied). Adsorption equilibrium isotherm was studied using MD red algae and its AC dosages of 2.5 g and 0.6 g, respectively, per 30 mL of aqueous Ni^{2+} solutions of initial concentrations ranged from 30 to 70 ppm for adsorbents using initial pH 5.0. All the adsorption experiments were carried out at room temperature (23 ± 2 °C). The pH of sample solution was adjusted with 1 M HCl or 1 M NaOH during the equilibrium period, at the obtained optimal values for heavy metal using agitation speed (200 rpm) for 2 h. Then the solution was filtered and filtrate was measured for ion content (C_e) by an atomic adsorption spectroscopy (GBC-932).

Adsorption studies

The effect of pH on the equilibrium adsorption was investigated by using different initial concentration of Ni^{2+} (10 mg L^{-1}) and different activated carbon dosages. The pH values were adjusted with diluted HCl and NaOH solutions. All the adsorption experiments were carried out at room temperature (23 ± 2 °C), using agitation speed (400 rpm) for the minimum contact time required to reach the equilibrium. Adsorption of Ni^{2+} was studied using different weights of AC and MD prepared from *Gracilaria* and different concentrations of Ni^{2+} and initial pH 5.0.

Equilibrium isotherm

Nickel uptake capacities and adsorption isotherm

Adsorption equilibrium isotherms were studied using MD and AC dosages of 0.2, 0.4, 0.7, 1.0 and 0.2, 0.4, 0.7 and 1.0, respectively, per 100 mL of aqueous Ni^{2+} solutions of initial concentrations ranged from 5 to 50 mg L^{-1} for alga and 5-250 mg L^{-1} for MD and AC using initial pH 5.0. For these experiments, the screw-cap conical flasks were shaken at a speed of 200 rpm and room temperature (25 ± 2 °C) for the required contact time. Then, the solution was filtered through a 0.45 µm membrane filter. The Ni^{2+} uptake was calculated by the simple concentration difference methods. The amount of metal adsorbed by activated carbon was calculated from the difference between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$q_e = \frac{(C_0 - C_t)V}{M} \qquad (1)$$

Where q_e is the metal uptake (mg metal adsorbed per g adsorbent), C_0 and C_e are the initial and equilibrium metal concentrations in solution (mg L^{-1}), V is the volume of the solution (mL) and M is the weight of activated carbon (g). To examine between adsorbed and aqueous concentration at equilibrium, adsorption isotherm models, Langmuir and Freundlich adsorption models were used for the data[13]. These isotherm constants for Ni^{2+} are presented in Table 1.

Table 1. Isotherm parameters obtained for biosorption of Ni

Isotherm model	AC		MD	
	0.4 g	0.6 g	2.5 g	3.5 g
Langmuir				
Q_m, mg g^{-1}	2.686	2.305	1.386	1.285
B, L mg^{-1}	0.673	1.100	0.043	0.048
R^2	0.924	0.993	0.999	0.999
Freundlich				
1/n	0.144	0.175	0.627	0.741
K_F, mg g^{-1}, L mg$^{-1\,1/n}$	1.595	1.322	0.092	0.075
R^2	0.979	0.982	0.972	0.999

Freundlich adsorption model

The Freundlich model[14] habitually gives a better fit for adsorption from liquids and can be expressed as:

$$q_e = K_f . C_e^{1/n} \qquad (2)$$

In this model, the rate of adsorption is of the constants 1/n and K_f (Lg^{-1}). For a good adsorbent, 0.2< 1/n <0.8 and a smaller value of 1/n show better adsorption and formation of rather strong bond between the adsorbate and adsorbent. Many researchers have used this model to interpret adsorption data for various systems[15-18].

