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A Comparative Study on Adsorptive Removal of Auramine O and Tartrazine dyes from Aqueous Solution using Activated Carbons

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ABSTRACT

Activated carbon was modified by oxidation with nitric acid to improve its adsorption capacity for the removal of cationic and anionic dyes from aqueous solution. The operational parameters investigated included initial concentrations, pH, temperature and contact time. The experimental data were analyzed by using Langmuir and Freundlich models of adsorption. The adsorption isotherm data for Tartrazine was best fitted to the Freundlich isotherm. While for Auramine O both isotherms fits with experimental data. The adsorption kinetics was modeled by the Lagergren first order and pseudo-second order model. The experimental data obeys pseudo-first order model for both dyes. Using a single batch adsorber design it has been revealed that as-received carbon sample act as good adsorbent for removal anionic dye and modified carbon is a better adsorbent for cationic dye removal.

Graphical Abstract



(a)AR[4,4' bis NMe₂Ph₂C⁺NH₂(λ_{max} =430nm)] (b) AR_{imine}[4,4' bis NMe₂Ph₂C = NH(λ_{max} =315nm)] (c) AR_{carbinol}[4,4' bis NMe₂Ph₂C (NH₂)OH(λ_{max} =370nm)]

Auramine-O and its conversion forms.

Keywords: Surface acidity, Tartrazine, Auramine O, Batch design.

INTRODUCTION

Most of the industries such as textile, paper, printing, food, cosmetics, etc. generate considerable amount of colored wastewater. Treatment of wastewater containing dyes is very difficult because dyes cannot be easily degraded due to their complex structure [1]. Depending on the exposure time and concentration, dyes can have chronic effects on organisms. Some dyes or their metabolites are mutagenic and carcinogenic. Auramine O (AO) is a basic dye used in paper, textile, and leather industries. It has also been used as food colorant, fungicide, antiseptic and component in brilliantine. AO may be carcinogenic for human beings because it can cause liver and lymphatic cancers in animals [2]. Oxygen carrying capacity of blood can be destroyed by AO. Tartrazine (TA) is used in foodstuffs (including weeds, chewing gum, jellies, puddings, juices, jams, mustard, sodas, and drugs), cosmetics, medicines and textile. TA is reduced in the organism to an aromatic amine which is highly sensitizing and known to cause allergic reactions such as asthma and urticaria [3]. It may cause thyroid tumors and chromosomal damage.

Therefore, TA and AO containing effluents have to be sufficiently treated before they are discharged into the water bodies. Various methods including ion exchange [4], electro coagulation [5], coagulation [6], algal decolorization [7] have been used for the removal of dyes but these methods tend to introduce metallic impurities into water. Among several chemical and physical methods, adsorption process is one of the effective techniques that have been employed for color removal from wastewater. Several types of adsorbents which include superabsorbent polymers [8], poly glutamic acid [9], sesame leaf [10], graphite loaded with Titania [11], fly ash [12] and bottom ash [13] have been used. Activated carbon has a great potential for the removal of dyes due to their extended surface area and microporous structure. Abundant information can be found in the literature on the use of activated carbons as adsorbents [14-18]. Most of these reported the results on the basis of surface area and porosity of activated carbons. However, very little attention has been given to the role of the activated carbon surface chemistry in the adsorption process. In this work, surface of activated carbon has been modified by oxidation with nitric acid and degassed at different temperatures.

Comparison of adsorption capacity of cationic and anionic dyes onto as received and modified activated carbons was carried out. Our aim is to account for the interactions of dyes with surface groups of activated carbons. Design of an adsorption system by using Freundlich and Langmuir isotherm equations has also been suggested to develop optimized carbon adsorbent.

MATERIALS AND METHODS

Material: The granulated activated carbons used in this studyACG-100 and Indcarb-50 are wood based materials. Which have been obtained from Industrial Carbons Private Limited, Ankleshwar, India. Auramine-O (C.I. 41000) is a basic dye. Tartrazine (C.I. 19140) is an acidic dye. Both dyes were supplied by CDH.

