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Extraction of anionic dye, *Alizarin Red S*, from industrial waste waters using active carbon derived from the stems of *Achyranthes Aspera plant* as bio-adsorbent

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ABSTRACT

The surface sorption nature of the activated carbon derived from Achyranthes aspera plant (ACAA) towards an anionic dye, Alizarin red S has been investigated by adopting batch modes of extraction using simulated water. The influence of various physicochemical parameters like pH, sorbent concentration, agitation time, temperature and initial concentration of the dye have been probed and the conditions have been optimized for the maximum removal of the dye. The effect of the presence of fivefold excess of co-ions on the % removal of the dye has been investigated. The adsorption data is analyzed for understanding the nature of adsorption using Langmuir and the Freundlich isotherms and found that the Langmuir model has better describes the adsorption process indicating the homogenous mono-layer nature of the adsorbate (Dye) layer on the adrsorbent, ACAA. The R_L*= 0.48 of the Langmuir model indicates that the adsorption of the dye is onto the surface of the active carbon, ACAA and further, the sorption of the dye is confirmed using FTIR data. The kinetics of adsorption has been analyzed using pseudo first order and pseudo second order models and observed that the adsorption kinetics follows pseudo second order as it has* R^2 *vale: 0.9757 which approaches to 1. The thermodynamics parameters namely;* ΔH, ΔS *and* ΔG *revealed the spontaneous and endothermic nature of adsorption process. The procedures developed in this investigation have been applied to the samples collected from the effluents of textile industries and found to be successful.*

Key words: Anionic Dye, Pollution and Control, active carbon, Achyranthes aspera plant, adsorption, applications.

INTRODUCTION

The contamination of water bodies with residues of synthetic dyes coming from the effluents of textile industries is endangering the biota and aquatic life prevailing in the water bodies due to the toxic nature of some of the dyes or their degradation products. Further, the color in water bodies due to the residues of dyes obstruct the sun-light to reach to the biota or aquatic life and thereby retarding or effecting the natural phenomenon such as photosynthesis, metabolisms etc [1].

It is reported that every year nearly 10% of dye used in Textile industry is lost through the sewage and if proper extraction and disposal methods are not envisaged by the industries, they enter into the water bodies causing grave threat to aquatic life [2, 3].

Alizarin red S (ARS) is widely used in textile industry and due its thermal, biological and optical stability, the effluents of industry contains adequate amounts of the said dye. This is an anthraquinone dye and it cannot be degraded naturally due to the complex structures of aromatic rings and hence its turns to be a potential toxic to the biota and aquatic life. The consumption or use of waters containing residual amounts of toxic Alizarin red S cause several harmful effects, such as gastritis, mal-functioning of lungs, severe headache, painful micturition, and methemoglobinemia [4].

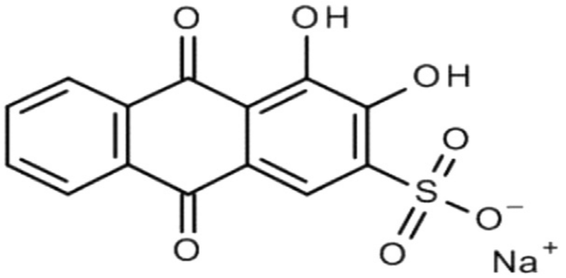


Figure 1: 3,4-Dihydroxy-9,10-dioxo-2-anthracene sulfonic acid sodium salt

Of the various methods being investigated for the extraction of the pollutants, the methods based on adsorption using bio-adsorbents derived from plant materials are proving to be versatile methods. Our research group has been investigating on these bio-remedial methods of pollution control and successfully developed methodologies for the removal of Chromium (VI) [5-8], Zinc [9, 10], Aluminum (III) [11-14], Fluoride [15-21], Nitrite [22, 23], Nitrates [24], Ammonia [25-27], Phosphate [28, 29] and some Dyes [30-33]. Further, methods also have been developed by exploring the advantage of mechanism of self purification in oxidation ponds in controlling heavy metal ions like Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, and Pb^{2+} by cultivating some bio-masses [34] right in the pond itself. Activated clay modified by Iron Oxide [35], mustard husk [36], and magnetic chitosan [37] have been investigated for removing Alizarin red S from polluted waters. Maryam Fayazi et al [38] worked on the adsorption of Alizarin red S from aqueous solution onto activated carbon/γ-Fe_2O_3 nano-composite. Ghaedi et al. [39] investigated the kinetic and equilibrium sorption characteristic of Alizarin red S on to magnetically activated carbon (MAC) nano-composite adsorbent. B. Ahmad et al [40] investigated the mechanisms of Alizarin Red S bio-sorption onto olive stone by-product. Filho et al. [41] studied the adsorption of Alizarin Red S on to graphite electrode by the complexation with Cu ions. Kurepa et al. [42] worked on the uptake and distribution of ultra small anatase TiO2 Alizarin Red S nano conjugates.

