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Equilibrium and Kinetic Modelling on the Removal of Reactive Red 120 using *Morinda Tinctoria*

R. Vijayalakshmi
Department of Chemistry, A.V.V.M. Sri Pushpam College, Poondi, Thanjavur, Tamil Nadu, India
R. Venkatachalam
Department of Chemistry, A.V.V.M. Sri Pushpam College, Poondi, Thanjavur, Tamil Nadu, India
T. Peria Thambi
Department of Chemistry, A.V.V.M. Sri Pushpam College, Poondi, Thanjavur, Tamil Nadu, India

Abstract:
In the present study the effect of biosorbent dosage (0.02-0.1g/100 m L^{-1}), the pH(1-7) and the initial concentration(10-50mgL^{-1}) on Reactive Red 120 removal from an aqueous medium using Morinda Tinctoria Batch experiments were carried out for biosorption kinetics and isotherm studies. The results showed that the dye uptake capacity was found to increase with decrease in the biosorbent dosage. The dye uptake capacity was found to be more at pH 2, when compared to with other pH value. The equilibrium sorption isotherms have been analysed by the Freundlich and Langmuir models. The Freundlich isotherms have the highest co-efficient of determination. The kinetic data of the biosorption was analysed using the pseudo-first order and pseudo-second order kinetic models. The data showed that the pseudo-second order equation was more appropriate. The surface morphology of the seeds of the Morinda Tinctoria was exemplified by scanning electron microscope. Fourier transform infrared analysis confirm the existence of a amine group in the Morinda Tinctoria

Keywords*: Equilibrium, Kinetics, Morinda Tinctoria seeds, Modeling, Reactive Red 120 dye*

1. Introduction

Many industries including textile, rubber, paper, leather, plastics, cosmetic, printing and others are using synthetic dye stuff during their various dyeing operations which are producing high volume of dye-bearing wastewater. This exhibits high colour and high chemical and biochemical oxygen demands. The discharge of these dye effluents in to the environment were worrying health and esthetical reasons. (Tan,I.A.,*et al.*,2007). In general, dyes are poorly biodegradable or resistant to environmental conditions and therefore create major problems in the treatment of wastewater management. Moreover, they cannot be completely removed by conventional biological treatment processes such as activated sludge and anaerobic digestions (Vimonses.,*et al*,2009). The removal of dyes in an economic way remains an important problem although a number of processes have been developed with adsorption techniques. Adsorption is a very effective separation technique and now it is considered to be superior to other techniques for water treatment in terms of initial cost, simplicity of design and ease of operation and insensitive to toxic substances (Mohammad.et al, 2010). The commonly used adsorbent, activated carbon has a high capacity for the removal of dye (Sharma,Y.C.,*et al.*,2010). Thus, there is demand for the other adsorbents which are made up of inexpensive material and does not require any additional pre-treatment such that the adsorption process will become economically viable. Recently, some agricultural and forestry products and wastes have been recognized as new adsorbent. Several kinds of agricultural by -products such as indica leaf powder (Bhattacharya,K.G., *et al.*,2003), giant duckweed ,sawdust , barley husk , orange peel and fly ash (Visa,M., *et al*.,2009), Castor seed shell (Oladoja,N.A., *et al*.,2008). However, sorption capacity of some of the low cost adsorbent is very low. So, there is a need to find an economical, easily available and highly effective sorbent .*Morinda Tinctoria* belongs to family Rubiaceae. The plant is extensively cultivated in India and its leaves and roots are used in traditional medicine and to relive pain in the gout *(*Nadkarni , A.K.,*,et al.*,1998).

In the present investigation, *Morinda tinctoria* biomass is used for removal of Reactive Red 120 dye from aqueous solution with different initial sorbent dosage, pH and dye concentrations in a batch mode. The equilibrium data was analyzed using Langmuir and Freundlich adsorption isotherm models. The kinetics data was analyzed using Pseudo first order and Pseudo second order kinetics models.

2. Experimental Methods

2.1. Preparation of Adsorbent

The *Morinda Tinctoria* seeds were broken up into small pieces and washed with water, dried in an oven and transferred to the muffle furnace and the seeds pieces were burnt distinctively in the furnace for 2 hours fixing the temperature at 400°C. Adsorbent

thus produced were withdrawn from the furnace, cooled, washed with water and dried in an oven at 110°C for 2 hours and ground in a mortar by means of a pestle applying moderate pressure. It was cooled in the desiccators for an hour then removed and ready for use as an adsorbent.

