Modeling and Sensitivity Analysis of Dyes Adsorption onto Natural Adsorbent from Colored Textile Wastewater

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ABSTRACT: In this article, adsorption modeling and sensitivity analysis were presented to describe the adsorption of textile dyes, Solophenyl Red 3BL (SR) and Pergasol Red 2B (PR), from colored wastewater onto the natural adsorbent (soy meal hull). The numerical model was used to solve the mathematical equations governing the adsorption procedure. The experimental results of SR and PR removal were compared with those results predicted by the numerical model. A sensitivity analysis of dye removal from solution phase has been carried out. The model predictions were compared to those results obtained from experimental tests for adsorption of dyes, and a close agreement was achieved. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 4043–4048, 2008

Key words: textile dye removal; natural adsorbent; adsorption modeling; sensitivity analysis

INTRODUCTION

The presence of organic contaminants in the hydrosphere because of their nonbiodegradability and potential carcinogenic nature of the majority of these compounds is of particular concern for the freshwater, coastal, and marine environments. The discharge of dye-bearing wastewater from textile industries into natural stream and rivers poses severe problems, because of toxicity of some dyes to the aquatic life and damaging to the esthetic nature of the environment.[1–11] As a result, the removal of color from waste effluents has become environmentally important. Considerable attempts have been done by many researchers to find appropriate treatment systems to treat effluents containing dyes from different industries, in particular, textile industry. The commonly used methods for dye removal from waste effluents are physicochemical, chemical, and biological methods. From the numerous techniques mentioned, adsorption is an effective process for the removal of dyes from industrial effluents. The adsorption process is economically cost-effective, efficient, and easy method for dye removal.[12–20] The high price, high operating costs, and problems with regeneration limit the applicability of activated carbon as an adsorbent for dye removal.[12,20]

Therefore, there is a growing interest to find an effective and ideal alternative material to be relatively cost effective and at the same time having high adsorption efficiency. These works include use of natural adsorbents such as agricultural wastes.

In the present study, the use of low-cost and eco-friendly adsorbent, soy meal hull, has been investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull were carried out at our previous work.[21] The main focuses of this article were adsorption modeling and sensitivity analysis of adsorption process for direct dyes removal from solution phase. A model that describes dye removal process from aqueous phase would facilitate the development of an appropriate treatment system and environmental management plan during the design stage of those industries that use dyes for dyeing process. The governing equation of the model was numerically solved using CTRN/W and SEEP/W models. A sensitivity analysis was carried out to evaluate the effects of changing model parameters on dye removal process.

EXPERIMENTAL

Material

Two anionic direct dyes, Solophenyl Red 3BL (SR) ($C_{45}H_{26}N_{10}O_{21}S_6Na_6$, MW 1372 g/mol) and Pergasol Red 2B (PR) ($C_{29}H_{19}N_5O_8S_2Na_2$, MW 675 g/mol), were obtained from Ciba and used without further purification. Other chemicals were Analar grade and achieved from Merck.

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Soy meal hull was obtained from Behpak Co. (Behshahr, Iran). The soy meal hull samples were first held for 24 h at room temperature and then were sieved to obtain the particle size of <0.125 mm.

Adsorption procedure and analyses

The adsorption measurements were conduced by mixing various amounts of soy meal hull (0.5–2 g) for SR and (0.2–1g) for PR in jars containing 250 mL of a dye solution (50 mg/L) at pH ranging from 2 to 10.[21] The pH studies were performed to determine the optimum pH at which maximum dye removal could be achieved with the adsorbent for each dye.

The adsorption experiments were performed using a 250 mL solution containing dye. The initial concentration of dye was 50 mg/L. Samples were withdrawn from colored solutions at certain time intervals (5, 10, 15, 30, 45, 60, 120, 180, 240, 300, 360, 420, 480, and 1440 min) during the adsorption process and analyzed for dye removal using a CECIL 2021 spectrophotometer. Dye removal was measured at the maximum wavelength (λ_{max}) of dyes (542.5 and 510.5 nm for SR and PR, respectively). The experimental conditions were amounts of soy meal hulls (0.075 g for SR and 0.15 g for PR), pH 2, and an agitating speed of 200 rpm for a time period of 24 h to reach equilibrium conditions. The pH adjustments of the solution were made by adding HCl or NaOH. An FC6S-VELP (Scientifica) jar test was used for agitating purpose. After adsorption experiments, the sorbent was separated from the solution by Hettich EBA20 centrifuge. Samples were withdrawn from solution at certain time intervals and analyzed for dye removal.