The present work is endeavored at developing simple, economical and effective methodologies in removing the toxic Alizarin red S (ARS), an anion, from industrial wastes or polluted waters using active carbon derived from stems of ***Achyranthes aspera*** plant.

MATERIALS AND METHODS

Plant description:

Achyranthes aspera (Fig No. 2) belongs to the family of Amaranthaceae and is distributed in many areas as a common weed. It is a branched herb or shrub grows up to 15 cm height. It has medicinal values and is used as astringent and diuretic and as an emmenagogue in curing skin eruptions.

Figure 2: *Achyranthes aspera plant identified to have affinity towards Alizarin red S dye*

Preparation of active carbon:

The stems of Achyranthes aspera were cut into small pieces, washed with distilled water and dried under sunlight for 3 days. The dried stem pieces were carbonized in muffle furnace at 250^0C for 2 hrs. After carbonization, the carbon was washed with distilled water several times and then filtered. The filtered carbon was dried in an oven at 110^0C

and was sieved by 75μm ASTM mesh. The screened carbon was activated by boiling the carbon powder in 1N $HN0_3$ for 2-3 hours on Bunsen burner flame. After treatment with the acid, the treated material was washed with distilled water repeatedly and brought the material to neutral pH and was dried in oven at 110^0C for 5hrs. The material was stored in an airtight container for further use. This active carbon is named as ACAA (Active carbon of Achyranthes aspera).

Reagents and Chemicals:

All the chemicals used were of Analytical Reagent Grade purchased from Merck. India Pvt. Ltd and Sd. Fine Chemicals and all the solutions were prepared using double distilled water throughout this study. Stock solution of 100 ppm of Alizarin red S Dye was prepared and was suitably diluted as per need.

Method: Batch modes of extraction were adopted [43-45]. 100 ml of Alizarin red S solution (20ppm) was taken into 250 ml conical flask and to it definite quantity the adsorbent was added. pH was adjusted to a desired value. Then the solution was shaken in horizontal shaker at 120 rpm. After a definite contact time, the conical flask was removed from shaker and the solution was filtered through Whatman No.1 filter paper and the filtrate was analyzed for the residual dye concentration using Spectrophotometric method.

Estimation of the Dye: The dye has λmax at 420 nm below pH: 3.7 and obeys Beers-Lamberts law even at low concentrations. The O.D. measurements were made at the said λmax using UV-Visible Spectrophotometer against blank. The obtained O.D value for un-known solution was referred to standard graphs (drawn between O.D and concentration) prepared with known concentrations of the dye by adopting method of Least Squares to know the concentration of the dye.

The influence of pH, sorbent dosage, equilibration time, initial concentration of the dye and temperature on the % removal of the dye with the Active carbon of Achyranthes aspera (ACAA) was studied and conditions were optimized.

The dye uptake capacity was calculated using Amount adsorbed qe $= \frac{(C_0 - C_e)}{m} \times V$, q_e is the amount of dye adsorbed, m is the mass of adsorbent (g), V is the volume of the solution (L), C_0 is the initial Concentration of dye (mg/ L), C_e is the equilibrium dye concentration (mg/ L) and q_e is the amount of dye quantity adsorbed at equilibrium (mg/g). The percent removal of dye from the solution was calculated by the following equation:

$$\% \text{ removal} = \frac{(C_0 - C_i)}{C_0} \times 100$$

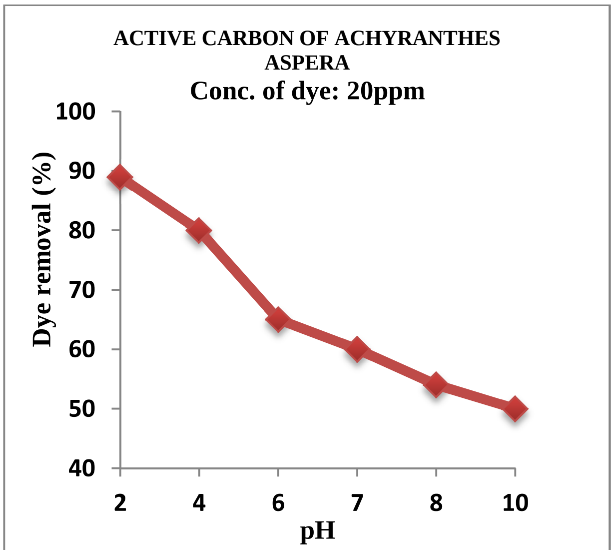
where C_0 (mg/L) and C_i (mg/L) are the initial and final dye concentrations.