2.2. Preparation of Dye Solutions

Reactive Red 120 were obtained from Balaji chemicals Ltd., Chennai, India. The dye stock solutions were prepared by dissolving accurately weighed dyes in distilled water to the concentration of 50 mg L^{-1}. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions for different initial dye concentrations. The chemical structure is illustrated in Figure 1.

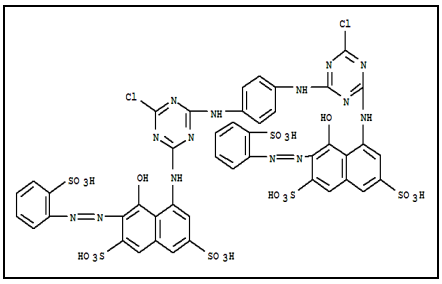

Figure 1: Chemical structure of Reactive Red 120 Dye

2.3. Batch experimental process

Biosorption experiments were carried out in a Rotary shaker at 180 rpm and at 30°C. Reactive Red 120 solutions were prepared to get required concentrations of *Morinda Tinctoria* biomass were added in the dye solutions. Samples were withdrawn at predetermined time intervals (0, 30, 60, 90, 120, 150 and 180 min), centrifuged at 12,000 rpm for 10 min and the absorbance of the supernatant were determined at maximum wavelength (λmax = 536 nm) (Naveen.N., *et al.*,2011) using UV-spectrophotometer. Results were reported on the basis of the dye uptake capacities.

2.3.1.Studies of biosorbent dosage

The dye solution 100 ml in each flask (concentration 50 mg/L) was equally dispersed into five conical flasks and added with different dosages (0.02–0.1 g/L) of biosorbent. These flasks were kept in a rotary shaker and absorbance values were determined using UV-spectrophotometer.

2.3.2. Studies of the pH

The dye solution with the concentration of 50 mg/L was prepared. The initial pH values ranging from 1 to 7 were adjusted with HCl and NaOH. The optimum dosage of the biosorbent were added into each flask and kept in a rotary shaker. The absorbance values were determined using UV-spectrophotometer.

2.3.3. Studies of initial Dye concentration

The dye solutions with five different concentrations ranging from 10 to 50 mg/L were prepared in different conical flasks. The optimum dosage of biosorbent were added into each flask and adjusted to optimum pH and kept in a rotary shaker at 30°C. The absorbance values were determined using UV-spectrophotometer.

3. Results and Discussion

3.1. Scanning Electron Microscopy Images

The Scanning electron microscopy images of the adsorbent before the adsorption is shown in Figure 2a. The surface morphology of the activated carbon observed by SEM indicates that the activated carbon has different sizes of cavities. This might be due to the presence of mesoporous nature of activated carbon. These pores are large enough to allow the molecules of the dye to be adsorbed. Figure 2b represents the SEM image of the adsorbent after adsorption which shows that the dye has been adsorbed.

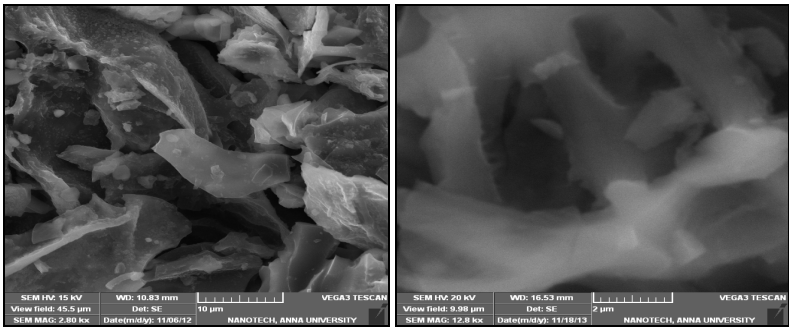

Figure 2 a: SEM image of Morinda Tinctoria before adsorption
Figure 2 b: SEM image of Morinda Tinctoria after adsorption

3.2. Fourier Transform Infrared spectroscopy analysis

Figure 3. represents the FTIR analysis of *Morinda Tinctoria* before adsorption. The peaks at 1575cm^{-1} representing the carboxylic groups (Parveena N *et al*., 2012).The FTIR spectrum showed some characteristics of an amine group such as N-H bonding bands at 2358 cm^{-1}, N-H out of plane bending band near 880 cm^{-1}and N-H rocking bands at 700-900cm-^{1} (Naveen N *et al*., 2011) .

