Utilization of Chemically Modified *Citrus reticulata* Peels for Biosorptive Removal of Acid Yellow-73 Dye from Water

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Summary: Textile effluents contain several varieties of natural and synthetic dyes, which are non-biodegradable. Acid Yellow-73 is one of them. In this research work, adsorptive removal of this dye was investigated using chemically modified *Citrus reticulata* peels, in batch mode. It was noted that adsorption of dye on *Citrus reticulata* peels increased by increasing contact time and decreased in basic pH conditions. Langmuir and Freundlich isothermal models were followed by equilibrium data, but the first isotherm fitted the data better, showing that chemisorption occurred more as compared to physiosorption, showing maximum adsorption capacity 96.46 $mg.g^{-1}.L^{-1}$. The thermodynamic study showed that adsorption of Acid Yellow-73 on chemically modified *Citrus reticulata* peels was favorable in nature, following pseudo-second order kinetics.

Keywords: *Citrus reticulata* peels, Acid Yellow-73, adsorption, waste-water, isotherms.

Introduction

Reactive anthraquinone dyes are extensively employed in textile industry due to their broad range of color shades and simplicity in application methodology. Their fused aromatic ring structures results in resistant to bio-degradation. Acid Yellow-73 is their common example, which is toxic, mutagenic and carcinogenic in nature. In this research work, Acid Yellow-73 has been used [1, 2]. Its structure is shown in Fig. 1.

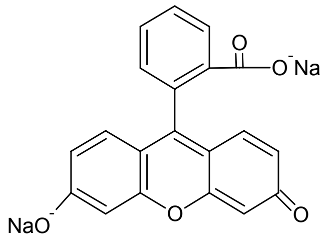

Fig.1: Chemical structure of Acid Yellow-73 dye.

These dyes are not easily removed by routine waste-water treatment methodologies like chemical precipitation, photo-catalytic degradation, coagulation and chemical or biological oxidation due to their thermodynamic stability and resistance towards photo-catalytical or biological oxidizing agents [3-5]. The adsorption process in recent years provides an attractive substitutive treatment of contaminated waters, particularly if the adsorbent is low-cost and indigenously available. Researchers are trying to find new economical adsorbents from their indigenous sources for treatment of waste-water by adsorption like: wheat husk, rice husk, plant leaves, seeds, peels of fruits and vegetables, chitin, straw, corn cobs, barley husks etc [6-16]. The adsorption of dye on agro-waste materials predominantly occurred by passive transport mechanisms due to these functional groups like: amino, hydroxyl, carboxylate and esters [17].

In this research work *Citrus reticulata* peels were used for the adsorption of Acid Yellow-73 dye from water. *Citrus reticulata* (common names: Kinnow, Mandarin orange, mandarin or mandarine) belongs to plant family Rutaceae, usually reach a height of 25 feet on average with a greater spread. Pakistan is the one of its largest producer in the world. This exclusive variety of citrus plants is indigenous to our country and approximately 95 % of the total Kinnow production of the world is grown in Pakistan. In traditional Chinese and Ayruvedic medicines, the dried peel of *Citrus reticulata* fruit is used to treat abdominal distension and reduce phlegm by enhancing digestion *Citrus reticulata* peels are already reported to remove several inorganic and organic pollutants from water on batch scale [18-21] The main aim of this study is to use them for removal of Acid Yellow-73, after treating with formaldehyde in order to improve its shelf life by preventing microbial attack. Various operational parameters of adsorption were optimized. Then kinetic modeling along with adsorption isotherms had been investigated in the batch mode.

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Results and Discussion

Characterization of Adsorbent

Citrus reticulata peels mostly consists of cellulosic material having reactive hydrogen atom. Formaldehyde undergoes addition reaction with compounds containing reactive hydrogen atom to form methylol derivatives as shown in Fig. 2. FT-IR spectrum of unmodified and chemically modified *Citrus reticulata* peels is shown in Fig. 3.