The obtained results were presented in the Graph No. 1-8; Table No.1-2.

RESULTS AND DISCUSSION

The sorption of characteristics of the active carbon , ACAA, towards the Alizarin red S dye by varying pH, adsorbent dosage, agitation time, temperature, initial concentration of dye and interfering ions has been investigated and the finding are presented comprehensively here under:

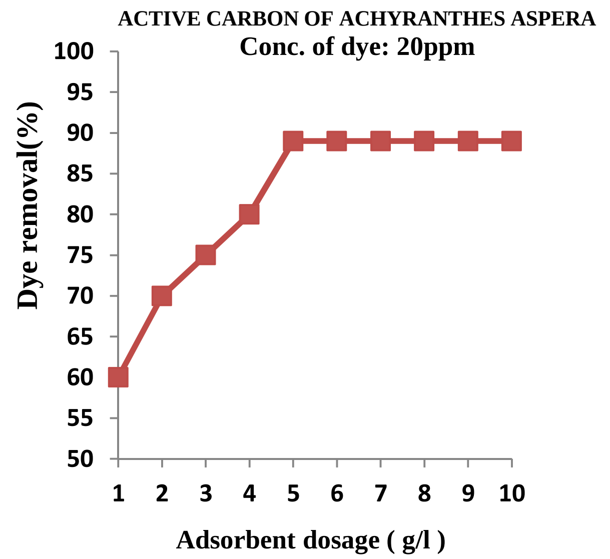
1: Effect of pH: The pH of the dye solution plays an important role in the whole adsorption process. The effect of pH has been studied by varying the pH from 2 to 10 under other optimum parameters: initial conc. of dye: 20ppm; adsorbent dosage: 5gm/l, contact times: 90minutes; rpm: 120 temperatures: 30^0 C. The results are presented in Graph No.1. It is observed from the Graph that 89% removal is possible at pH 2; and % of extraction is decreased to 50% as the pH increased further from 2 to 10. So it is inferred that acidic conditions favour the adsorption of dye.



Graph No: 1:Effect of pH on the adsorption of dye

This can be attributed to the function groups present on the surface of the adsorbent and anionic nature of the Alizarin red S. As the pH decrease, the protonation of the functional groups is more favoured and hence the surface of the active carbon is endowed with positive charge and consequently, the surface has affinity towards negatively charged species of the dye and hence, the % removal of anioinic dye Alizarin red S, is more at low pHs.

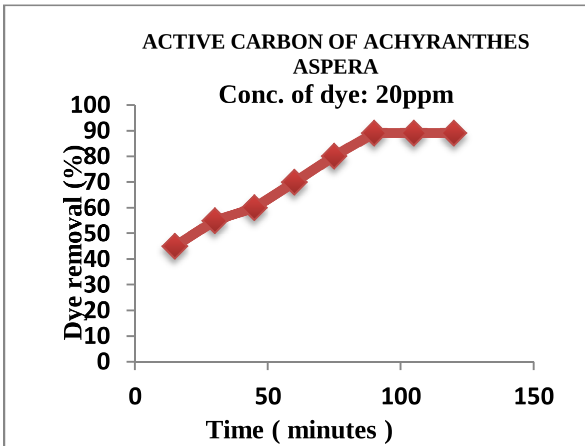
2: Effect of adsorbent dosage:
The effect of adsorbent dosage was studied by varying the sorbent dosage from 1-10gm/l at other optimum extraction conditions namely: pH: 2, time of equilibration: 90 min, rpm: 120; initial conc. of dye: 20 ppm; temp.:30^0 C. The results are depicted in the Graph No. 2.



Graph No: 2: Effect of adsorbent dosage on the adsorption of dye

From the graph it is inferred that with increasing the sorbent dosage, the % removal of the dye also increased but after certain dosage, it remains constant. It is observed from the Graph that the % removal of the dye is increased from 60% to 89% removal as the sorbent dosage is increased from 1 to 5gm/l. As the concentration of the sorbent is increased, the availability of active sites increases and hence, the increase in the % removal of the dye. But at high concentrations of the adsorbent, some of the active sites may be blocked resulting a study state at optimum dosages of the adsorbent concentrations.

