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Study of acid orange 7 removal from aqueous solutions by powdered activated carbon and modeling of experimental results by artificial neural network

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Abstract

In this work, removal of acid orange 7 (AO7) by powdered activated carbon, from aqueous solutions with initial concentrations of 150 ppm to 350 ppm and initial pH values of 2.8, 5.8, 8.0 and 10.5 at 25°C was studied. Experiments were done in batch mode and the experimental solutions were agitated periodically. All concentrations were measured spectrophotometrically at 483 nm and three times replicated. In most cases, after 75 min contact time, the most of AO7 removal is performed. The maximum equilibrium removal of acid orange 7 (AO7) was 96.24% for its initial concentration of 150 ppm at $pH_i = 2.8$, and minimum equilibrium removal was 48.05% for initial concentration of 350 ppm at $pH_i = 5.8$. At the similar experimental conditions, application of different initial pH values altered the AO7 removal percent no more than 9.06%. It is found that the adsorption system follows the second-order adsorption rate expression and the constants of the rate expression at different conditions were calculated which are comparable and often higher than other adsorbents in adsorption of other dyes. The constants of Langmuir equation, Q and b, and constants of Freundlich equation, K_f and $1/n$, were calculated and results show that the adsorption process is favorable. Comparison of R^2 values shows that fitting of Freundlich equation to experimental data is better than Langmuir equation. The experimental results were also modeled by artificial neural network with mean relative error of 5.81%. This model was developed in Matlab 6.5 environment using a 3-layer feed forward backpropagation network with 3, 2 and 1 neurons in first, second and third layers, respectively.

Keywords: Adsorption; Acid orange 7; Decolourization; Artificial neural network; Activated carbon; Aqueous solution

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1. Introduction

Many industries use dyes and pigments to colourize their products. Some dyes with concentrations that they are discharged to the environment, are often nonpoisonous, however, they give undesirable perspective to the water streams [1], whereas, some other dyes are poisonous and carcinogen and cause sever toxicity for aqueous microorganisms [2]. Dyes also can prevent from photosynthesis in aqueous ecosystems by absorbing sunlight. Sulfur dyes can rapidly reduce oxygen content of the water and so, are harmful to aqueous organisms [3]. It is important to know that weaving industries use large amounts of water and in these industries more than 30–60 L of water per kilogram of dyed fabric is used and large amount of wastewater (16% of used water), is produced [3]. Also, total dye consumption in the weaving world industries is more than 10^7 kg/y and approximately 10% of this amount, 10^6 kg, is discharged to water streams [2]. Therefore large amount of different types of dyes enters into the environment. In the other hand, dye producers and consumers are interested in its stability and fastness and so, dyes are difficult to degrade after use [2] and dyeing wastewaters are resistant to biological treatment methods [3,4]. Although various methods such as trickling filters, activated sludge, chemical coagulation, electrochemical coagulation, adsorption by carbon and photo-degradation process [2,5,6] and chemical substances such as hydrogen peroxide and sodium hyper chlorite [4] have been used in treatment of dyeing wastewaters, adsorption has some specific benefits. Adsorption processes can treat high-flow wastewaters with good final quality and no harmful substance production [2]. Among various adsorbents, activated carbon is the one that is widely used to treat polluted waters and wastewaters and its adsorption capacity is dependent on characteristics such as contact surface and pore size distribution [7].

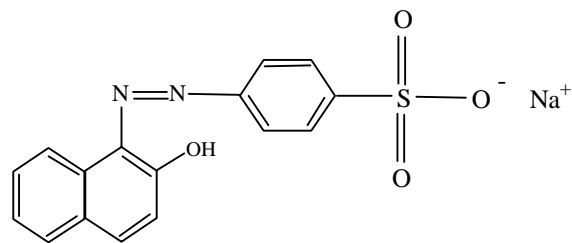AO7 (C.I. 15510) (Fig. 1) is a mono azo dye and is widely used in dyeing of synthetic fibers

Fig. 1. Structure of Acid Orange 7 (AO7) (hydrolyzed).

and wool and cotton and in paper industries [8]. Active azo dyes have double bound of nitrogen to nitrogen (–N=N–), which is bounded to an aromatic group [9] so, they can produce harmful health effects and it is essential to have a proper method to remove this dye from wastewaters.

