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KINETIC AND EQUILIBRIUM STUDY ON REMOVAL OF ACID ORANGE 7 BY USING ACTIVATED CARBON

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Abstract: In this work, the adsorption behaviors of Activated Carbon (AC) for removal of Acid Orange 7(AO7) were studied. Adsorption tests were conducted in various batch conditions where the effect of pH, contact time, dye concentration, and adsorbent dose were studied. Experiments performed at pH 2 show the optimal adsorption due to the best surface charge interactions. Adsorption kinetics is shown to be very fast and it follows pseudo second-order kinetics. The equilibrium was established in 1 h. Langmuir, Freundlich, and Temkin Isotherm models were applied on the system. Freundlich isotherm was found to be better fitted one.

Keywords: Acid Orange 7, kinetics, equilibrium, isotherms

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INTRODUCTION

Dyes containing azo-aromatic groups are highly dispersible pollutants. They contribute to water toxicity and represent an increasing danger for the environment and human beings. These effluents discharged from various industries (e.g. textile, paper, leather, food, etc.) are known to be toxic [1], carcinogenic [2], mutagenic [3], teratogenic [4], and their release in the environment's a considerable source of non-aesthetic pollution since the existence of low concentrations of dyes is clearly visible. Thus, the removal of these colored compounds from wastewater is an important target from the environmental point of view. However, this process faces a major problem represented in the high stability of these azo-dyes in aqueous media and their resistance to light and oxidation agents [5]. Most of the dyes are stable against photodegradation, biodegradation, and oxidizing agents several methods have been used for the removal of dyes from the aquatic environment, including physical, chemical, and biological processes. Among these methods, adsorption is a widely used for dye removal from wastewaters

In this work the dyes concentration was characterized by UV spectroscopy, and factors affected adsorption were evaluated. The effects of adsorbents dose, initial pH, initial dye concentration and contact time on dye removal were studied. Kinetic parameters were calculated from the experimental data to fit kinetic model. The equilibrium of adsorption and the adsorption data were describe by the Langmuir model, Freundlich model.

MATERIAL AND METHODS

The Activated Carbon (AC) used in this study was purchased from Poona Chemical Laboratory Pune. Scanning electron micrographs, FTIR analysis were obtained from Shivaji University Kolhapur. These data were used to characterize the Activated Carbon and its morphology. Stock solution of Acid Orange 7(1000mg/l) was prepared and then used for different experiments by diluting with distilled water. Adsorption experiment were carried out by shaking 0.1 g of AC with 100 ml aqueous solution of AO7 of given concentration in different glass flask. The effect of AC concentration on the amount of color adsorbed was studied by adding 0.05 to 1.2 g of AC in

100 mL of AO7 solution of initial concentration of 40 mg/L. All the experiments were carried out at 260C, pH of 2 and 150 rpm for 6 hr. For equilibrium study initial AO7 concentration used were 10, 20, 30 and 40 mg/L.

The amount of AO7 adsorbed in mg/g was determined by using the following mass balance equation

$$q_e = V (C_i - C_e) / m \quad (1)$$

Where C_i and C_e are AO7 concentration in mg/l before and after adsorption respectively, V is the volume of adsorbate in liter, and m is the weight of the adsorbent in grams. The percentage of removal of AO7 was calculated from the following equation

$$\% \text{ Removal} = 100 (C_i - C_e) / C_i \quad (2)$$

RESULT AND DISCUSSION

Characterization of the adsorbent: Fourier-transform infrared (FTIR) spectra of the AC before and after AO7 adsorption is presented in figure-1 and figure-2. FTIR spectrum of AC before AO7 adsorption shows peaks at 2324 cm^{-1} due to $-\text{C}\equiv\text{N}-$ stretching, the peak at 2119 cm^{-1} was attributed to stretching of $-\text{C}\equiv\text{C}-$ groups, the peak observed at 1864 cm^{-1} was assigned to a carbonyl bond ($\text{C}=\text{O}$). The peak observed at 1571 cm^{-1} is due to secondary amine group. In figure-3, scanning Electron Microscopy photographs before dye adsorption clearly revealed the surface morphology and the different level of porosity in AC. The surface after MB adsorption shown in figure-4 however shows that AC is loaded with AO7 dye