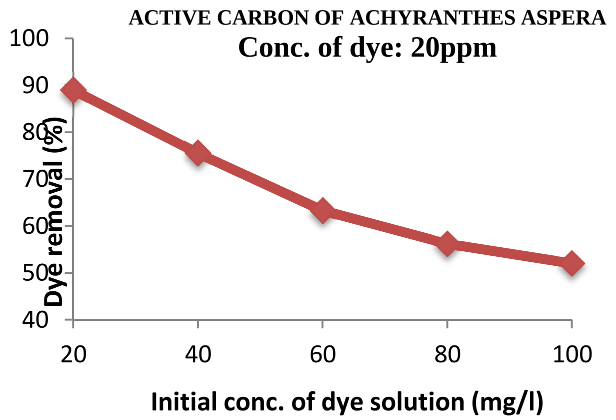
3: Effect of Contact time: To determine the optimum equilibrium time, the time is varied from 15 to 120 minutes at optimum conditions of pH: 2, dosage: 5 g/l, rpm: 120 and temp. 30^0C.



Graph No: 3:Effect of contact time on the adsorption

It is observed from the Graph No: 3, that the % removal of the dye is increased from 45 to 89% with increase in the contact time. This may be attributed to the fact that initially more active sites are available and hence, % removal is more and as the time progress,the active sites are progressively used up and so, % of removal becomes slow and eventually reaches a study state.

4: Effect of initial concentration:
In the Graph No. 4, the effect of initial concentration of the dye on the % of extraction when all the other conditions are constant is depicted. % of extraction of the dye decreases from 89 to 52% with the increase in the initial concentration from 20 to 100 mg/L for a fixed concentration of the adsorbent. This is expected because at low concentrations of the dye, many active sites are available on the adsorbent. At high concentrations of the dye, the demand of active sites is more but the available active sites are limited as the concentration of the adsorbent is constant and hence, % removal is less.



Graph No: 4: Effect of conc. of dye solution on the adsorption of dye

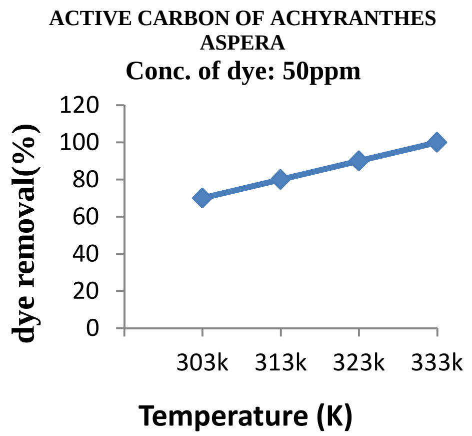
5: Effect of temperature:

The effect of temperature on the extraction of the dye has been studied in the temperature range: 303 to 333 k at optimum extraction conditions: pH: 2, agitation time: 90 minutes, rpm: 120 and dosage: 5 gm/l and the results have been depicted in the Graph No. 5a & b.

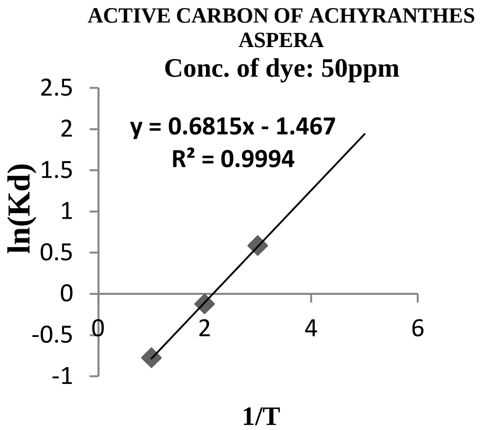
Free energy change (ΔG) (KJ/mole), enthalpy change (ΔH) (KJ/mole) and entropy change (ΔS) (KJ/mole) were determined using the equations; $\Delta G = -RT \ln K_d$; $\ln K_d = \Delta S / R - \Delta H / RT$; $K_d = q_e / C_e$; $\Delta G = \Delta H - T\Delta S$, where K_d: distribution co-efficient of the adsorption, q_e: the amount of dye adsorbed, C_e: equilibrium conc. of dye, T : the absolute temperature in Kelvin, R: the gas constant. The values of ΔH and ΔS were obtained from the slope and intercept of the plot between $\ln K_d$ and 1/T. [46-50]. The values are presented in the Table No: 1.

% of extraction increases from 70% to 100% with the increase in temperature from 303 to 333 k. With increase of temperature, the kinetic energy of the dye molecules is increased and hence, it penetrates deeper into the surface layers of adsorbent through micro pores resulting more extraction.

