

DOI No.: <http://doi.org/10.53550/EEC.2023.v29i04s.066>

Methylene blue Removal from Aqueous Solution of carbonized *Orthosiphon aristatus*

N. Vidhyulatha¹ and Kumaraguru^{*2}

¹ PG and Research Department of Chemistry, Poompuhar College (Affiliated to Bharathidasan University - 620 024) Melaiyur 609 107, Tamilnadu, India

^{*2} Thanthaiperiyar Government Arts and Science College, Tiruchirappalli 620 023 (Affiliated by Bharathidasan University)

(Received 11 April, 2023; Accepted 21 June, 2023)

ABSTRACT

The chemically activated carbon obtained from the stem of *Orthosiphon aristatus* was revealed to have an imperceptible feature of sorbent efficiency for the elimination of methylene blue from aqueous solutions of diverse concentrations. Adsorption tests were carried out in a batch procedure, and the influence of contact time, carbon dosage, and pH on percentage removal was investigated. Adsorption studies demonstrate that methylene blue uptake occurs at pH 6.7. The equilibrium adsorption data fit better with the Langmuir and Freundlich adsorption models. Kinetic modelling of the removal process was performed, and the removal process was discovered to follow a pseudo second-order model, the Elovich model, and the intraparticle diffusion model. The rate constant for the adsorption process was estimated. The thermodynamic parameters change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated, and negative values of (ΔG°) suggested that the removal process was spontaneous at all temperatures. It was concluded that activated carbon derived from the stem of *Orthosiphon aristatus* has a high capacity for methylene blue elimination.

Key words : Activated carbon of *Orthosiphon aristatus*, Methylene blue dye, Adsorption isotherm, Kinetics, Equilibrium models.

Introduction

The dumping of dyes has resulted in the growing pollution of water resources throughout the world. The removal of colours from water and wastewater as a result of industrialization has proven to be a severe issue. The discharge of dyes into water resources is one of the most critical pollution issues, as it can have a severe impact on the quality of the water supply (Allen *et al.*, 1989). Increasing dye concentrations in water resources have a significant impact on water quality and pose serious hazards to human health, owing mostly to their non-

degradability and toxicity. Malachite green, Rhodamine-B, Methylene blue, Basic Red, Methyl Orange, and more colours are available. Methylene blue is an important element in several sectors, including tanneries, paint and pigments, wood preservation, and alloy manufacturing. In humans, methylene blue harming may trigger everything from skin irritation to lung cancer, as well as kidney, liver, and stomach damage (Abu Al-Rub *et al.*, 2002).

Adsorption is the most easygoing vogue mode for the colour removal progress. Adsorption onto activated carbon is a common technique for removing dissolved colours from wastewater. Adsorbent-

(³ Associate Professor)

grade activated carbon, on the other hand, is prohibitively expensive. To replace activated carbon, it is vital to seek out low-cost adsorbents that do not require pretreatment. We reported in this work that the usage of natural biomaterials is an alternative due to their relative abundance and cheap commercial values, and *Orthosiphon aristatus* Tamilnadu's most ancient plant. It is widespread throughout India, particularly in Tamil Nadu, Kerala, Bengal, and the entire southern region. This research looked into the feasibility of employing the stem of an *Orthosiphon aristatus* plant as an adsorbent for the adsorption of the cationic dye Methylene Blue from an aqueous solution. A review of the literature reveals that no work has been done to revitalize *Orthosiphon aristatus* as an adsorbent.

Experimental Methods

All of the reagents used in the studies were analytical (AR) grade and were from the scientific equipment firm Trichy. The dye was dissolved in distilled water to make stock solutions of the test reagents.

Preparation of adsorbent

The *Orthosiphon aristatus* natural plant material used in this study was taken from a nearby Poompuhar, Mayiladuthurai District, Tamilnadu, India. The image of *Orthosiphon aristatus*. The stem was washed several times with distilled water to remove dirt and dust before being dried in a hot air oven at 110 °C. The stem was then carbonised by adding w/v ratio Con. H₂SO₄ to obtain the main carbon. To obtain activated carbon, the primary carbon was activated at >900 °C for 6 hours under optimum circumstances.