Significant band shifting from 3423.19 (O–H stretching), 2925, 2847 (C–H symmetric and asymmetric stretching), 1731.34 (stretching vibrations of –COOH and –$COOCH_3$), 1626.32, 1424.94 (C–OH of carboxyl), 1312.44 (C–O stretch in ester), 1262.67 (C–O of aliphatic acid groups), 1154.54 (C–O–C stretch in ether) and 1033.02cm^{-1} (stretching vibration of C–OH) on unmodified *Citrus reticulata* peels occurred after chemical modification. They were shifted to 3420, 2924, 1744, 1638, 1434, 1267 and 1068cm^{-1} respectively, in chemically modified *Citrus reticulata* peels. This shows that *Citrus reticulata* peels contain alcoholic, aliphatic and aromatic acidic and phenolic, esters and ketonic constituents, which can chemisorb pollutants effectively [22-25].

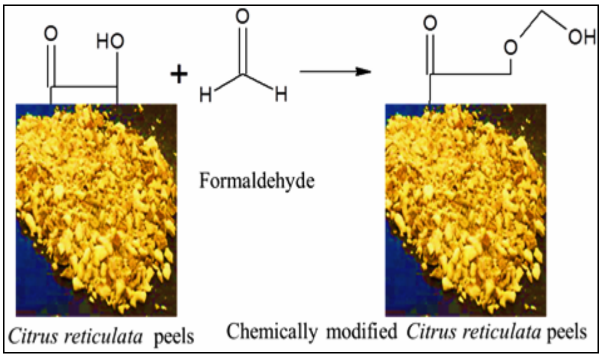

Fig. 2: Possible mechanism of chemical modification of C.R.P.

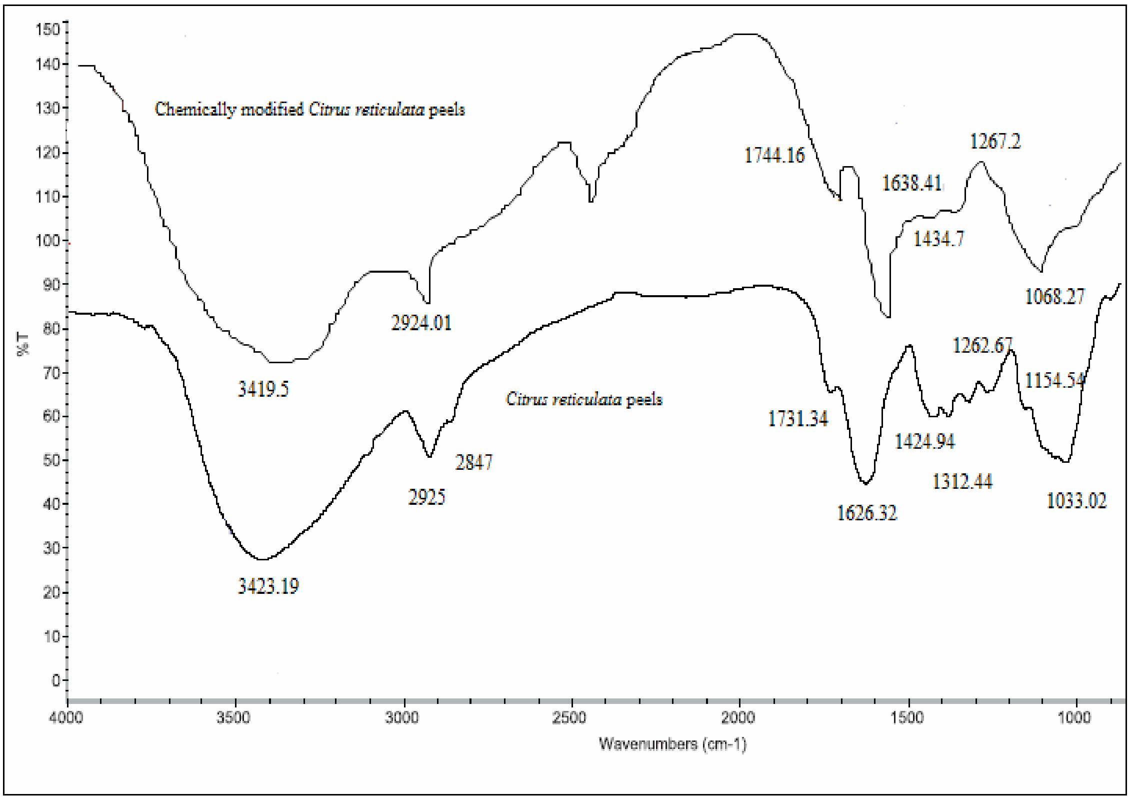

Fig. 3: FT-IR spectrum of unmodified and chemically modified *Citrus reticulata* peels.