Further, as ΔH value is positive, the adsorption process is endothermic in nature and as ΔG value is negative, the adsorption process is spontaneous (vide Table No. 1).



Graph No: 5(a): Effect of temperature on the adsorption of dye



Graph No: 5(b) : Effect of temperature on the adsorption of dye

Table No: 1 Thermodynamic Parameters of Adsorption of dye on ACAA

ΔH (KJ/mole)	ΔS (KJ/mole)	ΔG (KJ/mole)				R^2
5.66	12.19	-3.38 (303K)	-4.34 (313K)	-5.33 (323k)	-6.32 (333k)	0.999

6: Effect of Co-ions:

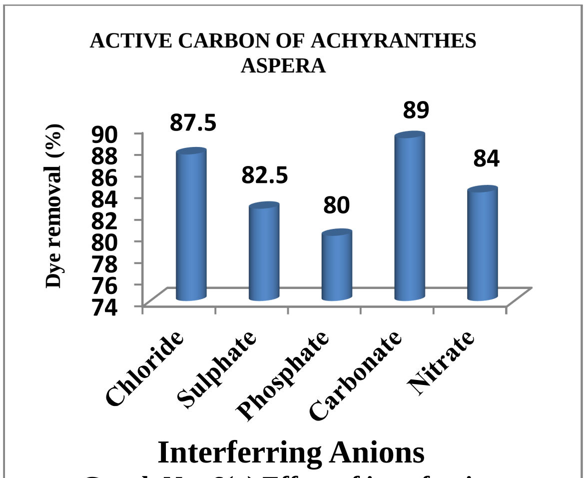
The interference of co-ions (fivefold excess) on the % of extraction of the dye has been presented in Graph No. 6a & b.

It is observed that Carbonate and Chloride have shown marginal effect while Sulphate, Phosphate and Nitrate have interfered in the order: Nitrate < Sulphate < Phosphate. Cations have sown less interference.

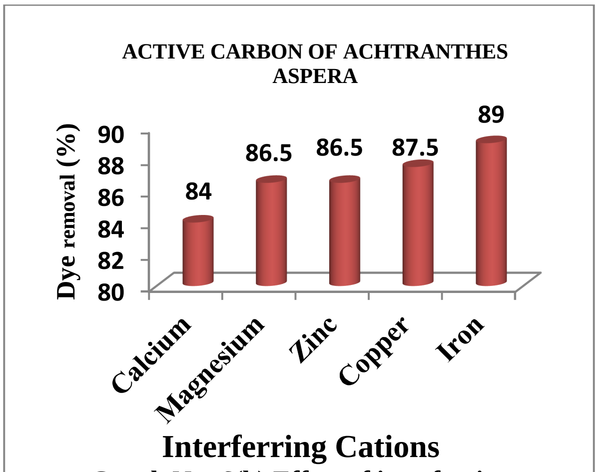
7: Adsorption Isothems:

The sorption nature is analyzed using the Freundlich [51] and Langmuir isotherms [52]. Linear form of Freundlich isotherm equation is: $\log (q_e) = \log k_F + (\frac{1}{n}) \log C_e$ and Langmuir isotherm is : $(C_e/q_e) = (a_L/k_L)\, Ce + 1/k_L$, where Kf and 1/n are the Freundlich constants, K_f is an approximate indicator of adsorption capacity, 1/n is a function of the strength of adsorption in the adsorption process, C_i and C_e *are the* initial and final concentration of the dye solution (mg L^{-1}) and q_e is the amount of dye quantity adsorbed at equilibrium (mg/g) and K_L and a_L are the Langmuir constants related to capacity and energy of adsorption respectively. From the Langmuir isotherm model dimensionless separation factor, R_L, is calculated using $R_L = \frac{1}{(1+a_L C_i)}$. The adsorption process is unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if: $0 < R_L < 1$ and irreversible if: $R_L = 0$.