Pedro Silva et al. [8] used spent brewery grains to remove AO7 from solutions and could obtain high levels of colour removal (> 90%) in contact times less than 1 h. They also modeled this process using response surface methodology [10]. Quan et al. [11] regenerated the AO7-exhausted granular activated carbon (GAC) by microwave irradiation, which improved the adsorption capacity of the treated GAC, resulting from modification of pore size distribution and surface chemistry by microwave irradiation. Chiou et al. [12] used ionically and chemically cross-linked chitosan beads to remove AO7 from aqueous solutions and the adsorption capacities (AC) had very large values of 1911 g.kg^{-1} to 2498 g.kg^{-1} at pH = 3 to 4 and 30°C. Those AC values of were 3.4–15.0 and 2.7–27.4 times those of the commercial activated carbon and chitin, respectively. Sánchez Jimenez and Salvador [13] proposed a new procedure for regenerating activated carbon based on thermal desorption with liquid water under subcritical conditions (300°C and 120 atm.) and in all cases, total recovery of the adsorption capacity was achieved, even after seven regenerations.

Due to large amounts of AO7 consumption, aim of the present work is to study the effect of

parameters such as initial concentration of dye, time and initial pH of solution on dye adsorption efficiency by powdered activated carbon (PAC), and to study the kinetic behavior of the adsorption process. Another important aim of this work is the calculation of the constants of Langmuir and Freundlich isotherms. Activated carbon has been widely used in adsorption of pollutants from water and wastewater but, there is a lack in experimental data on the removal of AO7 using powdered activated carbon. Also in this work, experimental data were modeled by artificial neural network (ANN). ANN is a new and accurate tool to model the experimental results obtained for different pollutants [14–16]. This novel modeling tool is newly grown and has not been used yet to model the above-mentioned experiments.

2. Experimental

Proper volumes of AO7 (technical grade) (C.I. 15510) (Fig. 1) stock solution with concentration of 1000 ppm were mixed with proper volumes of NaOH 0.1 N or H_2SO_4 0.2 N solutions and the mixtures were diluted with distilled water to prepare AO7 solutions with known concentration and pH_i. Volumes of 245 cm^3 of described solutions were contacted with 0.1 g PAC (Merck: 2184) in erlenmeyer flasks which were agitated periodically. Temperature of the experimental solutions was fixed at 25±1°C by an incubator (Sanyo-SMR-A290FE). Samples were drawn from the experimental solutions at different contact times and were filtered by 1.6 micron sintered glass filter. Absorbance of each filtrated solution was determined spectrophotometrically by a double beam Perkin Elmer spectrophotometer (model 550 SE) at 483 nm [17]. Each absorbance measurement was done three times, and concentrations were calculated using a calibration line with $R^2 = 0.9992$. A Metrohm pH meter (model 654) was used to measure the pH values. Initial concentrations of dye solutions were 150–350 ppm. Initial pHs of solutions were 2.8, 5.8,

8.0 and 10.5. The variance of the measurements and the maximum relative standard deviation of the results were calculated equal to 0.007 and ±0.005%, respectively.

3. Results and discussion

3.1. Adsorption kinetics

Fig. 2 shows remained concentrations of AO7 vs. time (time dependency of AO7 removal) in contact with 0.1 g PAC at 25°C and initial pH of 10.5 and initial AO7 concentrations of 150 ppm, 200 ppm, 250 ppm, 300 ppm and 350 ppm. It was seen that the removal percent of AO7, decreases with increasing its initial concentration (Fig. 2 and Table 1), which is due to equilibrium nature of adsorption process. This figure also shows that nearly after 75 min contact time, the most of AO7 removal is performed. Similar plots for AO7 removal in other pH values could be drawn.

