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Biosorption of Acid Orang 7 using dried Cyperus Rotundus: Isotherm Studies and Error Functions

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Abstract : Industrial wastewater is one of the major environmental pollutants. Discharge of the colorful industrial waste into the receptive waters leads to eutrophication and has mutagenic and carcinogenic properties In order to understand the biosorption of Acid Orang 7 (AO7) textile dye on dried Cyperus Rotundus (CR), batch experiments were conducted under various conditions. Adsorption isotherms were examined by six different isotherm and four Error Functions that finally showed the langmuir models closely fitted the experimental results. The maximum monolayer adsorption capacities of biomass are 32.21 mg/g at 273 K, 35.69 mg/g at 293 K and 38.45 at 313 K, respectively. Therefore adsorption capacity increases with increasing temperature, that shows the adsorption is an endothermic process. The results showed that the percentage of removal reached 98.9% from wastewater containing 25 mg/L AO7 dye, indicating that the Cyperus Rotundus biomass could be used as a potential biosorbent for the removal of AO7 dye from aqueous solution.
Keywords: Cyperus Rotundus, Acid Orang 7, Biosorption, Kinetic Mechanism.

Introduction:

Water pollution by organic chemicals is a major problem over decades[1,2]. Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid[3]. As a result, these industrial effluents have become one of the major pollutants to the aquatic environment and will cause considerable damage to the receiving waters if not properly treated[4]. Dyes in these industrial effluents are difficult to remove due to the variety of aromatic components which they contain and which are highly resistant to aerobic digestion and oxidization[5,6]. Due to low biodegradability of dyes, a conventional biological treatment process is not very effective in treating a dye wastewater[7, 8]. It is usually treated by physical or chemical processes[9, 10]. However these processes are costly and cannot effectively be used to treat the wide range of dye wastewaters[11]. Adsorption on activated carbon (ACR) has been found to be an effective process for dye removal, but it is too expensive[12]. Consequently numerous low cost alternatives have been proposed including Azolla[13], cashew nut shell[14], Canola[15, 16], sawdust[17], husk rice[18], Hazelnut Shells[19], coir pith[20], Lemna minor[21]. New economical, easily available and highly effective adsorbents are still needed. Cyperus Rotundus (CR) is one of the most invasive weeds known, having spread out to a worldwide distribution in tropical and temperate regions[22]. It has been called "the world's worst weed, as it is known as a weed in over 90 countries, and infests over 50 crops worldwide[23]. The difficulty to control it is a result of its intensive system of underground tubers, and its resistance to most herbicides[24]. Weed pulling in gardens usually results in breakage of roots, leaving tubers in the ground from which new plants emerge quickly[25]. Most herbicides may kill the plant's leaves, but most have no effect on the root system and the tubers and therefore poses many negative effects to aquatic ecology[22]. However, using CR as a bioabsorbent to remove dyes from the industrial effluents would be a "win–win" solution for both environmental problems[23]. In this study, dried CR was used as a biosorbent to remove Acid Orang 7 (AO7) as a target pollutant from aqueous solution. The aim was to study the affects influencing biosorption of AO7 on dried CR using batch experiments under different experimental conditions, including Contact time, initial dye concentration and temperature and initial AO7 concentrations.

Materials and Methods:

The dye used in the experiments was AO7, which was provided from Alvan Sabet Company of Iran and the other chemicals used in these experiments were the product of the Merck Company (Darmstadt, Germany). Double distilled water (DDW) was used throughout the study. Table 1 shows the structure of the investigated dye. The AO7 is azo and contain anionic sulphonate groups. Stock solutions of dye were prepared by dissolving the powder in double distilled water. Dye solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

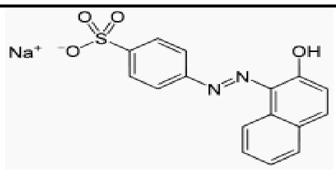
Cyperus Rotundus was collected from Tabriz agricultural school, Iran. The collected materials were then washed several times with distilled water to remove all dirt particles. The washing process was continued till the wash water contained no color. The washed materials were then dried at 50 °C for 12 h. The dried materials were then ground, using steel mill. The adsorbent was sieved through 1-2 mm sieve. The crushed particles were then treated with 0.1M HCl for 5 h followed by washing with distilled water and then kept for shaded dry[26]. The resultant biomass was subsequently used in sorption experiments.