Modification of carbons by oxidation: Oxidation with HNO_3 was performed by heating 5 g of an activated carbon sample with 200 mL of 50% nitric acid in a borosil beaker on a water bath maintained at about $80 \pm 5^{\circ}C$. When about 10 mL of the acid is left, the contents are diluted with distilled water and then filtered. The activated carbon was then washed with hot distilled water to neutral pH, dried in an oven at 110°C for 24 h and stored in stopperd glass bottles.

Degassing of activated carbons: Gradual elimination of carbon oxygen surface groups has been carried out by degassing the oxidized carbon samples at temperatures of 400°, 650°, and 950°C. Temperature controlled tube furnace is used for degassing. In quartz tube furnace, 5 g of a carbon sample is placed in a thin layer of about 5 inches in length. The tube furnace is then connected to a Hyvac. Cenco vacuum pump capable of giving vacuum to an order of 3×10^{-3} mm of Hg. Appropriate

voltage is then applied to set its temperature at desired level. The temperature is allowed to rise gradually and complete elimination of the gases at the preceding temperature is ensured before raising temperature by another 50° C. To avoid reformation of the carbon-oxygen complexes, degassed sample is allowed to cool in vacuum. The cooled sample is then transferred to stoppered bottles flushed with nitrogen.

Estimation of carbon-oxygen surface groups: 1 g of a carbon sample is dried in an oven at 150°C. It is then placed in a platinum boat $4" \times 1/2"$ in size. The opening is covered by a platinum foil, which is held in position by winding a platinum wire over it. The boat is then heated to the required temperature in a resistance tube furnace which is connected to a Hyvac. Cenco vacuum pump (capable of giving vacuum to the order of 3 X 10^{-4} mm) through weighed calcium chloride U-tubes and a series of Erlenmeyer flasks containing a known volume of standard barium hydroxide solution. The amounts of surface oxygen complexes are determined by analyzing the gases evolved. Calcium chloride U-tubes absorbs water, carbon dioxide is absorbed by barium hydroxide while the rest of the gases are collected over water, an aliquot volume of which is analysed for its CO and H₂ contents in Orsat – Lunge gas analysis apparatus. Oxygen evolved in the form of water, carbon monoxide, and carbon dioxide. The amount of total evolved oxygen is in close agreement with the oxygen obtained by ultimate analysis of the activated carbons.

Base neutralization capacity (Surface acidity): 1 g each of a carbon sample is placed in contact with 100 mL of 0.1 N sodium hydroxide solutions in a stoppered bottle. The contents are placed in a water bath kept at 80°C for 6 h. The contents are then cooled and an aliquot volume of supernatant liquid is titrated against standard hydrochloric acid solution. The amount of alkali neutralized gives the surface acidity of the carbon sample.

Fourier Transform Infrared Spectrometer (FTIR) Analysis: Surface functional groups of activated carbons before and after the dye adsorption have been analyzed by recording their FTIR spectra on PerkinElmer-Spectrum RX-1 Fourier Transform Infrared Spectrometer. The spectra of the carbon samples are measured as KBr pellets in the spectral range 4000-500 cm⁻¹ and 32 scan per sample. The KBr pellets are prepared by mixing and grinding the activated carbon with KBr (mass ration1:100) in a pestle mortar and then pressing the resulting mixture under pressure of 8×10^4 N in hydraulic press.

BET Surface Area and Pore Size distribution: Nitrogen adsorption-desorption isotherms are measured at 77 K by using a Quantachrome Instruments Nova 2200e Surface area and Pore size analyzer. From these isotherms BET surface area, total pore volume, average pore radius and pore size distribution of a particular activated carbon sample is determined. The activated carbon samples first degassed at 320°C temperature for 6 hrs before the analysis. Approximately 0.10 g of sample is used for this analysis. The surface area is determined using the BET equation, while the total pore volume is directly calculated from the volume of nitrogen held at the highest relative vapour pressure ($p/p^\circ = 0.99$). Micropore volume is calculated using the Dubinin-Radushkevich equation. Pore size radii are determined by Dubinin-Astakov equation. All calculations are done using NovaWin software provided with the analyzer.