The rate constants of the adsorption were determined from the second-order rate expression as follows [12]:

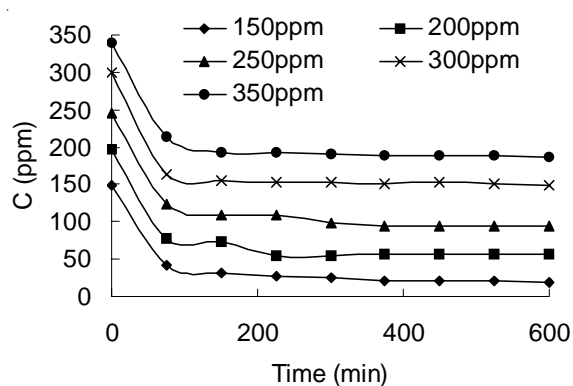$$\frac{t}{q_t} = \frac{1}{k \times q_e^2} + \frac{t}{q_e} \tag{1}$$

Fig. 2. Time dependency of AO7 adsorption by 0.1 g PAC at initial pH = 10.5 and $T = 25$°C and different initial concentrations of AO7 ($V_{sol} = 245$ cm^3).

Table 1

Equilibrium concentrations and removal percents of AO7 at its different initial concentrations and pH values and $T = 25°C$ in contact with 0.1 g PAC ($V_{sol} = 245$ cm^3)

pH$_i$ = 10.5		pH$_i$ = 8		pH$_i$ = 5.8		pH$_i$ = 2.8		C_i^a
R_e%	C_e	R_e%	C_e	R_e%	C_e	R_e%^{c}	C_e^b	
91.97	12.03	91.78	12.30	94.21	8.67	96.24	5.48	150
76.55	46.05	78.45	43.64	79.60	39.61	83.11	33.11	200
64.83	86.22	65.41	85.96	64.89	85.16	72.07	67.13	250
53.70	138.56	61.14	112.22	55.61	129.41	62.76	108.25	300
49.15	174.82	51.37	171.34	48.05	178.04	52.04	166.42	350

$^a C_i$: Initial concentration of AO7, ppm
$^b C_e$: Equilibrium concentration of AO7, ppm
$^c R_e$%: Equilibrium removal percent of AO7

Table 2

Second-order adsorption rate constants for adsorption of AO7 at its different initial concentrations and pH values and $T = 25°C$ in contact with 0.1 g PAC ($V_{sol} = 245$ cm^3)

pH$_i$ = 10.5		pH$_i$ = 8		pH$_i$ = 5.8		pH$_i$ = 2.8		C_i^a
R^2	k	R^2	k	R^2	K	$R^{2\ c}$	K^b	
0.9998	0.1364	0.9998	0.1645	0.9997	0.1735	0.9999	0.1809	150
0.9988	0.1818	0.9993	0.1414	0.9999	0.1448	0.9997	0.1911	200
0.9993	0.0925	0.9999	0.2836	1	0.2376	0.9998	0.3463	250
0.9996	0.2575	0.9992	0.1419	0.9997	0.2751	0.9992	0.5231	300
0.9998	0.1911	0.9997	0.1712	0.9998	0.3316	0.9999	1.1169	350

$^a C_i$: Initial concentration of AO7, ppm
$^b k$: Second-order adsorption rate constant, mg.mg^{-1}. min^{-1}
$^c R^2$: Linear regression coefficient

where q_t is milligrams of adsorbed material on one milligram of adsorbent (mg.mg^{-1}) at time t (min), q_e is milligrams of adsorbed material on one milligram of adsorbent at equilibrium condition (mg.mg^{-1}) and k is the rate constant of second-order adsorption (mg.mg^{-1}.min^{-1}). Table 2 shows the second–order rate constants (k) of AO7 adsorption at different initial AO7 concentrations and pH values, which calculated using the slopes and intercepts of t/q vs. t lines ($R > 0.9988$). Comparison of the reported k values (Table 2) with those reported by Chiou et al. [12] shows that the second-order rate constant of RY86 adsorption ($k = 4.76$ mg.mg^{-1}.min^{-1}) by chemically cross-linked chitosan beads at initial dye concentration of 1980 ppm and pH = 3.0 and temperature of 30°C is higher than the values calculated in our work and the greatest k value for AO7 adsorption ($k = 0.0864$ mg.mg^{-1}.min^{-1}) at initial dye concentration of 2233 ppm and pH = 4.0 and temperature of 30°C is lower than the values calculated in this work. The k values reported for adsorption of other dyes [12] (RB2, RR2, RY2, AO12, AR14) by chemically cross-linked chitosan beads at 30°C