Batch adsorption experiments were performed using 200 ml glass bottles with addition of 4 g CR Biomass and 100 mL of AO7 solution of increased initial concentrations (C_0) from 25 to 200 mg/L. The glass bottles were sealed and placed within a temperature control box to maintain water temperature. The pH of the samples was adjusted by adding 0.1 M HCl or 0.1 M NaOH to each 100 ml of the prepared solution to pH 7. The pH of solutions was measured with a pH meter. In the experiments on the effect of temperature, the temperature was held at 273, 293, and 313 K and the pH was fixed at 7. At the end of the equilibrium period, the suspensions were separated for later analysis of the dye concentration. The amount of AO7 adsorption at equilibrium q_e (mg/g) was calculated from the following equation[27-29]:

$$q_e = (C_0 - C_t)V/W$$

Where C_0 and Ce (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used. The concentration of AO7 after and before adsorption was determined using a spectrophotometer (λ_{max} = 452 nm).

Table1: the charactristics of AO7

chemical structure	Molecular formula	λ_{max} (nm)	Molecular weight	C.I. name
	$C_{16}H_{11}N_2NaO_4S$	452	350.32 g/mol	Acid Orang 7

Results and Discussion:

Effect of contact time and initial dye concentration:

The adsorption of AO7 onto CR was studied as a function of contact time in order to decide whether the equilibrium was reached. For this, 100 mg L^{-1} of AR88 solutions at pH 7 were contacted with 4 g L^{-1} of CR suspensions. The samples were taken at different periods of time and analyzed for their AR88 concentration (Fig. 1). Dye adsorption onto AO7 increased from 42.1% to 98.9% when the contact time was increased from

10 to 75 min. The AO7 adsorption rate is high at the beginning of the experiment because initially the adsorption sites are more available and AO7 ions are easily adsorbed on these sites[30-32]. The equilibrium can be reached within 75 min, and thus, further adsorption experiments were carried out for a contact time of 75 min. The equilibrium adsorption capacity of the adsorbent for AO7 increased with increasing initial dye concentration, as is also shown in Fig. 1. The dye adsorption capacity is highly concentration dependent. The increase in loading capacity of the adsorbent with relation to dye ions is probably due to a high driving force for mass transfer[33-35]. At 27 ℃ , when the initial dye concentration was increased from 25 to 200 mg/L, the loading capacity of dried adsorbent increased from 6.71 to 36.45 mg of AO7 per gram of CR biomass.

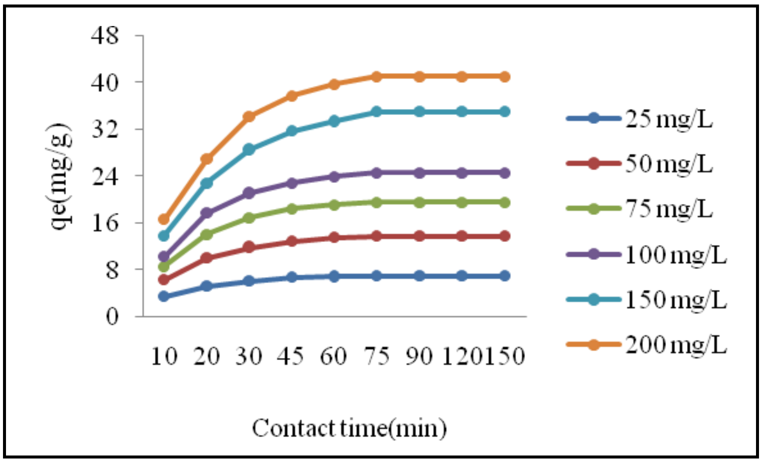


Fig. 1: Effect of contact time and initial AO7 concentration (pH = 7, Biomass dose: 4 g/L and temp: 27 ℃)

Adsorption Isotherms:

The experimental data at equilibrium between the amount of adsorbed dye (q_e) on the adsorbent and the concentration of dye in solution (C_e) at a constant temperature and pH were used to describe the optimum isotherm model. The linear forms of Langmuir, Freundlich, Temkin, Dubinin- Radushkevich (D-R), Harkin-Jura and Halsey isotherm models equations (Table 2) were used to describe the equilibrium data.