Scanning electron microscopy (SEM): SEM is widely used to observe the morphological features and surface characteristics of the adsorbent materials. In the present study, SEM is used to study morphological changes in the carbon surfaces before and after adsorption of the dyes. Hitachi S-4300 scanning electron microscope was used at an accelerating voltage of 10 kv to visualize the surface morphology and structure of activated carbons.

Adsorption Experiments: The stock solutions of acidic and basic dye were prepared by dissolving the 1 g of dye in 1 L distilled water. Standard solutions of different concentrations were prepared from stock solution by diluting with distilled water. Adsorption isotherms were obtained by placing 20

cm³ of dye solution of different concentrations (100–1000 mg/dm³) with 0.1 g of activated carbon. The suspensions were shaken occasionally at room temperature, until equilibrium was reached. Their main concentration of dye in solution was determined by UV-Vis spectrophotometer at wavelength 432.8 nm and 426 nm for AO and TA respectively.

RESULTS AND DISCUSSION

Effect of contact time: The effect of contact time on adsorption of dyes is presented in figure 1. A rapid increase is observed for the first 150 min and then proceeds slowly till equilibrium. This may due to large number of vacant surface sites available at initial stage. The equilibrium adsorption of TA and AO are 47.13 mg g⁻¹ and 44.02 mg g⁻¹ respectively. The adsorption of TA and AO achieve equilibrium in about 300 min and 240 min respectively. Data was recorded until 420 min to ensure complete equilibrium.



Figure 1. Effect of contact time on adsorption of AO and TA by ACG-100.

Equilibrium adsorption: The adsorption isotherms of TA and AO are presented in figure 2. The amount adsorbed is maximum in case of ACG-100 carbon sample as compared to I-50 for both dyes. But adsorption of TA (anionic dye) is more than AO (cationic dye) for both adsorbents. This indicates that the adsorption of the dye is not determined by the surface area alone. It is also influenced by the chemical structure of the carbon surface. Equilibrium characteristics of adsorption are described by Langmuir and Freundlich isotherms. The Langmuir and Freundlich isotherm parameters for both dyes are listed in table 1.



Figure 2. Adsorption isotherms of AO and TA on different as received activated carbons.

Values of correlation coefficients (\mathbb{R}^2) show that the Freundlich isotherms fit with experimental data of TA better than the Langmuir isotherm. But both isotherms fitted with adsorption of AO.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \qquad \text{Langmuir} \qquad \dots(1)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$
 Freundlich ...(2)

Table 1. Isotherm constants for the adsorption of AO and TA by ACG-100 and I-50

Icothorm	Doromotor	AO)	ТА		
Isotherm	r ai ailletei	ACG-100	I-50	ACG-100	I-50	
	$q_{max}(mg g^{-1})$	149.25	83.33	333.33	250.0	
Langmuir	$K_L(L mg^{-1})$	0.0129	0.0034	0.0039	0.0008	
	\mathbb{R}^2	0.977	0.985	0.717	0.665	
	$K_{\rm F}({\rm L~mg^{-1}})^{1/n}$	2.343	1.422	2.780	0.439	
Freundlich	n	1.97	1.72	1.35	1.23	
	\mathbf{R}^2	0.970	0.984	0.954	0.989	

Effect of modification of carbon surface on dye adsorption: Modification of ACG-100 was carried out by oxidation with nitric acid which leads to increase in carbon-Oxygen surface groups and then the oxidized samples degassed at gradually increasing temperatures to eliminate varying amounts of these surface groups.

The adsorption isotherms on the oxidized and degassed ACG-100 for TA and AO are shown in figure 3 and 4. It is seen that the adsorption increases on oxidation and decreases gradually as the temperature of degassing is enhanced from 400 to 950°C for cationic dye and reverse behavior is shown by anionic dye. Such adsorption results can be explained on the basis of electrostatic attractive and repulsive interactions.



Figure 3. Adsorption isotherms of TA on nitric acid oxidized ACG-100 before and after degassing at different temperature.