Orthosiphon aristatus



Experimental Procedure of Batch Method

Batch investigations (Annadurai *et al.*, 2002) were carried out to investigate the effect of key parameters, including pH, contact time, initial dye concen-

tration, other ions, and temperature, on the removal of MB onto activated *Orthosiphon aristatus* carbon. For adsorption isotherms, dye solutions of various concentrations (25-125 MB/l) and temperatures (30-60°C) with a known pH and a known amount of adsorbent (0.025 g/l) were agitated at 120 rpm until equilibrium was reached. The solution was then allowed to settle, and the residual concentration of MB was measured using a UV-visible spectrophotometer at 470 nm. For the elimination of MB dye from aqueous solutions, all studies were performed at a normal pH. The effect of pH on dye removal was examined throughout a pH range of 3.0-9.0 by adjusting the starting pH of the solution using dil. HCl or dil. NaOH. The influence of sorbent dosage on adsorption rate was studied using the same protocols described above, but with varied dosages (25-125 MB/50 ml). The following formula can be used to calculate the quantity of adsorption at time t, qt (MB/g).

$$q_t = V \times \frac{(C_0 - C_t)}{w} \quad \dots (1)$$

Where, q_t is the mass of adsorbed dye per unit mass of adsorbent (MB g⁻¹) C_0 and C_t are the initial and actual concentrations (g dm⁻³) of dye at the time, respectively. V is the volume of the treated solution (ml), and ' w ' is the mass of adsorbent (g). The removal percentage of MB dye can be calculated as following relationship

$$\% \text{ Removal} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad \dots (2)$$

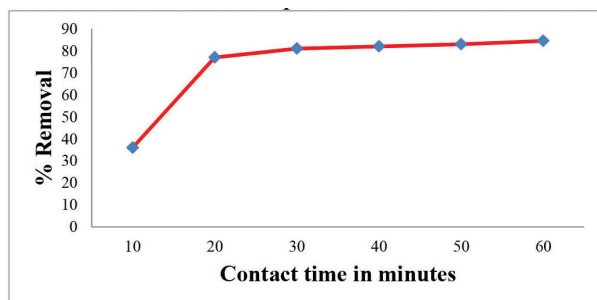
The process time for the equilibrium adsorption tests was chosen based on the adsorption kinetics experiments, as long as the considered sorbent / sorbate system is equilibrated. During these trials, the following process factors were altered: the kind and amount of adsorbent (AOAC), the particle size: All experiments were carried out at room temperature, with the starting pH of the solutions and the initial concentration of the considered ions.

Results and Discussion

Contact time

To determine the equilibration time (Demirbas *et al.*, 2002) for maximal absorption and to understand the kinetics of the adsorption process, MB adsorption on AOAC adsorbent was studied as a function of contact time, with the findings displayed in the graph.

The graph demonstrates that the absorption rate was initially brisk, with a maximum of adsorption completed in 30 minutes and equilibrium established in 50 minutes; hence, 60-minute equilibration duration was used for all subsequent tests.

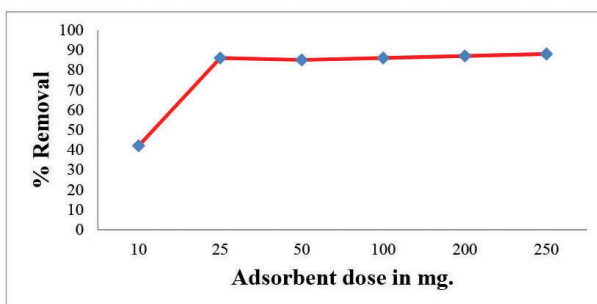


Effect of Contact Time on the Removal of MB dye [MB]=25mg/l; Temperature 30 °C; Adsorbent dose=0.025 g/50 ml.

The above graph depicts that the obliteration of MB on the adsorbent of AOAC was conducted in a distinct time range of 10 to 60 minutes via batch adsorption. It was discovered that the AOAC operated at a high efficiency of 35 percent in 10 minutes. The agitation time was increased, and suddenly the obliteration of MB was increased to 20 minutes and achieved the maximum at 50 minutes. The optimization uptake rate was 85 percent after 60 minutes.