Optimization of Adsorption Parameters

1. Solution pH

Fig. 4 is showing that when Acid Yellow-73 dye solution was treated with *Citrus reticulata* peels (C.R.P), it shows maximum adsorption in acidic pH range and 90 % of dye was removed at pH 3 and 41% at pH 10. In acidic conditions, protonation of oxygen containing functional groups and simultaneously hydrolysis of the dye species favors chemisorption [24].

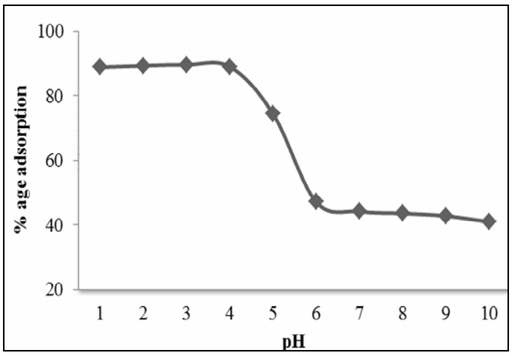

Fig. 4: Solution pH effect on % age adsorption of Acid Yellow-73 dye by chemically modified C.R.P.

2. Contact Time

It is indicated clearly from Fig. 5 that C.R.P adsorption power increased up to 72 % in 65 min. This increase in tendency for adsorptive removal of dye with increasing time is due to the fact that dye molecules form monolayer on the surface of C.R.P.

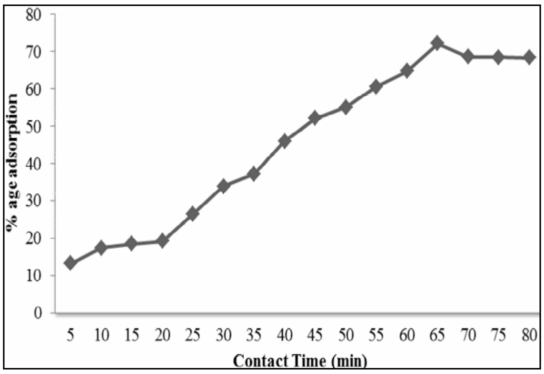

Fig. 5: Effect of contact time between Acid Yellow-73 and C.R.P on % age adsorptive removal of dye.

It favors the removal of dye from aqueous media by controlling the rate of transport of the adsorbate species from outer binding sites to inner sites of adsorbent. Adsorption of dye first occurred rapidly due to physiosorption on adsorbent upper surface, followed by slow mass transfer to inner binding sites of adsorbent and intra-particle diffusion. That's why, after attaining equilibrium, adsorption rate becomes nearly constant [12].

3. Temperature

It is clear from Fig. 6 that maximum 73% adsorptive removal of Acid Yellow-73dye occurred at 50 ^{o}C by *Citrus reticulata* peels keeping the other parameters are constant. The increase in removal of Acid Yellow-73 dye with increasing temperatures is because of greater mobility of the adsorbate molecules. Higher temperature results in swelling within the inner composition of *Citrus reticulata* peels, thus large molecules of dye enabled to go through further. It also increases solubility of dye [18-20].

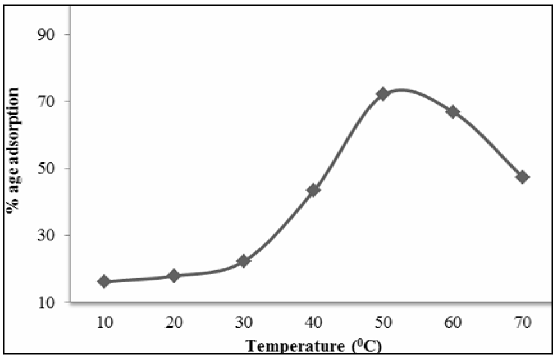

Fig. 6: Temperature effect on % age adsorptive removal of Acid Yellow-73 dye by chemically modified C.R.P.