Figure 1 FTIR of AC before Adsorption

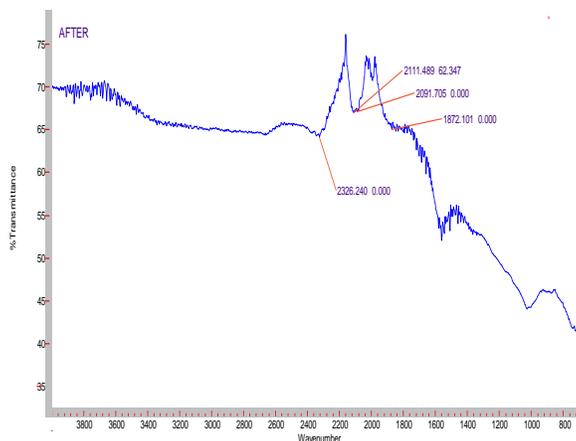


Figure2: FTIR of AC after Adsorption

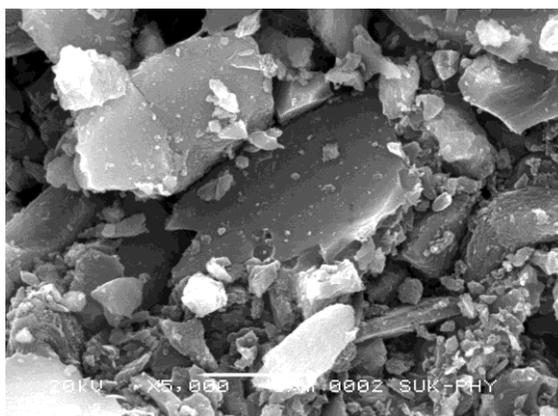


Figure 3: Scanning electron image before adsorption

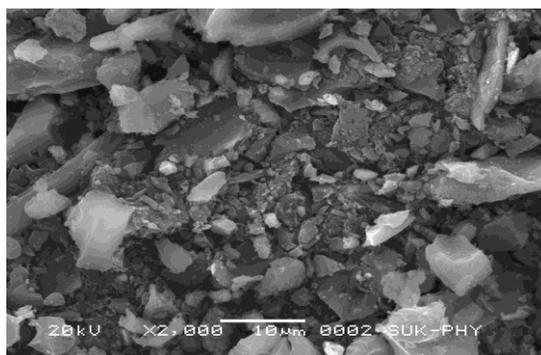


Figure 4: Scanning electron image after adsorption

Effect of initial pH: In the present study the effect of pH on the amount of dye removal was analyzed over the pH range from 2 to 12 and is presented in graphical form as given in figure 5.

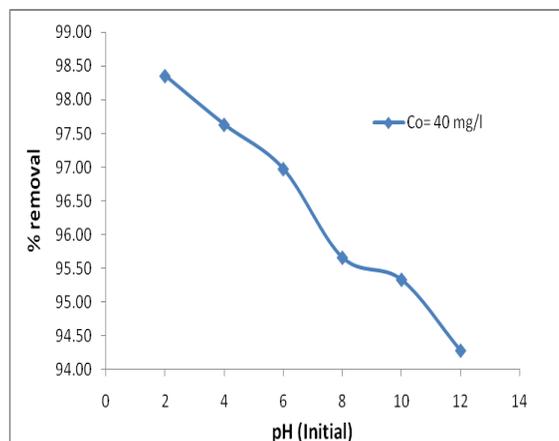


Figure 5: Effect of initial pH on percentage dye removal, 40 mg/l dye concentration and time 6 hr

The maximum dye sorption occurred at pH 2 and the removal decreased. As the initial pH increases, the number of negatively charged sites on the adsorbent surfaces increases and the number of positively charged sites decreases. A negative surface charge does not favor the adsorption of dye anions due to electrostatic repulsion [7], it is observed that % removal of AO7 at an initial solution pH 2 was found to be maximum i.e. 98.36 %.Therefore, further adsorption experiments were performed at pH 2.0.

Effect of adsorbent dosage: The effect of adsorbent dosage on the removal of Acid Orange 7 at $C_o=40\text{mg/L}$, pH2 is shown in the Figure 6. It can be seen that the removal increases up to a certain limit and then it remains constant. From figure 6, for an increase in AC dosage of 0.05-1.2 g/100ml, the q_e decreased from 65.89mg/g to 3.21mg/g, whereas the percentage removal increased from 82.37% to 99.36 % respectively.