Effect of adsorbent dosage

The effect of adsorbent dosage was investigated by placing various adsorbent doses (10, 25, 50, 100, 200, and 250 MB) in flasks holding 50 ml of 50 ppm MB solutions. For 60 minutes, flasks were shaken at 180 rpm and 30 °C. The findings of this investigation are depicted in the graph. The amount of MB absorbed per gram decreased as AOAC dose increased. This demonstrates that MB’s direct and equilibrium ca-



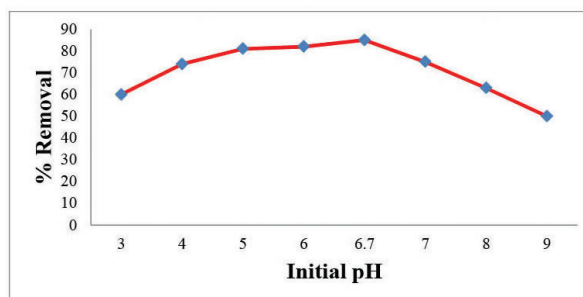
Effect of Adsorbent dose on the Removal of MB dye [MB]=25 mg/l; Temperature 30 °C; Contact Time 60 min.

pabilities are functions of activated AOAC dose.

The inquisition of adsorbent dosage was used with different dosages of AOAC in MB solutions, as seen in the graph above. It demonstrates that when the adsorbent dosage was increased, the AOAC quality improved due to an increase in active sites per unit surface. According to the findings obtained from this study, the maximum degradation of MB was 90% at 25 mg per liter and 180 rpm. Furthermore, with increasing dosage, the degradation of MB was reduced per gram, indicating that equilibration had occurred.

Effect of Initial pH

The effect of pH on dye methylene blue sorption was investigated by incorporating 0.25 g of adsorbent into flasks containing 50 ml of 50 ppm methylene blue solutions at various initial pH (3-9) with pH_{ZPC} fixed. Flasks containing the adsorbent and MB solution were shaken for 60 minutes at 180 rpm and 25°C. The greatest adsorption occurred at pH_{ZPC} because the surface of the adsorbent was more appealing to the adsorbate.



Effect of Initial pH on the Removal of MB dye [MB]=25 mg/l; Temperature 30 °C; Adsorbent dose=0.025g/50ml.

Experiments were guided with discrete pH values of (3 to 9) to confiscate MB solutions through the adsorbent of AOAC. Represents that at low pH, it vigorously influenced the sum of hydrogen ions encompassed on the boundary of the AOAC, which deterred the mitigation of MB solution. The conclusion of this examination implies that at higher pH, the competition of hydrogen ions and MB solutions for the degradation would be lowered and the mitigation efficacy would be increased at pH of 6.7.

Effect of other ions

The effect of chlorine ions (Bulgariu, 2013) on the adsorption process was investigated at various con-

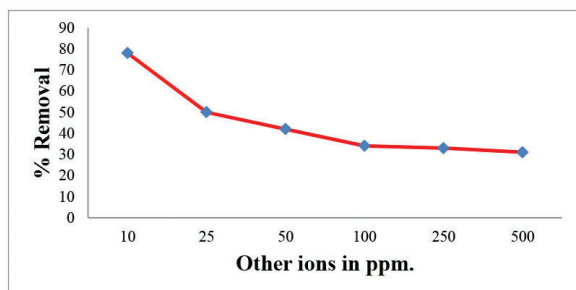
concentrations. Ions were added to 50 MB/l of MB solutions, and the mixture was agitated for 60 minutes at 30 °C. The graph shows that a low concentration of Cl⁻ has no influence on the percentage of MB adsorption on AOAC because the interaction of Cl⁻ at accessible sites of the adsorbent via competitive adsorption is ineffective. As the concentration of other ions grows, so does the interference of these ions at available surface sites of the sorbent via competitive adsorption, which reduces the percentage of adsorption.

Effect of other ionic strength on the removal of MB dye

The graph indicated that the 50 mg/l MB solutions be tested with various chlorine ion concentrations, which were designated as recognized equilibrated values. It was said that even at higher concentrations of chlorine ions, they could not defend the removal of MB and that at low concentrations of salt ions, they could not obstruct the integration of the activated pores on the AOAC and the MB solutions.