Table 2. Different isotherm models used in this study

		ref
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_e K_l} + \frac{C_e}{q_m}$	36,37
Freundlich	$\text{Log } q_e = \frac{1}{n} \log Ce + \log K_F$	38,39
Tempkin	$q_e = B_1 ln(k_t) + B_1 ln(C_e)$	40,41
D – R	$\text{Ln } q_e = \ln q_m - K\varepsilon^2$	42,43
H – J	$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \log C_e$	44,45
Halsey	$\text{Ln } q_e = (1/n \ln K) - (1/n \ln C_e)$	46,47

Error Functions:

The usual way to validate the isotherms is to consider the goodness-of-fit using the linear regression coefficients, R^2. However, using only the linear regression method may not be appropriate for comparing the goodness of fit of different isotherms. This is because an occurrence of the inherent bias resulting from linearization may affect the deduction. Therefore, in this study in addition to the linear regression analysis, the experimental data were tested with four non-linear error functions: the ARE, SD, χ^2 and SSE and to determine the best fitting isotherm. The error functions are given by[48-50]:

$$ARE = \frac{100}{n}\sum_{I=1}^{n}\left[\frac{q_{cal} - q_{exp}}{q_{exp}}\right]$$

$$SD = \frac{-b \pm \sqrt{\Sigma[\left(q_{exp}] - \frac{q_{cal}}{q_{exp}}\right)}}{n-1}$$

$$SSE = \frac{\sqrt{\Sigma[\left(q_{exp}] - q_{(cal)2}\right)}}{n}$$

$$\chi^2 = \frac{\Sigma(q_{exp} - q_{cal})^2}{q_{exp}}$$

The values of various isotherms constants are described in Table 3. The correlation coefficients was high for all isotherms. The ARE, SD, χ^2 and SSE values are smaller for the Langmuir isotherms, suggesting that langmuir models closely fitted the experimental results. Previously some researchers investigated several adsorbents such as rice husk[28], cashew nut shell[14], Canola[15], Hazelnut Shells[19] and Azolla[13] for the removal of dye from aqueous solutions. in this study adsorption capacity increases with increasing temperature then the adsorption is an endothermic process.

Table 2: Results of isotherm parameters for the adsorption of AO7 onto CR

Models	**parameters**	**Temperature (K)**			**Model**	**parameters**	**Temperature (K)**		
		273	**293**	**313**			**273**	**293**	**313**
Langmuir	q_m	32.21	35.69	38.45	D-R	q_m	24.18	27.11	31.69
	K_L	0.345	0.652	0.		E	0.691	0.783	0.938
	R^2	0.996	0.997	892		R^2	0.844	0.869	0.873
	ARE	11.25	9.69	0.999		ARE	21.97	25.64	28.33
	SD	16.12	12.85	13.22		SD	12.38	15.47	11.65
	χ^2	0.784	1.17	10.44		χ^2	18.11	20.36	16.43
	SSE	4.14	6.15	1.65		SSE	10.41	8.14	6.95
				5.47					
Freundlich	K_F	6.95	8.44	9.83	H-Jura	A	139.24	148.5	156.7
	1/n	0.22	0.34	0.56		B	0.711	1	4
	R^2	0.972	0.965	0.943		R^2	0.882	0.945	1.26
	ARE	33.49	29.61	26.89		ARE	21.25	0.896	0.904
	SD	18.35	22.28	25.13		SD	39.24	24.18	27.42
	χ^2	14.86	18.37	16.45		χ^2	23.11	42.61	36.15
	SSE	29.24	31.68	36.71		SSE	19.69	26.28	31.76
								23.86	28.93
Tempkin	K	0.041	0.065	0.057	Halsey	K	0.047	0.068	0.093
	β	7.81	9.64	11.95		n	7.14	6.45	8.32
	R^2	0.911	0.935	0.964		R^2	0.939	0.965	0.973
	ARE	19.36	22.69	18.25		ARE	44.29	49.16	41.18
	SD	28.64	31.38	29.34		SD	35.18	29.28	41.18
	χ^2	10.17	14.27	12.19		χ^2	14.52	16.51	21.62
	SSE	23.56	25.74	19.91		SSE	31.46	28.52	35.18

Conclusions:

Acid Orang 7 adsorption by Cyperus Rotundus biomass was studied in batch mode and it was strongly dependent on initial concentration and temperature. High initial concentration and temperature favor the AO7 adsorption on the biomass. The isotherm study indicates that adsorption data fit well with Langmuir models. R_L values from Langmuir model and 1/n from Freundlich model indicate that the removal of AO7 on the CR is favorable. The study showed that CR biomass could be used as a new and efficient adsorbent material for the removal of AO7 from aqueous solution.

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