The oxidized activated carbons were associated with acidic carbon-oxygen surface groups that ionized in solution to produce H^+ ions. Which were directed toward the liquid phase, leaving the carbon surface with a negative charge. So there is increase in the attractive forces of carbon surface with positively charged dye and repulsive forces with negatively charged dye. As the acidic surface groups are removed gradually on degassing at increasing temperatures the carbon surface tends to become



Figure 4. Adsorption isotherms of AO on nitric acid oxidized ACG-100 before and after degassing at different temperature.

less negatively charged. This decreases the adsorption of AO and increases the adsorption of TA with increase of degassing temperature. Such results also supported by surface acidity values (Table 2). Surface acidity is more for oxidized carbon and decreases as the temperature of degassing is enhanced. So adsorptive removal of basic dye will be more by sample having more surface acidity.

Table 2. Surface acidity of oxidized and degassed ACG-100

Carbon Sample	Surface acidity, meq 100 g ⁻¹
As-received	57.6
Oxidized	489
400°-degassed	252
650°-degassed	82
950°-degassed	traces

Effect of pH: The effect of pH_0 with blank dye solutions of $C_0 = 500 \text{ mg L}^{-1}$ over a pH_0 range of 2–13 for TA and AO is shown in figure 5. The colour intensity of AO remains stable below pH_0 7 and get reduced in the basic range. At pH_0 about 13 solution colour of TA lightens. This may be due to ionization of Tartrazine molecule in strong basic medium. Colour removal due to pH change alone may be due to the structural changes taking place in the dye molecules [19]. As in case of Auramine-O NH₂ bonded to central carbon of AO [Figure 6(a)] undergoes simultaneous conversion to its imine form AO_{imine} [Figure 6(b)] and carbinol form AO_{carbinol} [Figure 6(c)] in basic solution depending on the pH of solution[20]. Figure 5 also shows the effect of pH_0 in the range 3-7 on the removal of AO and in

120	7	◆TA on ACG-10 □AO on ACG-10 ▲TA black	0
100	_	×AO blank	
- 80	_	**************	
00 Ben 60	-	* ^ ^	
₹40	_		
20	_		
0	_		_
	0	⁵ _{PH} ¹⁰	15

Figure 5. Effect of pH on AO and TA adsorption. *www.joac.info*

the range 2-12 for the removal of TA by ACG-100. There is very slight increase in the removal of the cationic dye AO with the increase in pH. Maximum adsorptive removal of AO by activated carbon was found out at pH_0 7.0. In case of TA amount adsorbed is maximum at pH 3 then starts decreasing upto pH 7 and after that remains almost constant. This is caused by protonation of adsorbent surface at low pH which increases the interaction with anionic dye. Adsorption at pH 2 is low may likely due to protonation of both adsorbent and adsorbate [21].



(a)AR[4,4' bis NMe₂Ph₂C⁺NH₂(λ_{max} =430nm)] (b) AR_{imine}[4,4' bis NMe₂Ph₂C = NH(λ_{max} =315nm)] (c) AR_{carbinol}[4,4' bis NMe₂Ph₂C (NH₂)OH(λ_{max} =370nm)]

Figure 6. Auramine-O and its conversion forms.

Effect of temperature: Figure 7 shows increase in amount of the dye adsorbed at equilibrium with increasing temperature indicated that high temperature is favorable for the adsorption of TA. Similar behavior is shown by AO. This enhance in adsorption of both dyes with temperature is due to enlargement of pore size [22] and increase in mobility of dye molecules.

The thermodynamic parameters, *i.e.*, free energy, enthalpy, and entropy, were calculated using the following equations:

$$K_{c} = \frac{q_{e}}{C_{e}} \qquad \dots (3)$$
$$\Delta G = -RT \ln(K_{c}) \qquad \dots (4)$$
$$\log Kc = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad \dots (5)$$

Where, K_c , R (J·mol⁻¹·K⁻¹) and T (K) are the adsorption distribution coefficient, gas constant and absolute temperature, respectively. Thermodynamic parameters for the adsorption of both dyes on ACG-100 are presented in table 3. Negative values of free energy indicating the favourable and spontaneous adsorption process of both dyes.