Langmuir adsorption model

The most widely used isotherm equation for modeling equilibrium is the Langmuir equation. It is assumed that there is a finite number of binding sites that are homogeneously shared over the adsorbent surface. These binding sites have the same adsorption of a single molecular layer and there is no interaction between adsorbed molecules. The saturated monolayer isotherm can be represented as:

$$q_e = \frac{b.q_{max}\,C_e}{(1+b.C_e)} \qquad (3)$$

Where q_e is metal ion adsorbed (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), q_{max} is the maximum adsorption capacity and b is an affinity constant, whereas, q_{max} represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in comparison of adsorption performance, in cases where the adsorbent did not reach its full saturation in experiments and b is constantly related to the affinity of the binding sites[19].

Adsorption kinetic studies

The kinetics of adsorption describes the rate of nickel ions uptake on AC and MD prepared from *Gracilaria* which controls the equilibrium time. These kinetic models included the first order and second order equations.

Pseudo first order model

The pseudo first order rate expression is described by the following equation[20].

$$dq_t/d_t /= k_1 (q_e - q_t) \qquad (4)$$

Where q_e is copper sorbed at equilibrium per unit weigh of adsorbent (mg/g); q_t is copper sorbed (mg/g) and k_1 is the rate constant (min^{-1}). The integrated form of Eq. (4) becomes:

$$\log (q_e-q_t) = \log (q_e)-(k_1/2.303) \, t \tag{5}$$

A plot of $\log(q_e-q_t)$ *versus* (t) indicates a straight line of slope $(k_1/2.303)$ and an intercept of $\log (q_e)$. The adsorption first-order rate constants ranged between 0.013-0.071 and 0.012-0.103 $\min^{-1}$ for DM alga and AC, respectively (Table 2). The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. It was observed that kinetic model fits well for the first 40 min and thereafter the data deviate from the theory. Thus, the model shows the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Ho and McKay[18] reported that the sorption data were represented well by the Lagergren second-order model only for the rapid initial phase that occurs for a contact time of 0-30 min. This confirms that it is not appropriate to use the Lagergren kinetic model to predict the adsorption kinetics for chromium onto dried green alga and its activated carbon for the entire sorption period. While it gave predicted q_e far from the experimental q_e for both dried green alga and activated carbon, which shows that the pseudo second-order model can be applied but is not appropriate to describe the entire process and to predict the q_e.

Table 2. Parameters kinetic model for biosorption of Ni

Algae	Parameter Initial Ni concentration, mg L^{-1}	First-order kinetic model			Second- order kinetic model		
		K_2	q_e (calculated)	R^2	K_2	q_e (calculated)	R^2
0.6 g	30	0.00	0.04	0.67	0.057	1.00	1.00
AC	50	0.07	0.03	0.68	0.014	1.03	0.99
	70	0.05	0.02	0.76	0.007	1.08	0.99
2.5 g	30	0.01	0.15	0.92	0.003	0.99	1.00
DM	50	0.00	0.03	0.98	0.065	0.84	1.00
	70	0.00	0.02	0.91	0.004	0.91	1.00

Pseudo second order model

The adsorption data also analyzed a pseudo second order[20], given by

$$dq_t/d_t=K_2 (q_e-q_t)^2 \tag{6}$$

Where, K_2 is the equilibrium rate constant (g/mg, min). Q_e and q_t are the adsorption capacities at equilibrium at time t. The integrated form of Eq (5) becomes:

$$1/(q_e-q_t)=1/(q_e)+K_2 \, t \tag{7}$$

This has linear form:

$$t/q_t=1/K_2.q_e^2 +(1/q_e)t \tag{8}$$

A plot t/q_e *versus* t shows a straight line of slope $(1/q_e)$ and an intercept of $(1/ K_2.q_e^2)$[21].

As a result of failure in applicability of pseudo second-order, the adsorption kinetics was explained by Ho and McKay[18] Eq. (7). The second order rate constants K_2, the calculated q_e values and correlation coefficients were reported in Table 2. It was observed that the pseudo second-order rate constant (K_2) decreased with increased initial concentration for both DM and its AC. The calculated q_e values agreed very well with the experimental values and the regression coefficients were above 0.99 and 1.0 for AC and DM, respectively, which showed that the pseudo second-order model could be applied for the entire adsorption process and confirmed of Ni^{2+} onto DM and its AC.