Numerical modeling

A numerical finite element model has been used to simulate removal of dyes from colored wastewater, taking into account that the main mechanism for the removal process is an adsorption process.

RESULTS AND DISCUSSION

Adsorption isotherms and kinetics

The adsorption isotherm is an important tool in the design of adsorption systems. Many isotherm relationships have been previously used by several researchers. Two isotherms, Langmuir and Freundlich isotherms, were used in this study.

The Langmuir isotherm has been widely used to describe single-solute systems.[22,23] This isotherm assumes that intermolecular forces decrease rapidly with distance and consequently it can predict monolayer coverage of the adsorbate on the outer surface of the adsorbent. Further assumption is that adsorption occurs at specific homogeneous sites within the adsorbent, and there is no significant interaction among adsorbed species. An expression for the Langmuir isotherm is

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{1}$$

where q_e is the solid phase dye concentration at equilibrium (mg/g), C_e is the equilibrium concentration of dye (mg/L), Q_0 denotes the maximum adsorption capacity, and K_L is the Langmuir isotherm constant (L/mg). The linear form of Langmuir equation is

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \tag{2}$$

If C_e/q_e is plotted against C_e, it gives a straight line with a slope of $1/Q_0$ and an intercept of $1/K_L Q_0$.

Freundlich expression was also applied for the adsorption of SR and PR onto soy meal hulls. This empirical expression is used to describe heterogeneous systems.[20]

The Freundlich isotherm equation is given as

$$q = K_F C_e^{1/n} \tag{3}$$

where C_e is the equilibrium concentration of dye (mg/L); K_F and n are Freundlich isotherm constants indicating the extend of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. Equation (3) can be rearranged to a linear form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

If $\log q_e$ is plotted against $\log C_e$, it gives a straight line with a slope of $1/n$ and an intercept of $\log K_F$.

The Q_0, K_L, K_F, n, and R^2 (correlation coefficient) were calculated and given in Table I. As Table I shows, the adsorption process for both SR and PR

TABLE I
Isotherm Constants for Adsorption of SR and PR onto Soy Meal Hull

Dye	Langmuir isotherm parameters			Freundlich isotherm parameters		
	Q_0	K_L	R^2	K_F	$1/n$	R^2
SR	178.57	1.401	0.95	146.555	0.0534	0.91
PR	120.48	1.660	0.97	85.526	0.099	0.93

Condition: 250 mL solution, initial dye concentration 50 mg/L, soy meal hull (0.075 g for SR and 0.15 g for PR), pH 2, and an agitating speed of 200 rpm for a time period of 24 h.

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TABLE II
Kinetic Parameters for Adsorption of SR and PR onto Soy Meal Hull

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Dye	Pseudofirst-order parameters			Pseudosecond-order parameters		
	$k_{1,\mathrm{ad}}$	q_e	R^2	$k_{2,\mathrm{ad}}$	q_e	R^2
SR	0.775	111.25	0.991	0.0088	185.185	0.990
PR	0.529	33.02	0.991	0.053	105.26	0.990

Condition: 250 mL solution, initial dye concentration 50 mg/L, soy meal hull (0.075 g for SR and 0.15 g for PR), pH 2, and an agitating speed of 200 rpm for a time period of 24 h.

onto soy meal hulls adsorbent could be well described by the Langmuir isotherm equation with the correlation coefficients (R^2) of 0.95 for SR and 0.97 for PR.