4. Adsorbent Dose

The results of adsorbent dose variation on % age adsorptive removal of Acid Yellow-73 dye by C.R.P was are given in Fig. 7. This experiment was carried out in batch mode by changing adsorbent dose in between 0.1-1.0 g and keeping other parameters constant. Maximum removal of dye was found at 0.3 g of adsorbent dose and it is 92 %. Further increase in *Citrus reticulata* peels quantity reduces in %age adsorption of Acid Yellow-73 dye, because greater quantity results in agglomeration of adsorbent particle, which results in reduced exposure to dye molecules. That's why; increasing adsorbent dose further had depressing effect on adsorption efficiency [25].

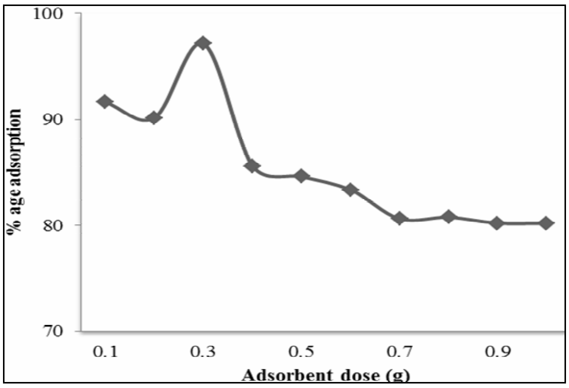

Fig. 7: Adsorbent dose effect on % age adsorptive removal of Acid Yellow-73 dye by chemically modified C.R.P.

5. *Initial Concentration of adsorbate*

The concentration of dye effect on adsorption efficiency had been tested in the range of 5-50 ppm and keeping other factors constant. The % age adsorptive removal of Acid Yellow-73 dye increased from 54 to 75 % using 0.5 g of C.R.P. The results in Fig. 8 indicated that the adsorption of dye is strongly dependent on its initial concentration. Lower concentration of dye can be effectively be removed by adsorption, but huge concentration of dye poses problems and had negative effect on adsorption capacity of adsorbents [12-19]

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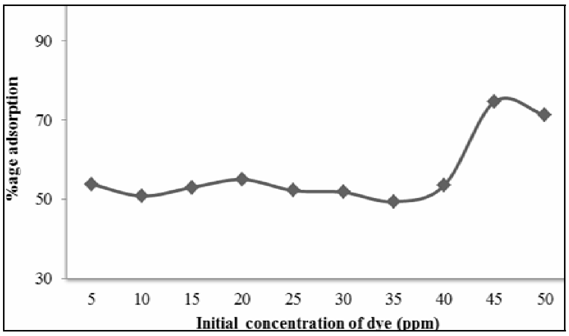

Fig. 8: Initial concentration of dye effect on % age adsorptive removal of Acid Yellow-73 dye by chemically modified C.R.P.

6. *Isothermal Investigation*

Freundlich and Langmuir isotherm model are applied using optimized conditions for determining mechanism of adsorptive removal of Acid Yellow-73 dye by C.R.P.

Langmuir Model

The equilibrium data obtained with varying concentration of adsorbate and fixed dose of adsorbent was applied to the Langmuir isothermal model as shown in Fig. 9.

$$1/ q_e = (1/bQ_{max}\, C_e) + 1 / Q_{max} \qquad \text{(Eq.1)}$$

here: b= Langmuir constant
Q_{max} = Maximum quantity of dye adsorbed per unit dry weight of *Citrus reticulata* peels.
C_e = remaining concentration of dye
q_e = quantity of dye adsorbed, calculated by $[(C_o-C_e)V/m]$.
C_o= initial concentration of Acid Yellow-73 dye
V= volume of Acid Yellow-73 dye solution
m= mass of C.R.P used [23].

Langmuir isotherm constant '*b*' is used to calculate a dimensionless separation factor constant 'R_L' by eq.2;

$$R_L = 1 / (1+ bC_o) \qquad \text{(Eq.2)}$$

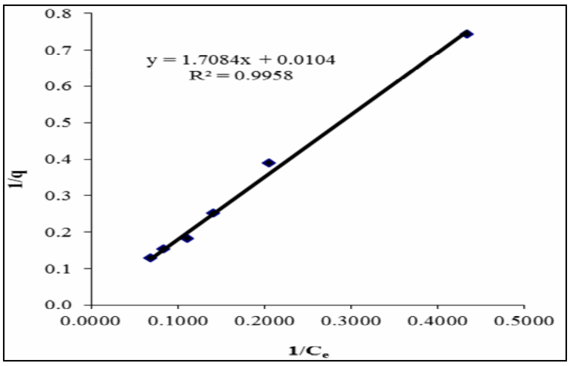

Fig. 9: Langmuir graph for adsorptive removal of Acid Yellow-73 dye by chemically modified C.R.P.