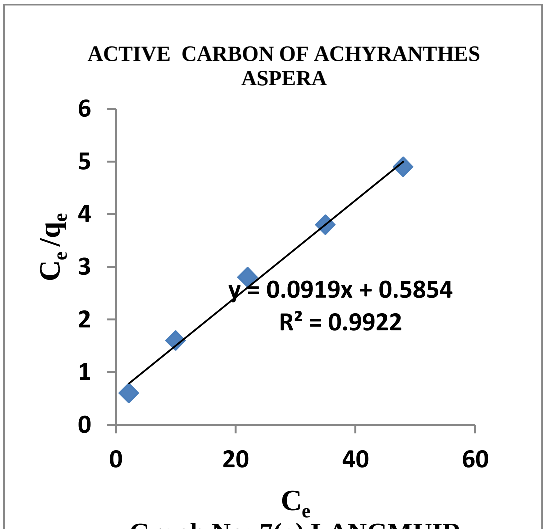
Langmuir isotherm (Ce/qe Vs Ce) and Freundlich isotherm {log (q_e) vs log (c_e)} have been presented in the Graph No. 7a and 7b respectively. The slope (a_L/k_L), intercept ($1/k_L$), and R^2 and R_L values have been calculated and presented in the Table No. 2.



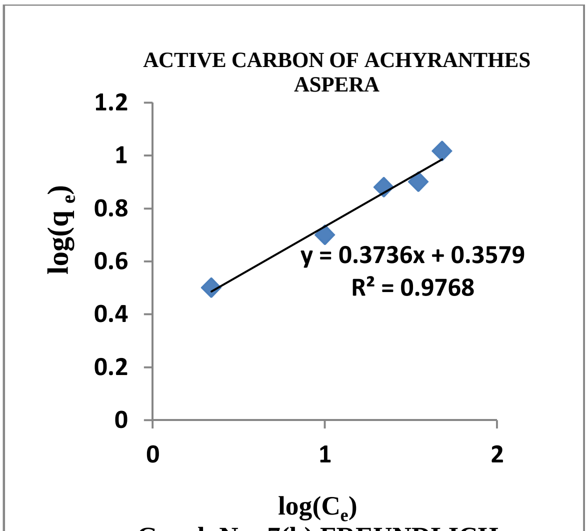
Graph No: 6(a) Effect of interferring anions on the adsorption of dye



Graph No: 6(b) Effect of interferring cations on the adsorption of dye



Graph No: 7(a) LANGMUIR ADSORPTION ISOTHERM

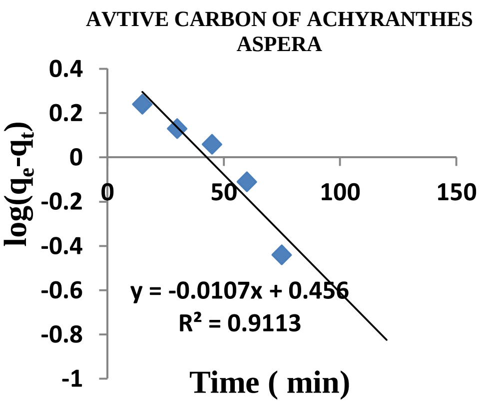


Graph No: 7(b) FREUNDLICH ADSORPTION ISOTHERM

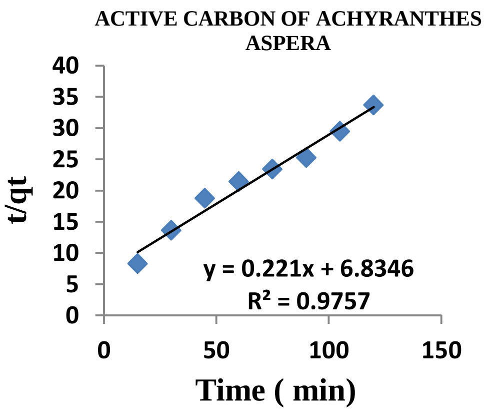
R^2 values are: 0.9922 for Langmuir isotherm model and 0.9768 for Freundlich model indicating that the Langmuir isotherms are more suitable for describing the adsorption proves. Further, R_L= 0.48 indicates that the adsorption of the dye is onto the surface of the active carbon, ACAA. Thus, the adsorption of the dye on the surface of the adsorbent is homogeneous and uni-layered.

8: Adsorption kinetics:

The kinetics of adsorption is analyzed using Pseudo first order: $\log(q_e – q_t)$ = $\log q_e - \frac{K_1}{2.303}.t$ and Pseudo second-order $\frac{t}{q_t}$ = $\frac{1}{K_2.q_e^2} + \frac{1}{q_e}.t$ equations , where q_t (mg/g) = amount of dye adsorbed on the active carbon, ACAA at various times (min), K_1 = the rate constant of the pseudo first order kinetic (min^{-1}), K_2 = the rate constant of the pseudo-second order kinetic (min^{-1}) as given in the Graph No. 8a & b [53-55].The slope, intercept and R^2 values calculated are presented in the Table No.2.