To investigate the kinetics of sorption, characteristic constants of sorption were determined using a pseudofirst-order equation of Lagergren and a pseudosecond-order equation.[24–26]

The rate constant for adsorption of SR and PR by soy meal hull was determined using Lagergren rate equation as given later:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_{1,\mathrm{ad}}}{2.303}\right)t \qquad (5)$$

where q_e is the amount of dye adsorbed at equilibrium (mg/g); q_t the amount of dye adsorbed at time t (mg/g); $k_{1,\mathrm{ad}}$ the pseudofirst-order rate constant (s^{-1}), and t is the time (s).

The pseudofirst-order rate constant ($k_{1,\mathrm{ad}}$) can be obtained from the slope of the plot between $\log(q_e - q_t)$ versus time t.

The rate of pseudosecond-order reaction is given as

$$\frac{t}{q_t} = \frac{1}{k_{2,\mathrm{ad}}q_e^2} + \frac{t}{q_e} \qquad (6)$$

where $k_{2,\mathrm{ad}}$ is the pseudosecond-order rate constant [g/(mg min)]. Plotting t/q_t against t, a line is obtained and the value for $k_{2,\mathrm{ad}}$ can be calculated.

The values of $k_{1,\mathrm{ad}}$, q_e, $k_{2,\mathrm{ad}}$, and R^2 (correlation coefficient) were calculated and shown in Table II. As Table II shows, the correlation coefficients (R^2) of the pseudofirst-order model resulted as 0.991 for both dyes. Furthermore, the correlation coefficients (R^2) for the pseudosecond-order model were given as 0.990 for both dyes. This means that the pseudofirst-order kinetics relative to dye removal is operative.

Mechanism of interaction between adsorbent and adsorbate

To understand the nature of the interaction between the surface of the soy meal hull and dyes, FT-IR and desorption studies were carried out. FT-IR studies revealed that the surface of soy meal hull has various functional groups, such as amine, hydroxyl, and carbonyl groups, which could also be affected by the pH of solutions.[21] Therefore, at various pH values, the electrostatic attraction as well as the organic property and structure of dye molecules and surface of adsorbent could play very important roles in dye adsorption on soy meal hull. At pH 2, a significantly high electrostatic attraction exists between the positively charged surfaces of the adsorbent, because of the ionization of functional groups of adsorbent and negatively charged anionic dye. As the pH of the system increases, the number of negatively charged sites is increased. A negatively charged site on the adsorbent does not favor the adsorption of anionic dyes due to the electrostatic repulsion.[27,28] Desorption studies by increasing the pH of the media showed resale of the adsorbed dyes to the bulk solution which can support the electrostatic interaction between soy meal hull and dyes. Therefore pH 2 was considered more effective pH in adsorption processes.[21]

Numerical modeling

Numerical models have been recognized as strong and powerful tools in prediction of many environmental problems associated with various industries. Furthermore, numerical models have been successfully used in designing effective remediation schemes based on the adsorption process.

In this study, the following partial differential equation was first modified and then numerically solved to simulate the dye removal from aqueous solution, taking into account that the adsorption is the only mechanism for dye removal in a batch system.[29]

$$\frac{\partial(\varphi C)}{\partial t} + \frac{\partial(\rho_b \bar{C})}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) - kC \qquad (7)$$

where C is the dye concentration in aqueous system (mg/L), $\bar{C}$ the sorbed concentration of dye in the solid phase (mg/g), k the rate constant (1/s), t the time (s), x the Cartesian coordinates (m), ρ_b the bulk density of the sorbent (g/mL), D the hydrodynamic dispersion coefficient (m^2/s), and φ is the porosity.

A numerical finite element model called CTRN/W was used to simulate the removal of direct dyes from aqueous solution.[29] For modeling purpose,
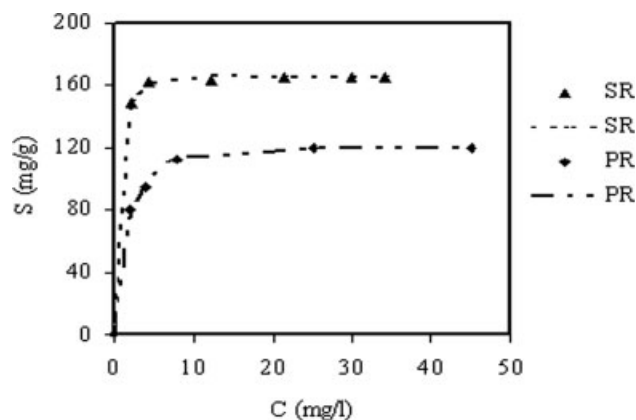
Figure 1 Experimental (▲,◆) and predicted (dotted line) isotherms for adsorption of SR and PR onto soy meal hull.