Q_{max}, *b* and R_L values are given in Table-1. Here in this case, maximum removal of Acid Yellow-73 by chemically modified C.R.P is 96.46 mg.g^{-1}. R_L is found to be 0.769 which indicates irreversible nature of favorable adsorption. These encouraging results prove the effectiveness of chemical modification C.R.P with formaldehyde [24].

Table-1: Langmuir isothermal and thermodynamical parameters for adsorptive removal of Acid Yellow-73 dye by chemically modified *Citrus reticulata* peels.

Langmuir Isotherm Parameters					*Separation factor*	*Thermodynamic parameter*
Slope	Intercept	R^2	Q_{max} (mg.g^{-1})	b (L.g^{-1})	R_L	ΔG^o (KJ.mol^{-1})
1.708	0.010	0.9958	96.46	0.006	0.769	-12.67

Freundlich Model

If equilibrium data followed Freundlich equation as given in eq.3, it indicates that physio-sorption occurred on heterogeneous surface of adsorbent.

$$\log q = \log K_f + 1 / n \log C_e \qquad \text{(Eq.3)}$$

where 'K_f' and 'n' are Freundlich constants related to adsorption capacity and adsorption intensity correspondingly. The values of 'K_f' and 'n' are calculated from regression analysis of Fig. 10 and given in Table-2. K_f is 0.58 $mg^{1-1/n}$ $L^{1/n}$ g^{-1} and *n* value is 1.021. The value of 'n' in the range of 0 to 1 corresponds to physio-sorption on heterogeneous surface of adsorbent and in this case, less physio-sorption occurred. It is also indicated by greater correlation coefficient of Langmuir model (R^2=0.9958) as compared to Freundlich model (R^2=0.9935) [23].

Table-2: Freundlich parameters for adsorptive removal of Acid Yellow-73 dye by chemically modified *Citrus reticulata* peels.

Freundlich Isotherm Parameters				
Slope	**Intercept**	**R^2**	**$K_f(mg^{1-1/n} L^{1/n} g^{-1})$**	**n**
0.979	**-0.233**	**0.9935**	**0.58**	**1.021**

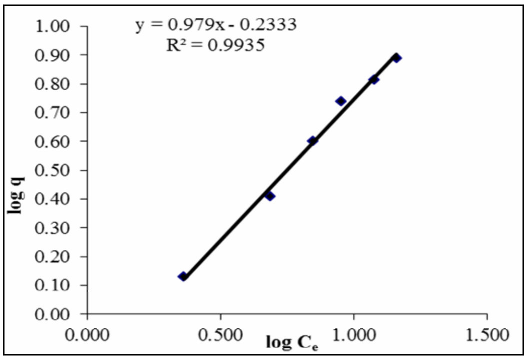

Fig. 10: Freundlich graph for adsorptive removal of Acid Yellow-73 dye by chemically modified C.R.P.

7. *Thermodynamical Investigation*:

Thermodynamic parameter ΔG^o is calculated by eq.4:

$$\Delta G^o = - RT \ln(K) \qquad \text{(Eq.4)}$$

where 'K' is the reciprocal of Langmuir constant 'b'. The negative value (-12.67 $KJ.mol^{-1}$) of ΔG^o as indicated from Table 1, indicates the spontaneous nature of adsorption [19-21].

8. *Kinetic Studies*:

They were carried out to predict basic mode of adsorption. Pseudo-first order kinetics is given by Lagergren rate eq.5:

$$\log (q_e - q_t) = \log q_e - k_{ad} / 2.303 \qquad \text{(Eq.5)}$$

where K_{ad} = rate constant of first order adsorption and q_t= is the amount of dye adsorbed at time. Its corresponding graph is shown in Fig. 11. Whereas pseudo-second order kinetics of adsorption is given by eq.6 and its corresponding graph is shown in Fig. 12:

$$t / q_t = 1 / k_2 q_e + 1 / q_e.t \qquad \text{(Eq.6)}$$

The comparison of both graphs indicated that correlation coefficient R^2 value is greater for pseudo-first order kinetic model (0.907) as compared to second one (0.765).