Graph No: 8(a) Pseudo first order kinetics



Graph No: 8(b) Pseudo second order kinetcs

Table 2: Adsorption and Kinetic parameters					
S.No.	Adsorption isotherms and Kinetic models		Slope	Intercept	R^2
1.	Freundlich isotherm		0.3736	0.3579	0.9768
2.	Langmuir isotherm	R_L= 0.48	0.0919	0.5854	0.9922
3.	Pseudo first order model		-0.0107	0.456	0.9113
4.	Pseudo second order model		0.221	6.834	0.9757

From the data, it may be inferred that Pseudo second order model well describes the kinetics of adsorption as the R^2 value for Pseudo second order model: 0.9757, is higher than Pseudo first order model: 0.9113.

9: I R Spectral Data:

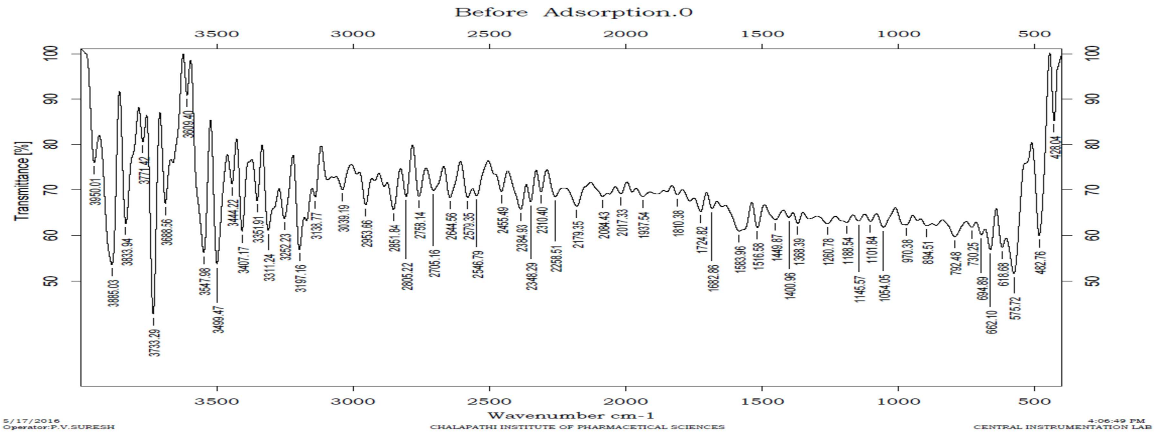


Figure 3(a): FTIR spectrum of the ACAA before adsorption of dye

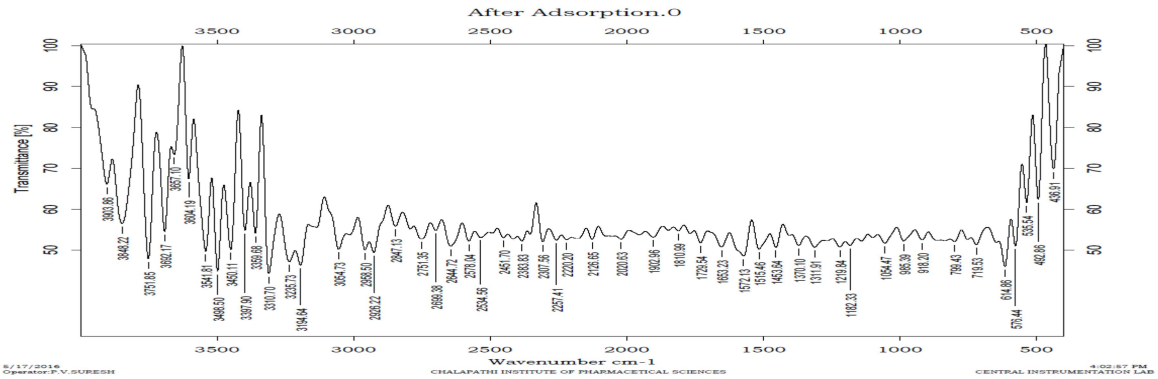


Figure 3(b): FTIR spectrum of the ACAA after adsorption of dye

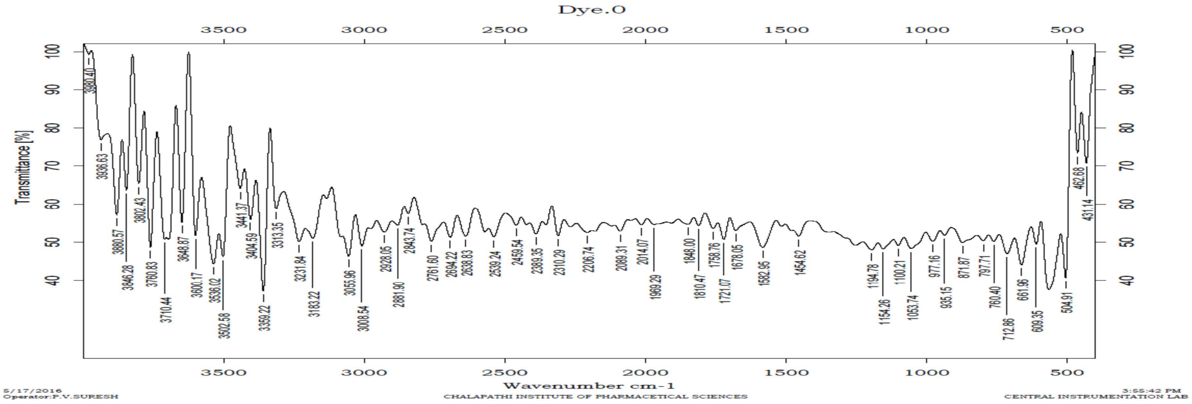


Figure 3(c): FTIR spectrum of the pure dye (ARS)

FTIR data before and after adsorption of the dye along with the pure dye(ARS) has been presented in the Fig No. 3a-c. It is revealed from the data that the surface of the active carbon has a number of functional groups: the frequencies in the range 3498– 310 for –OH/-NH stretching; 2699 to 2926 cm^{-1} for –CH_2 and –CH_3, 1311and 1054 cm^{-1} for C–O–C group; 1453 to 1653 for aromatic nature; 1729 and 1818 for C=O. On comparison of the frequencies before and after adsorption, it is inferred that many frequencies are shifted with less or more intensify and some new bonds pertaining to the dye appeared. These data confirms that the functional groups on the surface of the active carbon binding the dye.

4: APPLICATIONS

The procedures developed in this investigation were applied to the samples collected from effluents of textile industries at Mangalagiri and Machilipatnam of Andhra Pradesh. The samples were analyzed for the actual amounts of the said dye and then the samples were fed with known amounts of the dye.

Table 3: Removal of color in swages of dying industries

S. No.	Water samples	C_i (mg/lit) (initial concentration of dye)	C_f (mg/lit) (concentration of dye after removal)	% Removal
1	Sample 1	22	0	100
2	Sample 2	30	4	93.3
3	Sample 3	42	8	80.9
4	Sample 4	56	15	73.2