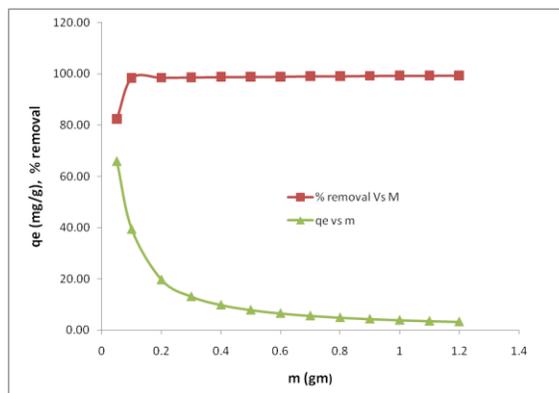


Figure 6: Plot of AC mass on adsorption of AO7 at 40 mg/l concentration and pH 2

The increase in the adsorption with the adsorbent (AC) dosage can be attributed to greater surface area and the availability of more adsorption sites [9]. The decrease in adsorption capacity q_e with increasing adsorption dosage may be due to overlapping of adsorption sites as a result of overcrowding of AC particles [10].

Effect of Initial AO7 Concentration and Contact time

The adsorption capacity versus time at different initial concentration were plotted in figure-7 and the result showed that as AO7 concentration increased, the q_t increased, primarily due to enhanced driving force to overcome mass transfer resistance and greater interaction between AO7 and AC.

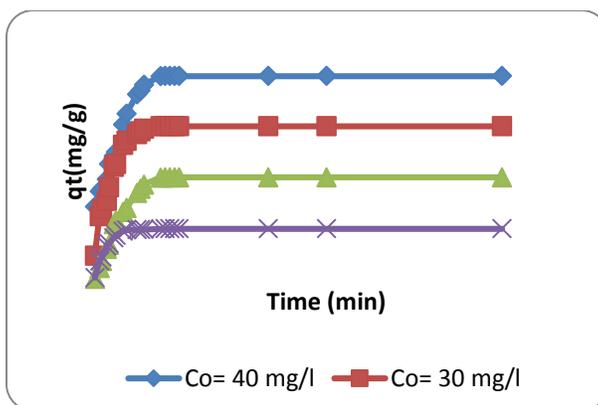


Figure 7: Effect of mass of adsorption of AO7 dye with time K and adsorbent mass 1 g/L

Figure-8 indicated very quick rate of adsorption of AO7 in the initial 15 min. and thereafter, the adsorption rate declined gradually and reached the equilibrium at about 1 hr. The higher adsorption rate at the initial stage may be due to availability of more number of vacant sites, as a result, there exists increased AO7 concentration gradient in solution and on the AC surface. After a certain period of time, this gradient is reduced due to accumulation of AO7 dye in the vacant sites, leading to a decrease in adsorption rate [11,12]

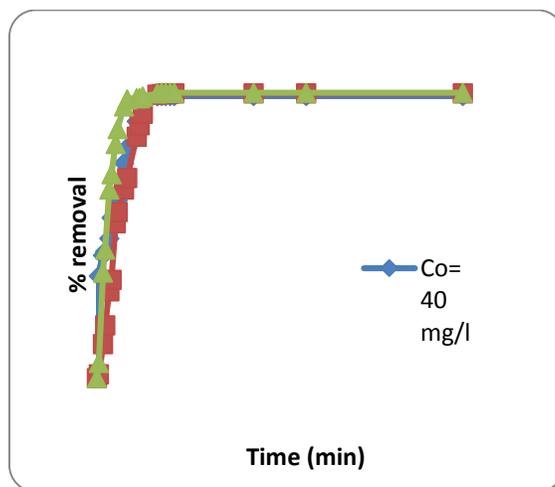


Figure 8: Plot of contact time on dye removal efficiency of ASD at temperature 303 K and adsorbent mass 1 g/ L

Adsorption Dynamics:

The Lagergren first order kinetic model:[8] The Lagergren first order rate equation is represented as :

$$\log (q_e - q_t) = \log q_e - k_1 * (t / 2.303) \quad (3)$$

where q_e and q_t are the amounts of AO7 adsorbed (mg/g) at equilibrium and at time t , respectively. k_1 is the Lagergren rate constant (min^{-1}) These values have been given in table-1

The pseudo-second-order kinetic model: [8] The adsorption data have been applied to pseudo-second-order kinetic model also. The equation is represented as:

$$t/q = 1/k_2 * q_e^2 + t/q_e \quad (4)$$

and $h = k_2 * q_e^2$

where K_2 is the rate constant of second order adsorption (g/mg/min.). h is the initial adsorption rate at time approaching zero (mg /g*min). Plots of t/q_t versus t has been shown in (figure-12). Values of K_2 and q_e have been calculated from the slope of the graph. These values have been given in table- 2.