Effect of Temperature

Temperatures ranging from 303 K to 333 K were utilised to probe methylene blue on AOAC during the degrading process. Throughout the MB degradation process, the agitation duration, pH, starting concentration, and adsorbent dose were all measured. According to the investigation's findings, which reveal that the rate of degradation of MB is greatly boosted at higher temperatures and provides more active sites for ingesting the MB, the degradation occurs via physisorption.



Adsorption Models

The adsorption equilibrium data were further analyzed into two well-known isotherm models via Freundlich and Langmuir models.

Freundlich model

The Freundlich model (Alpert *et al.*, 1970) which is

an indicative of surface heterogeneity of the adsorbent is described by the following equation.

$$\log q_e = \log K_f + \frac{1}{n_f} \log C_e \quad \dots (3)$$

Where, K_f and $1/n_f$ are Freundlich constants related with adsorption capacity and adsorption intensity respectively. The Freundlich plots drawn between $\log q_e$ and $\log C_e$ for the adsorption of MB were shown the graph and its make that correlation co-efficient (R^2) values amid 0.98 to 0.99, as a result temperature studied indicating that Freundlich model was applicable to the present study these values listed in table.

Langmuir model

The Langmuir adsorption isotherm (Maurya *et al.*, 2006) equation which is valid for monolayer adsorption on to a surface is given below.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \dots (4)$$

Where, q_e (MBg⁻¹) is the amount adsorbed at the equilibrium concentration C_e (mol l⁻¹), q_m (MBg⁻¹) is the Langmuir constant representing the maximum monolayer adsorption capacity and K_L (l mol⁻¹) is the Langmuir constant related to energy of adsorption. The plots drawn between C_e/q_e and C_e for the adsorption of MB was found linear and it's shown in the graph. The correction coefficient (R^2) values confirm good agreement our experimental results the values of the monolayer capacity (q_m) and equilibrium constant K_L have been evaluated from the intercept and slope of these plots and given in table. These facts suggest that MB is adsorbed in the form of monolayer coverage on the surface of the prepared adsorbent. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L by the equation.

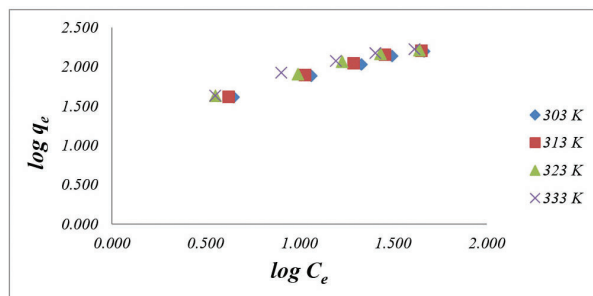
$$R_L = \frac{1}{1 + K_L C_0} \quad \dots (5)$$

Where, C_0 (MB/L) is the highest initial concentration of adsorbent and K_L (L/MB) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly.

- $R_L > 1$ -Unfavorable adsorption
- $0 < R_L < 1$ -Favorable adsorption
- $R_L = 0$ -Irreversible adsorption

➤ $R_L = 1$ -Linear adsorption

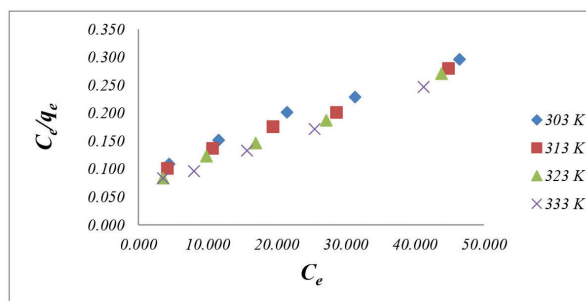
The R_L values in the middle of 0 to 1 indicate favorable adsorption for all initial concentration (C_o) and temperatures studied. The calculated R_L values are given in table. The values of K_L were increased with increasing the dose of adsorbent for AOAC High K_L values indicate high adsorption affinity the monolayer saturation capacity q_m were around 246.31 MB/L for AOAC.