Results and Discussion

The present study shows that AC and MD prepared of red algae *Gracilaria* have an ability to remove Ni^{2+} from the contaminated water. The data obtained from this work supports the view that the AC is effective for the removal of Ni^{2+} from aqueous solution. The adsorption of metal ions is dependent on AC and MD, concentration of metal ion, retention time and pH of the metal solution.

Effect of pH on adsorption

Figure 1 shows that the biosorption of Ni^{2+} was increased up to pH 5.0. The lower uptake at higher pH value is probably due to the formation of anionic hydroxide complexes. Due to these lower uptakes at higher pH values the ligands such as carboxylate and sulfonate groups could uptake fewer metal ions[12]. The initial pH of the metal solution is an important parameter affecting adsorption of metal ions[22]. The effect of initial pH on the removal of Ni^{2+} using AC and MD prepared of *Gracilaria* was studied (Figure 1). It is clear from the removal of Ni^{2+} decreased with an increase in pH from 1.0 to 9.0 and an optimum pH of about 5.0 was observed. In the literature[23], similar has been reported by the nature of the biosorption at different pH. The lower uptake at higher pH value is probably due to the formation of anionic hydroxide complexes. So in this study, relationship between adsorption and bioreduction is discussed. When pH increased 1.0 to 5.0, strange adsorption algae increased, because in the case algae entered heavy metals from ligands. In pH 5.0 reduction rate of algae is very high.
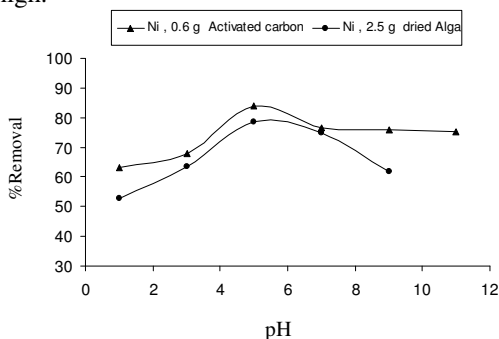

Figure 1. Effect of pH on adsorption of 50 mg L^{-1} Ni(II) by DM and MD after 15 min

At low and high pH, on the other hand, Ni^{2+} had a higher redox potential and favored Ni(II) bioreduction[24]. In addition, reductions on the biomass such as carbohydrate and protein could supply electrons for Ni(II) bioreduction, with partial release of soluble organics or final oxidized product[25].

Effect of metal ion concentration on adsorption

The initial concentration of metal ion provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases[26]. Figure 2 represented the effect of different initial concentrations of Ni^{2+} (30-70 mg $L^{-1)}$) on adsorption Ni^{2+} using marine algae *Gracilaria* (red algae) and its AC and MD. The results show the increase in initial concentration of Ni^{2+} which led to a decrease in the percentage of removal for both adsorbents due to saturation of the adsorption sites on adsorbents, the maximum uptake for nickel with initial concentration, 30 and 40 mg L^{-1} at pH 5.0 and 2.5 g MD and 0.6 g AC prepared in *Gracilaria* were obtained as 83.55% and 99.04%, respectively.
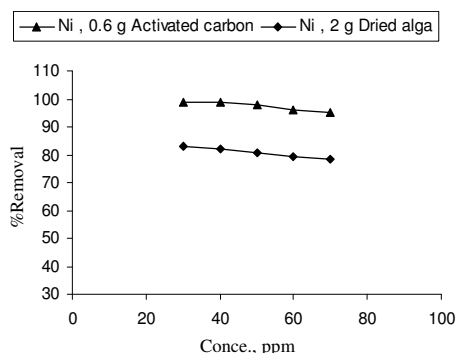
Figure 2. The effect of initial concentration of metal ion on the percentage of removal of Ni(II) at pH 5 and room temperature using MD and AC