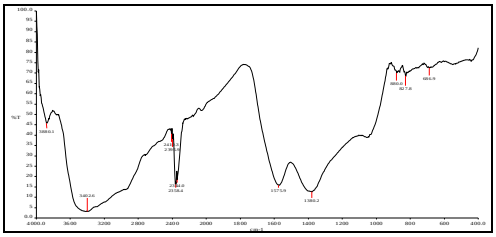

Figure 3: FTIR spectrum of biomass Morinda Tinctoria before adsorption of Reactive Red 120

3.3. Effect of biosorbent dosage

The effects of biosorbent dosage on the equilibrium dye uptake capacity were shown in Figure 4. It was observed that 0.02 g/L biosorbent dosage was found to be optimum for the dye removal. The equilibrium dye uptake capacity was found to be decreased with increasing in biosorbent dosage. This can be attributed to the difference in solute transfer rate on to the biosorbent surface. Further there is a distribution of the dye compounds to unit weight of biosorbent with increase in biosorbent dosage. The decrease in equilibrium uptake capacity may be due to the solute transfer rate on the adsorbent surface. In addition, the amount of dye compounds adsorbed on to the unit weight of the adsorbent was split with increasing adsorbent dosage.

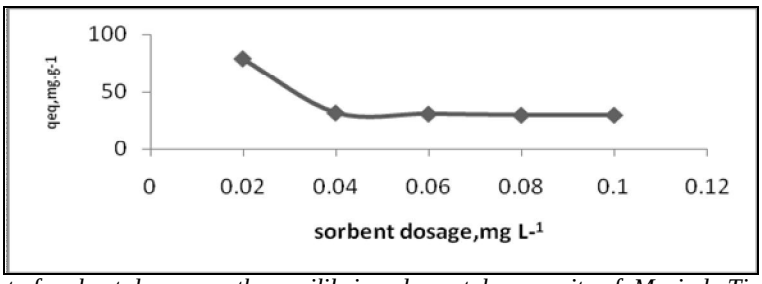

Figure 4: Effect of sorbent dosage on the equilibrium dye uptake capacity of Morinda Tinctoria biomass for Reactive Red 120 dye(initial dye concentration = 50mgL^{-1}; temperature=30^{o}C, agitation rate=180 rev min^{-1}).

3.4. Effect of pH

The influence of pH on the uptake capacity of reactive red 120 on dried *Morinda Tinctoria* seeds were studied with the optimum biosorbent dosage (0.02g 100mL^{-1}). It was found that the uptake capacity of dye increased with increase in pH value up to 2 and then decreased sharply with increase in pH value above 2. The equilibrium uptake capacity was found to be more at pH 2 when compared with all other pH values in the present investigation. Figure 5 shows the effect of solution, pH on the uptake capacity of dye at 30˚C.

At lower pH values, the biomass will have a net positive charge. The reduction in the uptake capacity of dye on *Morinda Tinctoria* with increasing pH can be attributed to a change in surface characteristics and charge. As the pH of the system increased, the number of negatively charged sites increased, and the number of positively charged site decreased in the biomass (Aksu,Z.,*et al* ., 2000). A negatively charged surface site on the sorbent did not favour the adsorption mechanism with respect to the pH. So, the pH 2 was taken as the optimum value for the corresponding experiments.

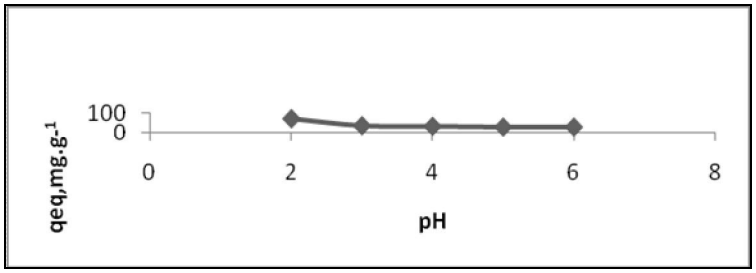

Figure 5: Effect of pH on the equilibrium dye uptake capacity of Morinda tinctoria biomass for Reactive Red 120 dye (initial dye concentration = 50mg L^{-1}; sorbent dosage = 0.02 g 100 mL^{-1} temperature = 30°C, agitation rate = 180 rev min^{-1}).