Freundlich isotherm

Freundlich adsorption isotherm for the removal of MB dye

Based on the plot of $\log Q_e$ Vs $\log C_e$, it was stated that the straight line showing the linear form of the Freundlich isotherm was feasible for this suppression of MB through AOAC. The apparently revealed that the efficiency of MB suppression was magnified by the dissimilar temperatures indicated in the the graph. Slope ($1/n$) and intercept ($\log K$) were analysed from the values recorded. K_f , and n were increased, which suggested that the more negative charges were appearing on the AOAC surface sites due to vanderwaal’s forces in between the MB and AOAC. The R^2 and adsorption intensity ‘ n ’ depict the multilayer adsorption on the heterogeneous surface with no stable energy and divulge the mechanism that transpired by means of physical adsorption.



Langmuir isotherm

Langmuir adsorption isotherm for the removal of MB dye

The outcomes obtained from the graph distinctly imply that the elimination of MB dye solutions on the adsorbent of AOAC at various concentrations and temperatures was operated on and discernibly explored. The process was matched with the Langmuir isotherm because the correlation coefficient of the R^2 value was close to 1. The plain line appears on the plot ‘ C_{eq}/Q_{eq} against C_{eq} ’ and the slope ($1/Q_m K_L$) and intercept ($1/Q_m$) data were measured from the assigned table,

Thermodynamic treatment of the adsorption process

Thermodynamic (Freidal *et al.*, 1956) characteristics related to adsorption were computed using standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0). The following equation gives the free energy of the adsorption process when the adsorption equilibrium constant K_0 is taken into account:

$$\Delta G^0 = - RT \ln K_0 \quad \dots (6)$$

Where, ΔG^0 is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin, R is the universal gas constant (8.314 J mol/K) and K_0 is the equilibrium constant for the ratio between C_{solid} is the solid phase concentration at equilibrium (MB/ L)

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	$K_f(\text{mg/g}) (\text{L/mg})^{1/n}$	17.718	18.802	22.31	23.501
	n_f	1.7163	1.7062	1.8119	1.7905
	R^2	0.9938	0.9865	0.9796	0.9629
Langmuir	$q_m(\text{mg/g})$	231.63	234.83	223.07	229.07
	$K_L (\text{L/mg})$	0.0443	0.049	0.0631	0.0685
	R^2	0.9894	0.993	0.9943	0.9973

and C_{liquid} is the liquid phase concentration at equilibrium (MB/L). The equilibrium constant ($\ln K_0$) may be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature, given in following mathematical forms.

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \dots (7)$$

Where, ΔH° is the standard heat change of sorption (kJ/mol) and ΔS° is standard entropy change (kJ/mol). The value of ΔH° and ΔS° can be obtained from the slope and intercept of plot of $\ln K_0$ against $1/T$. The value of thermodynamic parameter calculated from equation 6 and 7 are shown. The thermodynamic treatment of the sorption data indicates that ΔG° values were negative at all temperature. The results point out that physisorption is much more favorable for the adsorption of MB dye. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of MB adsorption increases, this rules out the possibility of chemisorptions. The low ΔH° value depicts MB dye is physisorbed onto adsorbent AOAC.

The negative ΔG° results confirmed the spontaneous nature of MB dye adsorption onto AOAC. The lower the value of ΔG° , the more physical the adsorption process. The fact that ΔH° is positive supports the endothermic character of the adsorption process. Positive ΔS° values indicated enhanced unpredictability of the solid solution interface during MB adsorption onto AOAC.

Kinetic models

Pseudo-second-order

Kinetic models (Gadsen, 1975) are commonly used to test experimental data in order to explore the process of adsorption. Assuming that the observed concentrations are identical to the surface concentrations, pseudo-second-order equations can be employed. This is the linearized form of the pseudo second order equation.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad \dots (8)$$

Where, q_t (MBg⁻¹) is the amount of adsorbed dyes on the adsorbent at time t , q_e the equilibrium sorp-

tion uptake and k_2 , (min⁻¹) is the rate constant of pseudo-second-order adsorption. The plot t/q_t versus t gives a straight line says second order kinetic model is applicable then q_e and k_2 are determined from the slope and intercept of the plot, respectively. The high regression value indicate the adsorption reaction exist a pseudo-second-order and these values shown.

The Elovich equation

The Elovich model equation is generally expressed as

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad \dots (9)$$

Where α is the initial adsorption rate (MB g⁻¹ min⁻¹) and β is desorption constant (g/MB) during any one experiment. If MB adsorption fits with the Elovich model, a plot of q_t Vs $\ln(t)$ yields a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$. The Elovich model parameters α , β , and correlation coefficient (R^2) are summarized. This model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second order kinetics models. This may be due to increase the pore or active site on the AOAC adsorbent.