CTRN/W is incorporated with SEEP/W. The CTRN/W utilizes the finite element grid made by SEEP/W software to model adsorption process of dyes from aqueous solution. The partial differential equation solved by CTRN/W has the following general form:

$$\left(\theta + \rho_d \frac{\partial S}{\partial C}\right)\frac{\partial C}{\partial t} = \theta D \frac{\partial^2 C}{\partial x_j^2} - U_j \frac{\partial C}{\partial x_j} - kS\rho_d - k\theta C \quad (8)$$

where θ is the volumetric water content (dimensionless), C the concentration (mg/L), D the hydrodynamic dispersion coefficient (mm²/s), x_j the Cartesian coordinates (mm), U_j the Darcian velocity in the x_j direction (mm/s), ρ_b the bulk density of the medium (1/1000 mg/mm³), S the concentration in the solid phase (mg/g), t the time (s), and k is the decay constant (1/s).

To solve eq. (7) numerically, it is necessary to specify the appropriate initial and boundary conditions to constrain the problem and make the solution unique. The numerical modeling for the adsorption of SR and PR from the aqueous solution using soy meal hulls adsorbent was performed in three different steps as explained later:

A one-dimensional finite element grid incorporating 10 elements and 53 nodes was first constructed using SEEP/W software. The hydraulic head differential and hydraulic conductivity were selected to produce zero velocity to neglect the advection term in eq. (8). The volumetric water content θ was defined as a constant equal to 1. A steady state simulation was then performed.

The associated SEEP/W model was included with the CTRN/W software. To specify the input data, the material properties box was selected from the KeyIn menu. The longitudinal and transverse dispersivities were set to 1.0×10^{-20} mm. The decay half-life was considered to be zero. A value equal to the

initial dye concentration in the solution system was specified at all nodal points of the finite element grid. A small time step of 1.0×10^{-20} s was assigned to consider the simulation as a steady-state condition. The SOLVE window was then used to perform this steady-state simulation and provide the initial conditions for the main transient modeling of the dye removal process. This model should be used as an initial condition for the transient simulation of the dye removal process (third step).

The main step in the numerical modeling is to simulate the removal of direct dyes from the solution system by adsorbent. To carry out this stage of the simulation, the initial dye concentration was first removed from all nodal points. A total iteration of 100 was assigned for the simulation. A central difference time integration scheme was considered. For transient modeling, 65 time steps were assigned.

The experimental and the predicted model for the equilibrium isotherms of SR and PR onto soy meal hull are shown in Figure 1. The predicted outputs of the model match the experimental measurements satisfactory.

For comparison purposes, the changes of dye concentration were only determined at certain time intervals (60, 120, 180, 240, and 300, seconds for SR and 120, 240, 360, 480, and 600 s for PR) during the adsorption process. Figure 2 compares the dye concentration for SR in solution system as a function of time predicted by the numerical finite element model and those determined as experimentally, showing a close agreement. Figure 3 gives the same comparison for PR. The predicted outputs of the model match the experimental measurements satisfactory.