3.5. Effect of initial dye concentration

The dye uptake capacity were found to be increased linearly with contact time in the beginning, then non-linearly at slower rate and finally attained saturation called equilibrium time(Figure 6) The uptake capacity of dye with the influence of initial dye concentration 10, 20, 30, 40 and 50 mg/L were studied. The optimum biosorbent dosage 0.02 g of adsorbent was added to 100 ml of dye solution with pH value of 2. These flasks were then kept in the rotary shaker at 180 rpm and 30°C. The samples were withdrawn at pre determined time interval. The samples were centrifuged at 12,000 rpm for 10 min. The biosorption capacities of biomass for Reactive Red 120 were determined. Increase in the dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases, thus increases the uptake. In addition, higher initial dye concentration increases the number of collisions between the dye molecules and sorbents, which enhances the sorption process.

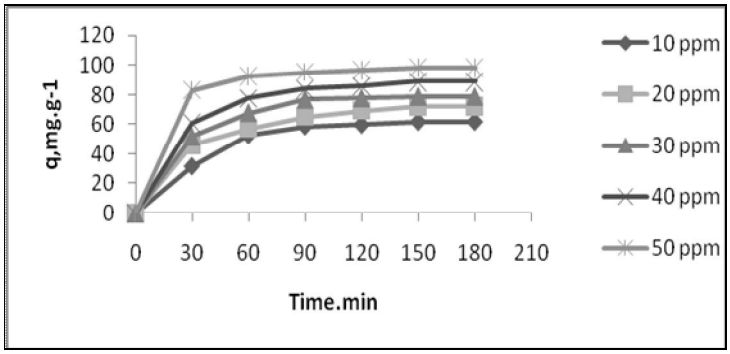

Figure 6: Effect of initial dye concentration on the uptake capacity of Morinda tinctoria seeds biomass for reactive red 120 dye (sorbent dosage=0.02g 100mL^{-1}; pH =2 ; temperature = 30°C; agitation rate=180rev min^{-1}).

3.6. Equilibrium modelling

Langmuir and Freundlich isotherm models were utilized for the mathematical description of the biosorption of the dye in an aqueous waste effluent.

3.6.1. Langmuir Isotherm

Equilibrium studies were described by a sorption isotherm characterized by certain constants whose values expressed the surface properties and affinity of the sorbent. The monolayer coverage of the sorbate on a sorbent surface at constant temperature is represented by the Langmuir isotherm. The Langmuir isotherm expression is presented by,

$$q_{eq} = \frac{Q^{\circ}\, b\, C_{eq}}{1 + b\, C_{eq}} \qquad \text{(1)}$$

Where q_{eq} is the quantity of dye adsorbed per unit weight of biosorbent at equilibrium (mg/g); Q^{o} is the maximum possible amount of dye that can be adsorbed per unit dry weight of biosorbent to form a complete monolayer on the surface (mg/g); C_{eq} is the equilibrium concentration of unadsorbed dye in the solution (mg/L); b is the empirical constant, indicating the affinity of sorbent towards the sorbate . Figure 7 shows the equilibrium data fitted to the Langmuir isotherm expressions.

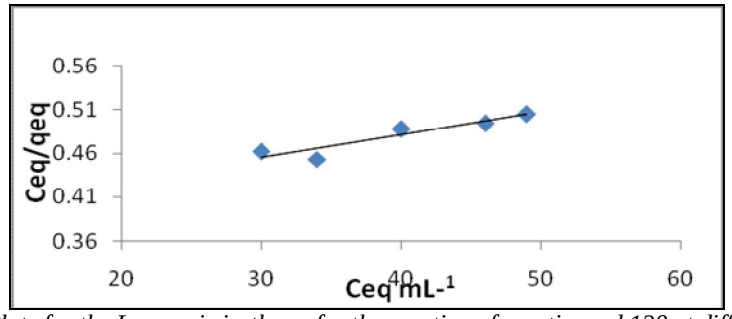

Figure 7: Plots for the Langmuir isotherm for the sorption of reactive red 120 at different initial dye concentrations (sorbent dosage = 0.02 g 100 mL^{-1}; pH= 2; temperature= 30^{o}C; agitation rate = 180 rev min^{-1}).