Intra-particle diffusion model

Kinetic data was further investigated using the Intraparticle diffusion model (Gupta *et al.*, 1988), which is based on the equation below.

$$\log R = \log K_{id} + a \log t \quad \dots (10)$$

Where, k_{id} is the intra-particle diffusion rate constant and it's related to the thickness of the edge. According to above equation a plot of $\log R$ versus $\log t$ gives a straight line that's says the adsorption mechanism follows the intra-particle diffusion process and the evidence of correlation co-efficient values are close to unity.

Conclusion

The composite adsorbent was effective in removing MB dye from the aqueous solution. Solution pH, adsorbent concentration, contact time, and starting ion concentration all had an effect on removal efficiency. The Langmuir and Freundlich models fit the adsorption data nicely. However, because of the larger correlation coefficient that the former exhibited, the Langmuir isotherm fit the model better than

the Freundlich isotherm, showing the applicability of monolayer coverage of the dye on the surface of the adsorbent. According to the study's findings, the prepared *Orthosiphon aristatus* activated carbons could provide an effective, inexpensive, accessible, and low-cost adsorbent for the eradication of methylene blue from aquatic habitats.

References

- Abu Al-Rub, F. M., Kandah, N. and Aldabaibeh, 2002. Nickel removal from aqueous solutions using sheep manure wastes, *Eng. Life Sci.* 2 111–116.
- Allen, S. J., McKay, G. and Khader, K. Y. H. 1989. Intraparticle Diffusions of Basic Dye During Adsorption onto Sphagnum Peat. *Environ. Pollut.* 56: 39.
- Alpert, N. L., Kesi, W. E. and Szymanaki, H. A. 1970. *Theory and Practice of Infrared Spectroscopy*. Plenum: New York. 2nd ed.
- Annadurai, G., Juang, R.S. and Lee, D.J. 2002. Adsorption of heavy metals from water using banana and orange peels, *Water Sci. Technol.* 47 (1): 185–190.
- Crank, J. 1956. *The Mathematics of Diffusion*. Clarendon Press: Oxford.
- Demirbas, E., Kobya, M., ncel, S. O. and Sencan, S. 2002. Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies, *Bioresour. Technol.* 84 (3): 291–293.
- Freidal, R.A. and Queiser, J. A. 1956 "Infrared Analysis of Bitumenous Coal and Other Carbonaceous Materials. *Anal. Chem.* 28: 22.
- Gadsen, J. A. 1975. *Infrared Spectra of Minerals and Related Inorganic Compounds*. Butterworths: London.
- Gupta, G. S., Prasad, G. and Singh, V. N. 1988. Removal of Chrome Dye from Carpet Effluents using Coal II (Rate process). *Environ. Technol. Lett.* 9: 1413.
- Maurya, N. S., Mittal, A. K., Corner, P. and Rothar, E. 2006. Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH. *Bioresour. Technol.* 97: 512-521.
- Poongodi Vijayakumar, R. Swaminathan Senguttuvan, 2023. One Pot Facial Fabrication and Characterization of Ag-Fe Nanocomposite – As Photocatalytic Removal of Methyl Red Dye and Pharmacological Applications: Volume-12, Issue-1: Page:1419-1440. DOI: 10.31838/ecb/2023.12.1.118.
- Veeravelan, K. Arivoli and S. Marimuthu, V. 2017. Adsorption Characteristics of AZJ-NC for Removing basic Red (III) Dye from Waste Water, Volume-6, Issue-1.
- Veeravelan, K. Arivoli and S. Samu Solomon, J. 2022. Adsorption Characteristics Study on the Removal of Therapeutic Drug Ibuprofen Pollution on the Acid Digested Carbon of Waste Leathers. *Eco. Env. & Cons.* 28.
- Vidhyulatha, N., Arivoli, S. and Ajithkumar, M. 2022. Removal of Fe (II) ion from aqueous solution by sorption onto Activated *Orthosiphon aristatus* carbon (AOAC). *Eco. Env. & Cons.* 28; pp. (S411-S417) DOI No.: <http://doi.org/10.53550/EEC.2022.v28i06s.069>