and pH = 3 or 4.0 and initial dye concentrations ranging from about 2000–5200 ppm, are sometimes less and sometimes more than the amounts calculated for AO7 adsorption in this study.

3.2. Adsorption isotherms

A contact time of at least 24 h between AO7 solutions and PAC was necessary to reach full equilibrium condition. Table 1 shows equilibrium concentrations and equilibrium removal percents of AO7 in contact with 0.1 g PAC and different pH values and initial concentrations of AO7 solutions at 25°C. It can be seen that maximum removal percent of AO7 is 96.24% at $pH_i = 2.8$ and $C_i = 150$ ppm and the minimum one is 48.05% at $pH_i = 5.8$ and $C_i = 350$ ppm. Table 1 also indicates that at the similar experimental conditions, application of different initial pH values altered the AO7 removal percent no more than 9.06%.

Constants of Langmuir and Freundlich isotherms are very important in water and wastewater treatment industry and so, they were calculated for the used PAC. Langmuir isotherm can be shown as follows [18]:

$$\frac{1}{q_e} = \frac{1}{Q \times b} \times \frac{1}{C_e} + \frac{1}{Q} \tag{2}$$

where q_e is milligrams of adsorbed material on one milligram of adsorbent (mg.mg^{-1}) in equilibrium condition, C_e is equilibrium concentration of AO7 (ppm) in solution, and Q and b (L.mg^{-1}) are constants of Langmuir equation. Q is maximum milligrams of adsorbed material on one milligram of adsorbent (mg.mg^{-1}). Plots of $1/q_e$ against $1/C_e$ is linear ($R^2 > 0.9$) (Fig. 3 as a sample of similar plots) and thus, Langmuir equation can be used as a mathematical model of adsorption process at equilibrium condition and Q and b can be calculated from intercept and slope of the $1/q_e$ vs. $1/C_e$ plots, respectively.
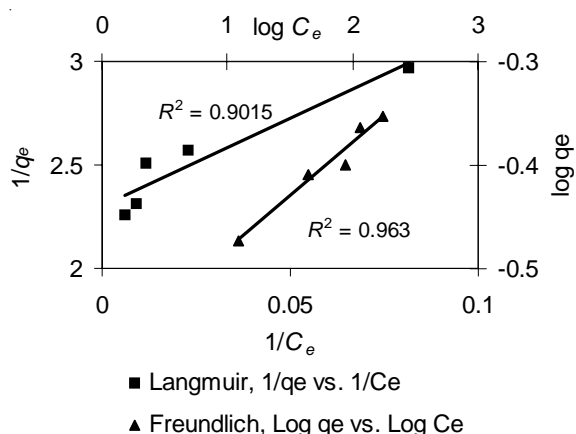
Freundlich isotherm can be shown as follows [18]:

Fig. 3. Langmuir and Freundlich isotherms for adsorption of AO7 by 0.1 g PAC at initial pH = 8 and $T = 25°C$ and initial AO7 concentrations ranging from 150 ppm to 350 ppm ($V_{sol} = 245$ cm^3).

$$\log q_e = \log K_f + \frac{1}{n} \times \log C_e \tag{3}$$

where q_e and C_e are as explained above, and K_f (mg.mg^{-1}.(L.mg^{-1})$^{1/n}$) and $1/n$ are constants of Freundlich equation. Because plots of $\log q_e$ against $\log C_e$ are also linear ($R^2 > 0.9$) (Figs. 3 as a sample of similar plots), Freundlich equation can also be used as a mathematical model of adsorption process at equilibrium condition and $1/n$ and K_f can be calculated from slope and intercept of the $\log q_e$ vs. $\log C_e$ plots, respectively (Table 3).