3.6.2. Freundlich isotherm

The Freundlich adsorption isotherm equation explains the adsorption on the heterogeneous surface and is given by the expressions

$q_{eq} = K_F C_{eq}^{1/n}$ ----------(2)

Where K_F and n indicators of adsorption capacity and adsorption intensity, respectively. The value of K_F and n are obtained by plotting ln q_{eq} versus ln C_{eq} is shown in Figure 8. The calculated isotherm constants at different temperature are given in Table 1. In view of the values of linear regression coefficients in Table 1, the Freundlich model exhibited a slightly better fit to the equilibrium data when compared to the Langmuir model studied. The best fit of equilibrium model was determined based on the coefficient of determination R^2 and the plot is shown in Figure 8.

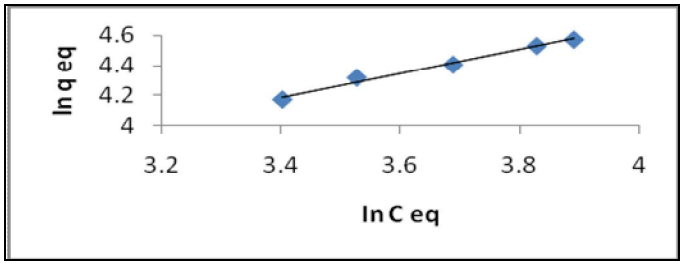

Figure 8: Plots for the Freundlich isotherm for the sorption of Reactive Red 120 at different initial dye concentrations (sorbent dosage=0.02 g 100mL^{-1}; pH= 2; temperature= 30^{o}C; agitation rate=180rev min^{-1}).

Parameters	**Isotherm constants for the biosorption of reactive red 120using *Morinda Tinctoria***
	Langmuir adsorption isotherm
Q^o (mg g^{-1})	384.6
b (L mg^{-1})	0.00097
R^2	0.8778
	Freundlich adsorption isotherm
K_F (mg g^{-1})	30.05
N	1.2550
R^2	0.9875

Table 1: Langmuir and Freundlich isotherm constants and coefficient of determination for the sorption of Reactive Red 120 using seeds bio Morinda Tinctoria biomass.

3.7. Kinetic modelling

The biosorption mechanism and potential rate controlling steps have been investigated by using the Pseudo first -order and Pseudo second-order models.

3.7.1. Pseudo-first order kinetic model

pseudo-first order rate expression of Lagergren,1898 is represented in eqn (3)

$$\frac{dq}{dt} = k_{1,ad}(q_{eq}-q) \quad \text{----------(3)}$$

Where q_{eq} , q are equilibrium uptake capacity and uptake capacity at any time, respectively. The $k_{1,ad}$ is the first order biosorption rate constant (min^{-1}). The integrated form of eqn (3) is given by eqn (4).

$$\log(q_{eq}-q) = \log q_{eq} - \frac{k_{1,ad}}{2.303} t \quad \text{----------(4)}$$

The pseudo-first order rate constant, $k_{1,ad}$ and q_{eq} were determined from the slope and intercept of the plot (Figure 9). The pseudo-first order rate constant values were presented in Table 2 for different initial dye concentrations.

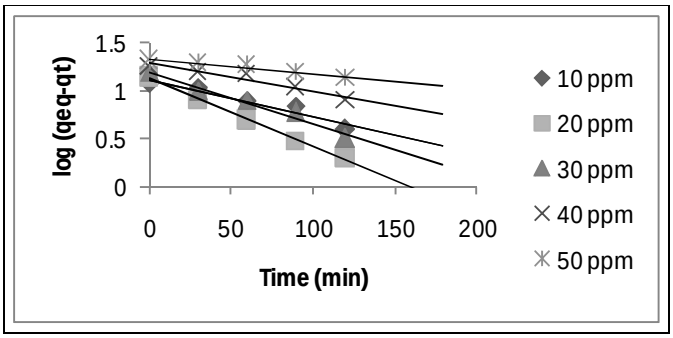

Figure 9: Plots for the pseudo-first order for the sorption of reactive red 120 at different initial dye concentrations (sorbent dosage = 0.02 g 100mL^{-1}; pH=2; temperature= 30^{o}C; agitation rate =180 revmin^{-1}).