Figure 7. Effect of contact time and temperature for adsorption of TA on ACG-100. *www.joac.info*

The positive values of ΔS for each dye suggested increased randomness at the solid/solution interface and positive values of ΔH revealed the endothermic nature of overall adsorption process. Similar results have also been observed by Karagozoglu *et al.* [23] for the adsorption of Astrazon Blue and by Aber and Esfahlan [14] for adsorption of basic yellow 2.

		ТА		AO			
T(°C)	ΔG (kj mol ⁻¹)	ΔH (kj mol ⁻¹)	ΔS (j mol ⁻¹ K ⁻¹)	ΔG (kj mol ⁻¹)	ΔH (kj mol ⁻¹)	ΔS (j mol ⁻¹ K ⁻¹)	
30°C 40°C 50°C 60°C	-7.049 -7.665 -8.374 -9.283	15.28	73.51	-5.030 -5.897 -6.568 -10.08	42.51	155.40	

Table 3	3. Thermo	odynamic	parameters	for adsor	ption of	TA a	nd AO	by .	ACG-	100
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Adsorption kinetics: The kinetic data at different temperature have been analyzed by using pseudofirst order, second order and intra particle diffusion models.

The pseudo-first order equation of Lagergren [24] is generally as follows

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \qquad \dots (6)$$

The second order equation for the equilibrium adsorption is expressed as Ho and Mckay [25]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e 2} + \frac{1}{q_e} t$$
...(7)

The amount of dye adsorbed at equilibrium (q_e) and first order rate constant (k_1) calculated from intercept and slope of the plot $log(q_e-q_t)$ vs time and the values of second order rate constant (k_2) and q_e were calculated from the intercepts and slopes of the plot of t/qt vs t are presented in table 4. The experimental values of amount adsorbed at equilibrium are very close to values calculated from pseudo first order model, therefore the first order kinetic model is more suitable to describe the adsorption process for both dyes.

Table 4. Pseudo- first order and pseudo second-order kinetic parameters for removal of
TA and AO by ACG-100 at different temperature.

	ТА					AO					
T(°C)	q _e (exp) mg g ⁻¹	Pseudo First		Pseudo Second			Pseudo First		Pseudo Second		
		Order	Model	Ord	er Model	q _e (exp) mg g ⁻¹	Order Model		Order Model		
		q _e (cal) mg g ⁻¹	\mathbf{R}^2	q _e (cal) mg g ⁻¹	R ²		q _e (cal) mg g ⁻¹	R ²	q _e (cal) mg g ⁻¹	\mathbf{R}^2	
30°C	47.13	47.86	0.983	62.50	0.995	44.02	45.49	0.949	52.63	0.993	
40°C	47.50	48.64	0.980	58.82	0.998	45.30	45.08	0.998	52.63	0.991	
50°C	47.88	40.45	0.995	55.56	0.998	46.01	53.33	0.995	58.82	0.990	
60°C	48.31	43.05	0.977	55.56	0.998	48.72	50.23	0.995	62.50	0.953	

Intra particle diffusion model has also been applied to study the diffusion mechanism. The intraparticle diffusion Weber and Morris [26] model as

$$q_t = K_{id} t^{1/2} + I$$
 ...(8)

Where, k_{id} (mg/g min^{1/2}) is the intra-particle diffusion rate constant. Intercept I gives an idea about the thickness of the boundary layer, i.e., the larger the intercept, the greater is the effect of boundary

layer. Figure 8 shows the intraparticle diffusion plot of the adsorption of AO and TA on ACG-100. The shape of curve confirms that the intraparticle diffusion is not the only rate-limiting step. First line depicts Macropore diffusion and the second represents micropore diffusion until equilibrium was achieved.



Figure 8. Intraparticle diffusion plot for AO and TA adsorption on ACG-100.

Effect of adsorbent dose: It has been found that by increasing the adsorbent dose, adsorption density i.e. the amount adsorbed per unit mass decreases and the percentage removal increases. This increase in the amount of adsorbed dye is because of increase in the number of available adsorption sites with increase in adsorbent dosage. The decrease in adsorption density may be due to unsaturation of adsorption sites [27] with an increase in the adsorbent dose.