According to R^2 values, fitting of Freundlich equation to experimental data is better than Langmuir equation. For all data, R_L which is shown as the following:

$$R_L = \frac{1}{1 + b \times C_0} \tag{4}$$

is in the range of zero and 1, and n is greater than 1 which indicate that adsorption of AO7 by the used powdered activated carbon is favorable [18]. Comparison of the results shown in Table 3 with

Table 3
Constants of Langmuir and Freundlich isotherms for adsorption of AO7 at its initial concentrations ranging from 150 ppm to 350 ppm and different pH values and $T = 25°C$ in contact with 0.1 g PAC ($V_{sol} = 245$ cm^3)

R^2_{Fr} [b]	R^2_{La} [a]	$1/n$	K_f(mg.mg^{-1}.(L.mg^{-1})$^{1/n}$)	b (L.mg^{-1})	Q (mg.mg^{-1})	pH$_i$
0.9768	0.9264	0.08	0.30	0.65	0.44	2.8
0.9198	0.9567	0.05	0.32	0.73	0.40	5.8
0.963	0.9015	0.10	0.26	0.27	0.44	8
0.9893	0.9281	0.07	0.29	0.44	0.40	10.5

[a]R^2_{La}: Linear regression coefficient of Langmuir equation
[b]R^2_{Fr}: Linear regression coefficient of Freundlich equation

those reported by Chiou et al. [12] shows that Q (constant of Langmuir equation) values which are calculated for PAC in this work, all are lower (about 1/5 or 1/6) than those reported for removal of dyes such as RB2, RR2, RY2, RY86, AO12, AR14, AO7 and DR81 by chemically cross-linked chitosan beads at pH = 3 or 4 and $T = 30°C$. The b (constant of Langmuir equation) values calculated in this work are also higher than (up to several times) those reported for above dyes [12]. Furthermore, $1/n$ and K_f values (constants of Freundlich isotherm) in our experiments are respectively lower and greater (at least 100 times as much) than those reported by Tsai et al. [19] for adsorption of AO10 by activated carbons prepared from bagasse by ZnCl$_2$ activation at dye concentrations ranging from 5 ppm to 25 ppm and temperatures of 20°C and 40°C.

4. Modeling with artificial neural network

Artificial neural network (ANN) modeling was studied as a replacement for kinetic studies to predict the time dependency of the AO7 removal by PAC which some of its experimental data are shown in Fig. 2. This new and powerful Prediction tool uses some experimental data to predict the response of the experiments at new similar conditions. Modeling of experimental results using ANN was performed in Matlab 6.5 environment using a 3-layer feed forward backpropa-

gation network with 3, 2 and 1 neurons in first, second and third layers, respectively. Transfer function of neurons at first and second layers was tan-sigmoid and at output layer was log-sigmoid. Training function was trainscg. Total 219 experimental points were randomly split between training and prediction sets with 2:1 ratio, respectively. That is 146 points were used as training set and 73 points were used as prediction set. C_i, pH$_i$ and t were inputs of the network and C_t was the output (data which some of them are shown in Fig. 2). All inputs and outputs were normalized using the following equation [20]:

$$A_i = \frac{X_i - X_{min}}{X_{max} - X_{min}} \times (r_{max} - r_{min}) + r_{min} \tag{5}$$

where X_i is input or output of the network, A_i is the normalized value of X_i, X_{min} and X_{max} are extreme values of X_i, and r_{min} and r_{max} define the limits of the range where we want to scale X_i. In this work input data were normalized between –1 and 1 and output data were normalized between 0.2 and 0.8. After modeling, results were converted to original state.