Effect of retention time

Figure 3 indicates that removal ability increased with increasing contact time and concentrated heavy metals before equilibrium reached. Other limits such as dose of adsorbent, pH of solution and initial concentration were kept optimum. While temperature was kept at (23±2 ^{o}C) it can be seen from Figure 3 that Ni removal efficiency increased when contact time was increased from 15 min. Optimum contact time for both adsorbents was found to be 15 min. In previous literature, similar has been reported by the evaluation of the MD *Gracilaria corticata* for the adsorption of Cu(II) from wastewater in a packed column reported[27].
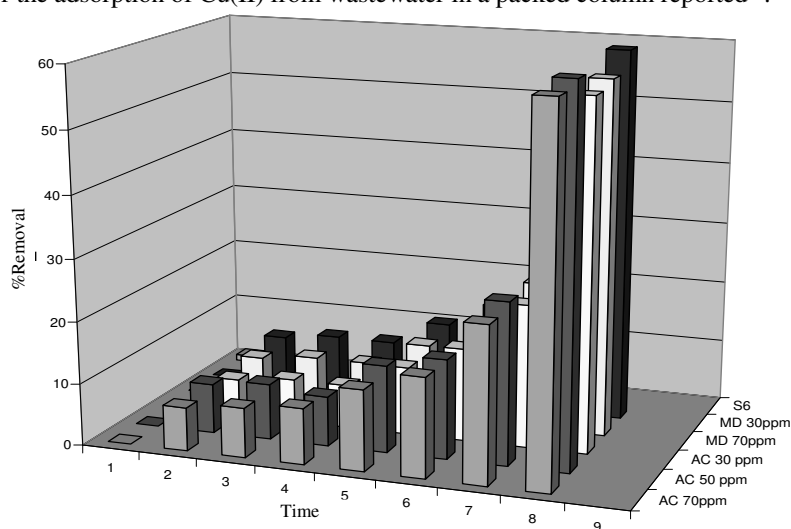

Figure 3. The effect of time on the percentage of removal of Ni(II) at pH 5 and room temperature using DM and AC

Effect of adsorbent dose on adsorption

The initial concentration of metal ion provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases[26]. The results show that the equilibrium concentration of Ni^{2+} increased with an increasing adsorbate concentration. It showed that the increase in initial concentration of Ni^{2+} led to a decrease in

the percentage of removal for both adsorbents. When initial Ni^{2+} concentrations increased from 0.2 to 3.5 g, the removal percentages decreased from 66 to 45% for MD and when initial chromium concentrations changed from 5 to 250 mg g^{-1}, the percentage of removals was decreased from 100 to 90% for the AC. This was due to the saturation of the sorption sites on adsorbents[28-29].

Adsorption isotherm

Adsorption isotherms are important for describing how adsorbate will interact with an adsorbent and are critical in the use of adsorbent. Equilibrium studies in adsorption isotherm are characterized by certain constants whose values express the surface properties and affinity of the adsorbent. Equilibrium between adsorbent and adsorbate was described by adsorption isotherms, usually the ratio between the quantity adsorbed and the remaining in the solution at a fixed temperature (23±2 ^{o}C), at equilibrium. To study the adsorption isotherm, two models were analyzed.

Langmuir and Freundlich isotherms

The Langmuir adsorption isotherm is the most widely applied adsorption isotherm. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. The applicability of the empirical Freundlich isotherm was also analyzed based on the adsorption on heterogeneous surface, using the same set of experimental data of dried red and MD and its AC. The isotherm experimental results showed the data could be well modeled according to the Langmuir adsorption isotherm. The Langmuir constant (q_{max}) is dependent on experimental conditions such as solution pH.

Another importance in evaluating adsorbent performance is the initial gradient of the adsorption isotherm, since it indicates the adsorbent affinity at low metal concentrations. In the Langmuir equation, this initial gradient corresponds to the affinity constant (b). As we can see from Table 1 data could be well modeled according to the Langmuir, adsorption isotherm. In previous investigation, similar method with DM *Gracilaria* for the biosorption of Ni(II) has been reported[28].