Design of batch adsorption: Langmuir and Freundlich equation adsorption data has been used to design a single batch adsorber [28] for the adsorption of dyes onto both oxidised and unoxidised activated carbons. The design objective is to reduce the dye concentration from C_o to C (mg/L). The mass balance for dye adsorption system is given by:

$$V(C_o - C) = W(q_1 - q_o) = Wq_1 \qquad ...(9)$$

Where, *V* is the volume of dye solution. *W* is the amount of the activated carbon added to the solution when the amount of the dye adsorbed on carbon changes from $q_0=0$ to q_1 . At equilibrium $C \rightarrow C_e$ and $q_1 \rightarrow q_e$

$$V(C_o - C_e) = Wq_e \qquad \dots (10)$$

It has been shown earlier that the both isotherms fit with the adsorption data of AO and Freundlich fits with adsorption of TA. Rearrangement of the above equation on substituting the value of q_e from Langmuir equation gives adsorbent/solution ratio as

$$\frac{W}{V} = \frac{(C_o - C_e)}{q_e} = \frac{C_o - C_e}{q_m b C_e / (1 + b C_e)} \qquad \dots (11)$$

From Freundlich isotherm as

$$\frac{W}{V} = \frac{(C_o - C_e)}{q_e} = \frac{C_o - C_e}{K_f C_e^{1/n}} \qquad \dots (12)$$

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Figure 9 shows the predicted amounts of as-received and oxidised carbon to remove 95% of 500 mg L^{-1} of AO solution from different volumes of dye solutions in a single-batch adsorber. It can be seen, that the amount of oxidized ACG-100 as adsorbent is less by about 57% compared to the amount of as-received ACG-100 for the removal of 95% AO from the solution. Use of as-received carbon sample as adsorbent reduces by approximately 91% the amount of modified carbon for removal of TA.



Figure 9. Adsorbent mass against treated volume of water for 95 % removal of AO by as- received and oxidized ACG-100 activated carbons.

Mechanism of adsorption: FTIR spectrum of oxidized ACG-100 before and after adsorption of AO and TA is shown in figure 10. Band at 1713 cm⁻¹ is assigned to CO from carboxylic acid. Strong band at 1580 cm⁻¹ represents C-C stretching of aromatic rings [29]. After adsorption of dye intensity of bands at 1713 cm⁻¹ and 1580 cm⁻¹ decrease and shift towards lower wave number for both TA and AO dyes. That indicated the participation of carboxyl groups present on the activated carbon surface in adsorption process. The SEM images of as received ACG-100 and TA adsorbed ACG-100 at a magnification of 400× are shown in figure 11(a) and (b) respectively. Surface morphology of the activated carbon is different before and after adsorption of the dye. It is seen that before adsorption considerable number of pores are present on the surface of the activated carbon and after adsorption the surface becomes smoother and the pore size appears to be reduced [30].



Figure 10. FTIR spectra of oxidized ACG-100 (a) before (b) after adsorption of AO (c) after adsorption of TA



Figure 11. SEM images of as-received ACG-100 sample (a) before adsorption and (b) after adsorption of TA at a magnification of 400×.

APPLICATION

A present study shows the adsorptive removal of carcinogenic dyes Auramine O and Tartrazine from aqueous solution using activated carbons. Effect of surface chemistry on comparative study of cationic and anionic dyes has been discussed.

CONCLUSION

The equilibrium adsorption of cationic and anionic dyes on activated carbons depends on the amount of acidic carbon-oxygen groups present on the carbon surface. The adsorption of cationic dye increases on oxidation of the carbon surface due to increase of acidic groups and decreases on degassing when these surface groups are eliminated from the carbon surface. Reverse behavior is shown by anionic dye. The adsorption of Tartrazine and Auramine O are found to be maximum at pH 3 and 7 respectively. The adsorption follows first order rate law for both dyes. Amount of oxidized carbon required to remove 95% of cationic dye is about 57% less and to remove anionic dye is 91% more than the amount of unoxidised carbon.

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