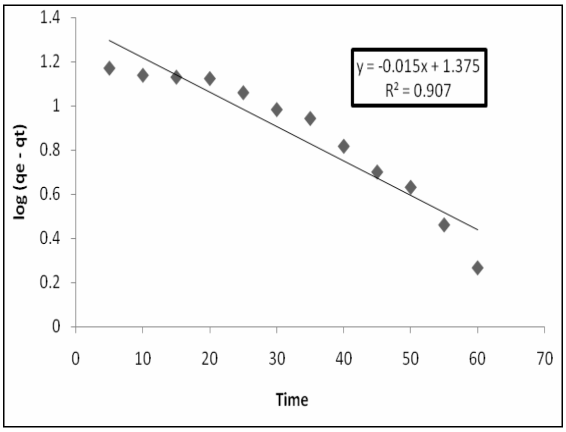

Fig.11: Pseudo-first order graph for adsorptive removal of Acid Yellow-73 dye by chemically modified C.R.P.

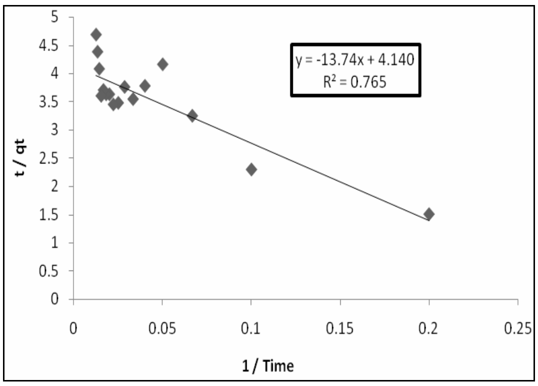

Fig. 12: Pseudo-second order graph for adsorptive removal of Acid Yellow-73 dye by chemically modified C.R.P.

Experimental

Preparation of Adsorbate

Stock solution of Acid Yellow-73 (Sigma-Aldrich, $C_{20}H_{10}Na_2O_5$, mol. wt. 376.27 g.mol^{-1}, CAS No.: 518-47-8) was synthesized by taking 1.0 g of dye / L of de-ionized water. Further solutions were prepared by its dilutions as per requirements.

Preparation of Adsorbent

The adsorbent *Citrus reticulata* were purchased from local markets and washed. They were peeled off and dried in sun light for a week. Peels were soaked in 10 % formaldehyde solution in order to prevent fungal attack and removal of coloring materials from peels. Then after air drying for 3 days, they were kept in oven at 80 ^{o}C for 2 hours for complete removal of moisture. Possible mechanism of chemical modification of cellulosic material with formaldehyde is given in Fig. 2. Finally, they were ground and sieved through 50 ASTM mesh and the resulting fine powder was stored in plastic jars till further use. They were analyzed by recording their FT-IR spectrum (Perkin Elmer-RX). Non chemically modified *Citrus reticulata* peels were not used for adsorption studies of Acid Yellow-73 dye because of extrusion of yellowish coloring matter from dried adsorbent in aqueous medium.

Adsorption Experiments

They were carried out as explained by Rehman *et al*., [23] using 50 mL of dye solution with 20 ppm concentration. Residual dye concentration in filtrate was determined spectrophotometrically at λ_{max} 488 nm (Labomed, Inc. Spectro, UVD= 3500) [24, 25].

Conclusion

It is obvious from this study that Acid Yellow-73 dye can be removed from waste-water by adsorption on formaldehyde modified *Citrus reticulata* peels using following optimized conditions of various parameters: 45 ppm initial dye concentration, 65 minutes contact time between adsorbent and dye solution, 3 pH and 50 ^{o}C temperature. Isothermal studies indicated that both chemisorption and physiosorption are occurring during biosorptive removal of dye from water with maximum adsorption capacity 96.46 mg.g^{-1}.L^{-1}. The developed adsorption system is useful and can be used for the removal of Acid Yellow-73 dye from contaminated water.

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