Kinetic modeling

The Legergren first order rate constant ($k_{1,ads}$) and q_e determined from the model indicated that this model failed to estimate q_e since the experimental values of q_e differed from those estimated in Table 2. Subsequently, the rate of uptake of Ni^{2+} onto the biomass increased quickly to 15 min and no further adsorption was observed beyond this period. The Ni^{2+} uptake by the biosorbents was best described by pseudo second-order rate model. The pseudo second order model is based on the supposition that adsorption follows a second-order which means the rate of occupation of adsorption sites is proportional to the squares of number of unoccupied sites[6,23]. Previous literature for the evaluation of the AC prepared from the algae *Gracilaria* for the adsorption of Cu(II) it has been observed that the adsorption follows second order kinetics reported[29].

These isotherm constants for Ni^{2+} are presented in Table 2 Subsequently, the rate of uptake of Ni^{2+} onto the biomass increased quickly till 15 min and no further meaningful adsorption was observed beyond this period. The nickel(II) uptake by the biosorbents was best described by pseudo second order rate model. The pseudo second order model is based on the supposition that biosorption follows a second order mechanism which means that the rate of occupation of adsorption sites is proportional to the squares of number unoccupied sites[30].

Relationship between bioreduction and adsorption of Ni(II)

In order to study the effect of salinity and real wastewater on the capability of the alga *Gracilaria* and its developed AC to adsorb Ni^{2+} from its aqueous solution, removal studies were achieved using synthetic seawater, natural seawater and real wastewater. A near 100% removal of toxic nickel from synthetic seawater, natural seawater and wastewater was detected for activated carbon developed from *Gracilaria*. Moreover, the maximum adsorption capacities were not changed by the changing of the type of chromium solution. The presence of salt had no effect on the adsorption of Ni^{2+} on both adsorbents, which leads to deduce that there was no interaction between the salt and the surface of the adsorbent nor the salt and the solute (Ni). In addition, the high concentration of Ni^{2+} ions may make them more preferable to be absorbed by the adsorbents. On the other hand the real wastewater may contain very low concentrations from several metal ions that will not have much effect on the removal percentage of nickel ions. These results indicate that the two sorbents MD and AC of *Gracilaria* are applicable material for removal of Ni^{2+} from different types of aqueous solutions including wastewater.

Conclusion

1. In this research two methods used in the investigation of the batch removal of Ni^{2+} from aqueous solution, and wastewater using marine dried (MD) red algae *Gracilaria,* and its activated carbon (AC).

2. A suitable indigenous MD and its developed AC have been identified as effective adsorbents to remove Ni^{2+} ions from different types of aqueous solutions. The adsorption kinetic data can be described by the second-order kinetic models.

3. The adsorption capacity is related to the pH of solution and pH 5.0 is optimal. Furthermore, the equilibrium data of adsorption are in good agreement with the Langmuir's model. The MD and its AC are inexpensive effective adsorbents for the removal of Ni^{2+} ions from aqueous solutions.

3. The AC developed from MD alga biomass exhibited high biosorption capacity. The adsorption of Ni^{2+} was found to be pH dependent and maximum removal was observed at pH 5.0. The kinetics studies showed that both *Gracilaria* and its AC have poor fit with pseudo first-order kinetic equation while they have a good agreement with the pseudo second-order kinetic equation. Moreover, the intra-particle-diffusion was also investigated and the adsorption process was found to be controlled by the film diffusion at lower concentrations of the adsorbate and shifted to particle diffusion at high concentration.

4. The maximum efficiencies of Ni^{2+} removal were 83.55% and 99.04% for MD and AC developed from it, respectively.

5. We conclude that absorption by AC is higher than the MD red algae.

6. This process is environment friendly and reduces the huge amount of indiscriminate effluent discharges around the small industry concerns. It may provide an affordable technology for small and medium-scale industry.

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