The pseudo second order kinetic model fitted better than Lagergren model

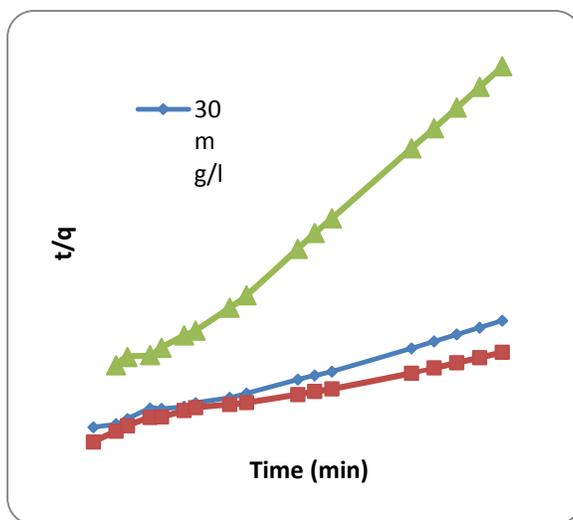


Figure- 9: Second order plot of AO7 adsorption onto AC

Adsorption Isotherms

In this study, adsorption data were fitted to two parameter models namely Langmuir, Freundlich, Temkin. The Langmuir isotherm is given in equation

$$q = q_m * K_L * C_e / (1 + K_L * C_e) \quad (5)$$

Where q_m is the maximum amount of dye adsorbed per unit mass of adsorbent corresponding to complete coverage of the

adsorption sites in mg/g , KL is the Langmuir constant related to energy of adsorption in L/mg. The Freundlich isotherm is given by

$$q_e = K_F * C_e^{1/n} \quad (6)$$

where K_F ($\text{mg/g} * (\text{L/mg})^{1/n}$) and $1/n$ are constants related to adsorption capacity and intensity of adsorption, respectively. The Temkin isotherm is presented by;

$$q_e = B_1 * \ln(KT * C_e) \quad (7)$$

where $B_1 = (R * T/b)$, T (K) is the absolute temperature, R (8.314 KJ/Kmol K) is the universal gas constant, A (L/mg) is equilibrium binding constant and b (KJ/mol) is the variation of adsorption energy

Table-1: Definition of error functions used[20]

| Name of error function | Definition |
|---|--|
| The Sum square errors(ESQ) | $\sum_{i=1}^p (q_{e,cal} - q_{e,exp})_i^2$ |
| The hybrid fraction error function (HEF) | $\frac{100}{(n-p)} \sum_{i=1}^n (q_{e,exp} - q_{e,cal})^2 / q_{e,exp}$ |
| Marquardt's standard deviation (MSD) | $100 * (1/(n-p) \sum_{i=1}^n (q_{e,exp} - q_{e,cal})^2 / q_{e,exp})^{0.5}$ |

p is number of parameter in the isotherm

Isotherm Analysis: In this work the non-linear regression technique has been used. This method solved by using the Microsoft Excel to predict the error function [6]. The various mathematically rigorous error function used in this analysis are given in table -3. The figure-10 shows the

experimental equilibrium data and the predicted Langmuir, Temkin, Freundlich isotherm got by minimizing the R2 function using non-linear method.

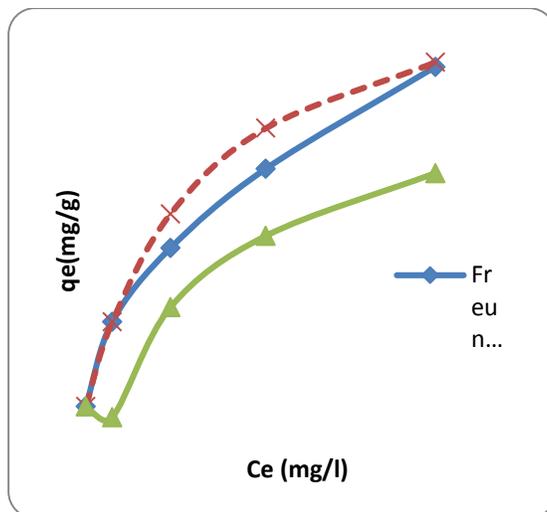


Figure-10: Plot of predicted equilibrium isotherm for the adsorption of AO7 onto AC