Sensitivity analysis

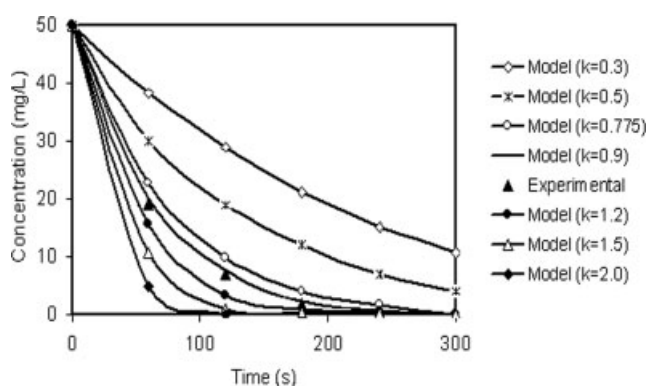A sensitivity analysis of the major parameters that influence the rate of dye removal from the solution
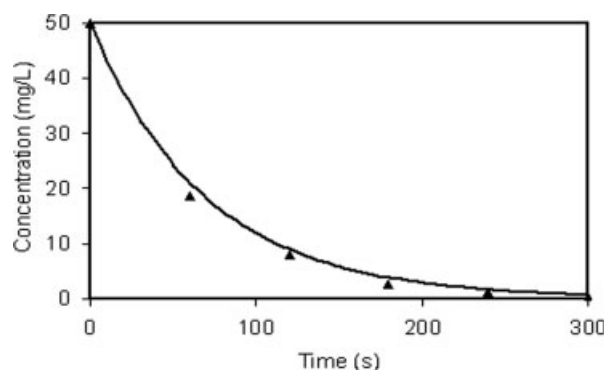
Figure 2 Comparison of concentrations of SR in aqueous phase versus time predicted by numerical model (solid line) and determined at laboratory (▲) at pH 2 and for an initial concentration of 50 mg/L.
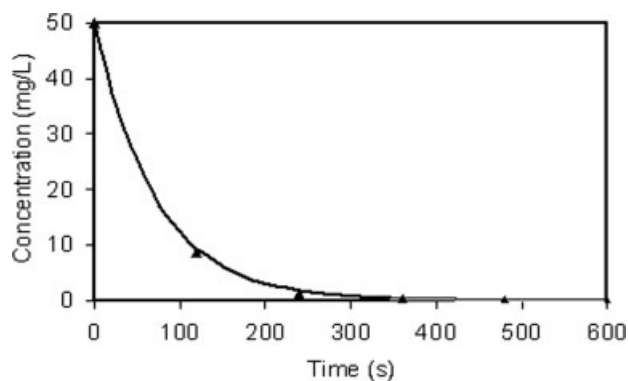
Figure 3 Comparison of concentrations of PR in aqueous phase versus time predicted by numerical model (solid line) and determined at laboratory (▲) at pH 2 and for an initial concentration of 50 mg/L.
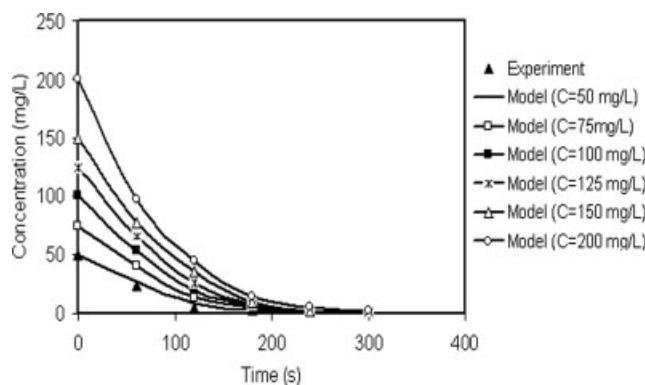
phase during the course of the adsorption process was carried out. Two of the main parameters taken into account were the kinetic rate constant and initial dye concentration. In this analysis, only SR was considered.

The first analysis was carried out to assess the sensitivity of the model to changes in kinetic rate constant. The rate constants ranged from 0.3 to 2 (Fig. 4). Under the low rate value of 0.3 s^{-1}, more than 10 mg/L of SR remained in the aqueous system after 300 s, compared with an adsorption system with high rate value of 2 s^{-1} where the dye concentration reduced to about 0.1 mg/L after 120 s.