Fig. 4 shows predicted results of AO7 adsorption against experimental ones for prediction set of points. It shows that the points are well distributed around $X = Y$ line in a narrow area. The mean relative error of modeling is 5.81%, which is good enough (Fig. 4) to predict experimental results and
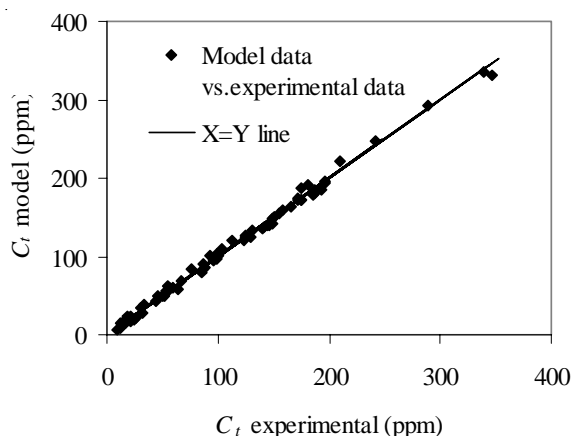
Fig. 4. Predicted AO7 concentrations (using ANN) at different conditions vs. experimental ones.

we can use artificial neural network as a new predictive method in this field of study.

5. Conclusion

Results of this study show that removal percent of acid orange 7, decreases with increasing its initial concentration. It can be seen that maximum removal percent of AO7 is 96.24% at $pH_i =$ 2.8 and $C_i = 150$ ppm and the minimum one is 48.05% at $pH_i = 5.8$ and $C_i = 350$ ppm. The results indicate that at similar experimental conditions, application of different initial pH values altered the acid orange 7 removal percent no more than 9.06%. The plots of t/q vs. t show good linear relationships with R^2 values greater than 0.9988. This indicates that the adsorption system belongs to the second–order kinetic model. Linear regression coefficients of $1/q_e = f(1/C_e)$ and $\log q_e = f(\log C_e)$ plots are greater than 0.9 and so, the equations of Langmuir and Freundlich are well fitted to the experimental data at equilibrium conditions. Of course, according to R^2 values, fitting of Freundlich equation to experimental data is better than Langmuir equation. The mean relative error of modeling of the experiments by artificial neural network is 5.81%, which is good enough to predict experimental results and we can use it, as a new predictive method and as a replacement of kinetic studies in this field.

Acknowledgement

Symbols

A_i	—	Normalized value of X_i
AC	—	Adsorption capacity
ANN	—	Artificial neural network
AO12	—	Acid Orange 12
AO7	—	Acid Orange 7 (Orange II)
AR14	—	Acid Red 14
b	—	Constant of Langmuir equation, $L.mg^{-1}$
C.I.	—	Color index number
C_e	—	Equilibrium concentration of AO7 in solution, ppm
C_i	—	Initial concentration of AO7 in solution, ppm
C_t	—	Concentration of AO7 in solution after t min, ppm
DR81	—	Direct Red 81
GAC	—	Granular activated carbon
k	—	The rate constant of second-order adsorption, $mg.mg^{-1}. min^{-1}$
K_f	—	Constant of Freundlich isotherm, $mg.mg^{-1}.(L.mg^{-1})^{1/n}$
n	—	Constant of Freundlich isotherm
PAC	—	Powdered activated carbon
pH_i	—	Initial pH of the experimental solution
Q	—	Maximum milligrams of adsorbed material on one milligram of asorbent, $mg.mg^{-1}$; constant of Langmuir equation
q_t	—	Milligrams of adsorbed material on one milligram of adsorbent at time t, $mg.mg^{-1}$

q_e — Milligrams of adsorbed material on one milligram of adsorbent at equilibrium condition, mg.mg^{-1}

R^2 — Linear regression coefficient

R^2_{Fr} — Linear regression coefficient of Freundlich equation

R^2_{La} — Linear regression coefficient of Langmuir equation

RB2   — Reactive Blue 2

$R_e\%$ — Equilibrium removal percent of AO7

r_{max} — Upper limit of the range where we want to scale X_i

r_{min} — Lower limit of the range where we want to scale X_i

RR2   — Reactive Red 2

RY2   — Reactive Yellow 2

RY86   — Reactive Yellow 86

T — Temperature, °C

t — Time, min

V_{sol} — Volume of experimental solution, cm^3

X_i — Input or output of the network

X_{max} — Upper extreme value of X_i

X_{min} — Lower extreme value of X_i

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