Initial concentration (mg L^{-1})	$Q_{eq.exp}$ (mg g^{-1})	Pseudo-first order			Pseudo-second order		
		$k_{1,ad}$ (min^{-1})	$q_{eq.cal}$ (mg.g^{-1})	R^2	$k_{1,ad}$ (min^{-1})	$q_{eq.cal}$ (mg.g^{-1})	R^2
10	68	.00870	13.30	0.9211	0.0022	69	0.9949
20	79	0.0163	13.44	0.9970	0.0038	80	0.9988
30	82	0.0124	15.84	0.9676	0.0024	90	0.9809
40	85	0.00644	19.38	0.9230	0.0014	95	0.9910
50	90	0.04130	22.18	0.9090	0.0060	99	0.9909

Table 2 : Pseudo-first and pseudo-second order rate constants, calculated and experimental values for the biosorption of Reactive Red 120 using Morinda Tinctoria seeds biomass.

3.7.2. Pseudo-second order kinetic model

The expression for the pseudo-second order kinetic model is

$$\frac{dq}{dt} = k_{2,ad}(q_{eq}-q)^2 \quad \text{----------(5)}$$

Where $k_{2,ad}$ is the second order biosorption rate constant(g mg^{-1} min^{-1}).

Integrating eqn (5) gives eqn (6):

$$\frac{t}{q} = \frac{1}{k_{2,ad}\, q_{eq}^2} + \frac{1}{q_{eq}} t \quad \text{----------(6)}$$

The pseudo-second order rate constant, $k_{2,ad}$ and q_{eq} were determined from the slope and intercept of the plot (Figure. 10). The pseudo-second order rate constant values were presented in Table 2 for different initial dye concentrations. The calculated coefficients of determination for Pseudo-second order kinetic model was found to be closer to unity when compared to Pseudo-first order kinetic model. The equilibrium adsorption capacity was found to be increased with increase in initial dye concentrations. The $q_{eq,cal}$ calculated values were found to be very closer to q_{eq} experimental values in Pseudo-second order kinetic model when compared to the Pseudo-first order kinetic model (Table 2). Therefore, the kinetic data were found to be fitted very well with the Pseudo-second order kinetic model when compared to Pseudo-first order kinetic model for the biosorption of Reactive Red 120 using *Morinda tinctoria*

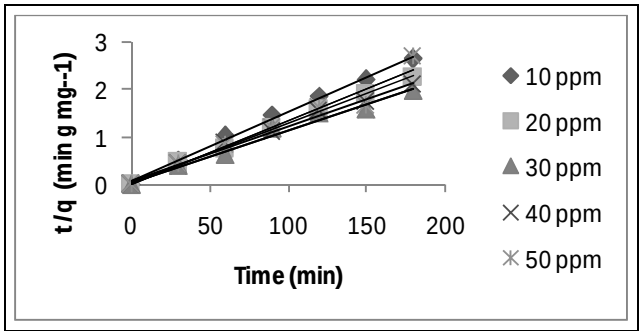

Figure 10: Plots for the pseudo-second order for the sorption of Reactive Red 120 at different initial dye concentrations (sorbent dosage=0.02 g 100mL^{-1}; pH=2; temperature=30^{o}C; agitation rate=180 rev min^{-1}).

4. Conclusion

Batch experiments were conducted to study the effect of sorbent dosage, initial dye concentration. The equilibrium data were found to be fitted very well with the Freundlich adsorption isotherm model with higher coefficient of determination when compared to the Langmuir adsorption isotherm model. The kinetic data fit very well with the pseudo second-order rate equation when compared to pseudo first-order rate equation. The surface morphology of the sorbent was analyzed using SEM micrograph. The functional groups were analyzed using FTIR. From the present study, it was found that *Morinda Tinctoria* biomass could be used as a potential low cost readily available sorbent to remove Reactive Red 120 dye from an aqueous textile effluents.

5. References

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