As Figure 4 shows, the accuracy of the finite element model (solid line) for the SR concentration was evaluated and verified by comparison with the experimental data, shown as black rectangles for a pseudofirst-order kinetic constant of 0.775 s^{-1}. The agreement is somewhat close. An outstanding agreement is obtained when a rate constant of 0.9 is selected.
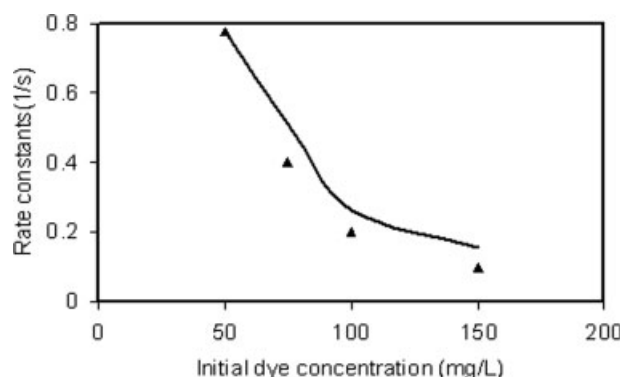
In the second analysis, the kinetic rate constant was assumed to be constant equal to 0.775 s^{-1}. This time, the sensitivity of the model to changes in initial dye concentration of SR was examined. Values of the initial dye concentration considered in this analysis ranged from 50 to 200 mg/L. Figure 5 shows SR concentration plotted against time for different values of initial dye concentration. It is clear that higher initial dye concentration caused a lower rate of dye removal from the solution system. As Figure 5 depicts, at early times of the adsorption process when the rate of dye removal is very fast, the sensitivity of the model to initial dye concentration is very obvious. Dye with a lower initial concentration is removed faster than that with a higher concentration.

Figure 6 shows the first-order rate constant as a function of initial dye concentration predicted by the finite element model. Comparison was also made with those rate constants determined in laboratory. As this figure shows, the kinetic rate constant reduced as SR concentration increased from 50 to 150 mg/L.

Figure 5 SR concentration as a function of time plotted for various initial dye concentrations.

Figure 4 SR concentration versus time for different kinetic rate constants.

Figure 6 Model predictions for the pseudofirst-order rate constants versus initial dye concentrations of SR.
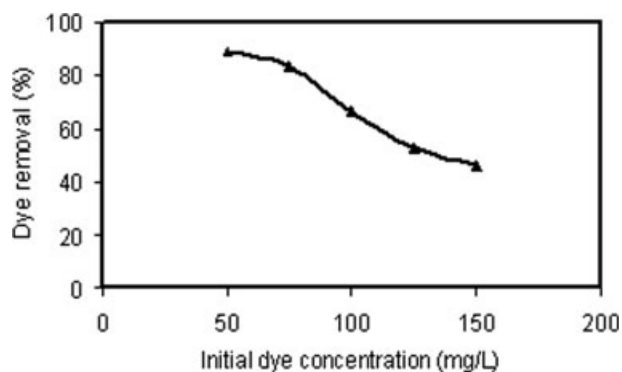
Figure 7 Percent of dye removal versus initial dye concentration for SR after 240 s of the adsorption process.

Figure 7 shows the percent of the removal of SR from the aqueous phase. In this figure, modeling predictions were compared with the experimental measurements in a fixed time of 240 s. The increase in the initial dye concentration decreased the percent of dye removal. As shown, the rate of removal decreased gradually from 96 to 90% when initial dye concentration increased from 50 to 75 mg/L. The percent of dye removal decreased again with a linear trend when the initial concentration was changed from 75 to 150 mg/L. After 240 s of the adsorption process, about 47% of the dye with an initial concentration of 150 mg/L was removed from the solution phase.

CONCLUSIONS

The results of this research show that soy meal hull has suitable adsorption capacity for the removal of SR and PR from their aqueous solutions. Adsorption obeys Langmuir isotherm for both SR and PR. A numerical finite element model has been presented. The governing equation of the model was numerically solved using CTRN/W and SEEP/W packages to simulate SR and PR removal from the aqueous system by soy meal hull adsorbent. The model takes into account the adsorption process incorporating the Langmuir isotherm and pseudofirst-order kinetic model. The predicted outputs of the model are in close agreement of the experimental data. A sensitivity analysis was performed to investigate the effects of changing model parameters on dye removal process. It was found that the model is most sensitive to the initial dye concentration and the rate and kinetic of dye sorption. Quantifying the effect of variations in model parameters is important in developing an appropriate treatment system and controlling pollution load discharging to the environment.

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