Table2: Kinetic constants for the adsorption of AO7 by AC , agitation time 120 min. and adsorbent dose of 1 g/L

| Conc. | qe, exp | First Order | | | Second Order | | | |
|-------|---------|-------------|----------------|----------------|--------------|----------------|----------------|-------|
| | | qe,cal | k ₁ | R ² | qe,cal | k ₂ | R ² | h |
| 10 | 9.95 | 2.977 | 0.108 | 0.993 | 9.090 | 0.134 | 0.990 | 11.11 |
| 20 | 19.84 | 4.254 | 0.064 | 0.965 | 16.666 | 0.072 | 0.991 | 20.01 |
| 30 | 29.66 | 3.807 | 0.048 | 0.955 | 25.641 | 0.05 | 0.993 | 33.33 |
| 40 | 39.34 | 3.991 | 0.029 | 0.964 | 28.571 | 0.122 | 0.983 | 100 |

Table3: Isotherm values for adsorption of AO7 by AC for initial concentration range of 10-40 mg/L, time of agitation 6 hr and adsorbent dosage 1g/L

| | SSE | HEF | MSD |
|-------------------|---------|--------|-------|
| Freundlich | | | |
| K_F | 49.2426 | 50.13 | 49.6 |
| n | 0.5031 | 1.91 | 1.99 |
| MEF* | 2.4488 | 5.74 | 32.51 |
| Langmuir | | | |
| q_m | 52.078 | 52.05 | 54.78 |
| K_L | 4.172 | 3.89 | 3.67 |
| MEF* | 8.1833 | 52.078 | 39.7 |
| Temkin | | | |
| B_1 | 11.3306 | 10.776 | 10.64 |
| K_T | 42.9645 | 47.64 | 47.66 |
| MEF* | 8.26 | 18.61 | 52.12 |

CONCLUSION

This study shows that AO-7 can be successfully removed from the aqueous solution by adsorption on AC and this can be an effective and valuable mean for controlling water pollution due to dyes. These results shows that initial AO7 concentration, contact time, pH and have marked effect on adsorption. The equilibrium data are best explained by Freundlich adsorption isotherm. Kinetics of adsorption follows second order rate equation.

REFERNCES

1. M.S. Tsuboy, J.P.F. Angeli, M.S. Mantovani, S. Knasmüller, G.A. Umbuzeiro, L.R.Ribeiro, Genotoxic, mutagenic and cytotoxic effects of the commercial dye CI Disperse Blue 291 in the human hepatic cell line HepG2, *Toxicology in Vitro* 21(2007) 1650–1655.
2. K. Golka, S. Kopps, Z.W. Myslak, Carcinogenicity of azo colorants: influence of solubility and bioavailability, *Toxicology Letters* 151 (2004) 203–210.
3. K.T. Chung, Mutagenicity and carcinogenicity of aromatic amines metabolically produced from azo dyes, *Journal of Environmental Science and Health, Part C* 18 (2000) 51–71.
4. A.R. Beaudoin, M.J. Pickering, Teratogenic activity of several synthetic compounds structurally related to trypan blue, *The Anatomical Record* 137 (1995) 297–305.

5. S. Seshadri, P. L. Bishop, A. M. Agha, Anaerobic/ aerobic treatment of selected azo dyes in wastewater, *Waste Management* 14 (1994) 127–137.
6. Kini S.M., Saidutta M.B., Murty V.R.C. and Kadoli S.V., Adsorption of basic dye from aqueous solution using ACI treated saw dust (*Lagerstroemia microcorpa*) : Kinetic, Modeling of Equilibrium, Thermo dynamic, *I. Res. J. Environment. Sci.*, 2(8), 6-16 (2013)
7. Namasivayam, C., and D. Kavitha. 2002. Removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, *Dyes and Pigments*, 54: 47-58.
8. Lagergren S., About the theory of so-called adsorption of soluble substances, *der Sogenannten adsorption geloster stoffe Kungliga Svenska psalka de Miens Handlingar.*, 24,1-39(1898)
9. Mane, V.S., I.D. Mall, and V. C. Srivastava. 2007. *Dyes and Pigments*, 73:269-278
10. Ho Y.S. and McKay G., The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res* 34(3), 735-742 (2000)
11. Mane V.S. and Vijay Babu P.V., Studies on the adsorption of Brilliant Green dye from aqueous solution onto low-cost NaOH treated saw dust, *Desalination*, 273, 321–329(2011)
12. Kumar K.V. and Porkodi K., Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum notatum*, *J. Hazard Mater*, 146 , 214– 226(2007)