Then these samples were subjected to extraction adopting the methodologies developed in this work. The obtained results were presented in the Table No. 3. It can be seen from the table that the procedure developed in this work successfully remove the said anionic dye.

CONCLUSION

- Active carbon is derived from the stems of Achyranthes aspera plant (ACAA) and its adsorption nature towards the Alizarin red S, an anionic dye, is probed at various conditions of extraction namely, pH, sorbent concentration, agitation time, temperature and initial concentration of the dye adopting Batch methods of extraction and using simulated water. The extraction conditions are optimized for the maximum removal of the dye.

- 89% of the dye is removed from simulated waters at the optimum conditions of extraction viz., pH: 2; extraction time: 90 minutes; 120 rpm, temp: 30^0C, initial conc. of the dye: 20 ppm and sorbent dosage: 5 g/lit.
- % removal of the dye when fivefold excess of co-ions commonly found in industrial sewages namely, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, CO_3^{2-} , Ca^{2+} Zn^{2+}, Fe^{2+}, Mg^{2+} and Cu^{2+}has been investigated.
- The adsorption process is analyzed using Langmuir and the Freundlich isotherms and found that the Langmuir model better describes adsorption process. This indicates homogenous mono-layer nature of the dye layer on the surface of the adrsorbent, ACAA. Further, the R_L= 0.48 of the Langmuir model indicates that the adsorption of the dye is onto the surface of the active carbon.
- The FTIR data also confirms the adsorption of the dye is on to the surface of the adsorbent.
- The kinetics of adsorption is analyzed using pseudo first order (R^2 value: 0.9113) and pseudo second order models (R^2 value: 0.9757) and found that the latter model is better fit.
- The effect of temperature on the % removal of the dye has been studied in the temperature range: 303 to 333 k and found that the % removal increases with the increase in temperature. The thermodynamics parameters namely; ΔH, ΔS and ΔG have been calculated and found that the adsorption process is endothermic in nature and also spontaneous.
- The Methodolology developed in this investigation have been applied to the samples collected from the effluents of textile industries and found to be successful.

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