Volume-6, Issue-1, January - 2017 • ISSN No 2277 - 8160 IF : 3.62 | IC Value 80.26

Original Research Paper Home Science

ADSORPTION CHARACTERISTICS OF AZJ-NC FOR REMOVING BASIC RED 111 DYE FROM WASTEWATER

S Arivoli PG and Research Department of Chemistry, Thiru Vi Ka Government Arts College, Thiruvarur, Tamilnadu, India.

K Veeravelan PG and Research Department of Chemistry, Thiru Vi Ka Government Arts College, Thiruvarur, Tamilnadu, India.

V Marimuthu PG and Research Department of Chemistry, Thiru Vi Ka Government Arts College, Thiruvarur, Tamilnadu, India.

ABSTRACT *Dyes are one of the most important industrial pollutants, especially in textile industries. Many methods have been proposed in order to remove color from wastewater among which, adsorption is more acceptable due to the ability for its use in the large scale. The objective of this study was to investigate Activated Zizyphus Jujuba seed shell (AZJ-NC) as an inexpensive adsorbent for removal of Basic Red 111 from aqueous solutions. In this work the Modified Activated Zizyphus Jujuba seed shell (AZJ-NC) has been applied for removal of the Basic Red 111 dye from aqueous environments. The effect of pH, contact time, initial concentration and amount of adsorbent were considered. In order to investigate the mechanism of the adsorption process, several kinetic models including pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion were used. In addition, equilibrium data was analyses to Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Hurkins-Jura, Halsay, Radlich-Peterson, Jovanovic and BET isotherm models. Results showed that the adsorption of the Basic Red 111 was enhanced with increasing initial dye concentration, pH and contact time. The optimum pH was 9. Considering the values of R2 (0.999), BET isotherm model and pseudo-second order kinetic model had the best fitness. This study has demonstrated that the Physical modified Activated Zizyphus Jujuba seed shell (AZJ-NC) can be employed as effective and inexpensive adsorbent for the removal of Basic Red 111 from aqueous environments.*

KEYWORDS : Basic Red 111 (BR-111), Activated Zizyphus Jujuba seed shell Nano Carbon (AZJ-NC), Isotherm Models, Thermodynamic and Kinetic studies.

1. Introduction

Industrial wastewater is considered as one of the major pollutants of the environment [1]. Moreover, textile industries are among each country's basic industries and have coloured wastewater due to making use of coloured materials [2]. Overall, coloured wastewater is produced by various industries, such as textile, dyeing, pharmaceutical, food, cosmetics and healthcare, paper and leather industries. Such colours not only change the water's colour, which is important regarding aesthetics, but they also prevent light from penetrating through water, disturb photosynthesis and destroy the aquatic ecosystem as well as several aquatic species [3]. One of the high consuming materials in the dye industry is Basic Red 111 (BR-111) which is used for cotton and silk painting [4]. Chemical structure of BR-111 is illustrated in Fig. 1. Up to now, a great number of methods have been proposed in order to remove dyes from the industrial wastewater among which adsorption is the most acceptable due to its cost effectiveness and its capability to be used in large scales [5].

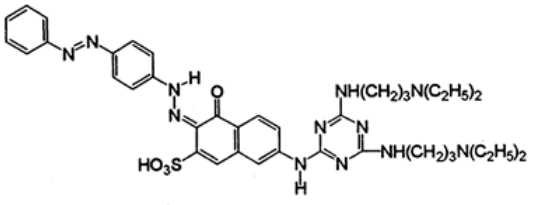


Fig.1. Molecular Structure of Basic Red 111

The methods of colour removal from industrial effluents include biological treatment, coagulation, flotation, adsorption, oxidation and hyper filtration [6]. Among the treatment options, adsorption has been found to be superior to other techniques for water treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity of toxic substances [7]. Different adsorbents have been used for the removal of various materials from aqueous solutions, such as dyes, metal ions and other organic materials including perlite [8], bentonite [9], silica gels [10], fly ash [11], lignite [11], peat [12], silica [13], etc.

Among these natural materials, *Activated Zizyphus Jujuba seed shell* (AZJ-NC) which has a low weight and a fine micro-porous structure (up to 90%) and can be found in many regions of southern part of TamilNadu, India. Because of its fine micro-porous structure, *Activated Zizyphus Jujuba seed shell* (AZJ-NC) has a high specific surface area and can float in water owing to its low density. Recently, many researchers have used Activated Carbon for removal of cadmium [14], disinfection by-products [15], heavy metals [16], sulfur dioxide [17] and azo dye [2].

1.1 Objectives

Due to several advantages of the *Activated Zizyphus Jujuba seed shell (AZJ-NC)* and its accessibility in India, the aim of the present work was to investigate its effectiveness for the removal of BR-111 at various experimental conditions. Since initial *Zizyphus Jujuba seed shell* (AZJ-NC) has some impurity, shows low sorption capacity and is negatively charged, the acidic treated *Activated Zizyphus Jujuba seed shell* (AZJ-NC) was used in this work. Therefore, the purpose for acidic treatment of *Zizyphus Jujuba seed shell* (AZJ-NC) was to improve the positive surface charge of adsorbent and its sorption capacity since initial *Activated Zizyphus Jujuba seed shell* (AZJ-NC) shows low sorption capacity. The present study aims to use modified *Activated Zizyphus Jujuba seed shell (AZJ-NC)* for removing BR-111 dye from aqueous solutions.

2. Materials and Methods

2.1 Instruments and Reagents

Stock solution was prepared by dissolving the required amount of BR-111 in double distilled water. The test solutions were prepared by diluting stock solution to the desired concentrations. The concentration of the BR-111 was determined at 620 nm. The pH measurements were done using Digital pH meter (Equip-Tronics EQ 614A, India) and adsorption studies were carried out on UV-Vis Double Beam spectrophotometer (Systronics 2203, India). All chemicals included NaOH, HCl and BR-111 with the highest available purity and were purchased from Scientific Equipment Company, Tiruchirapalli, (Merck, All solutions were stirred on a hotplate and stirrer (JENWAY, model-1000, India).

2.2 Adsorbent Features

In the present experimental study, *Activated Zizyphus Jujuba seed shell* (AZJ-NC) samples as adsorbents were gathered from southern part of Tamil Nadu, India. The chemical properties of the AZJ-NC are presented in Table 1. As Table 1 depicts, the utilized adsorbent, which shows the high capability of this adsorbent for absorption process.

Table: 1

Analysis	Value
pH_{slurry}	5.5
pH_{zpc}	6.00
Moisture content, %	0.105
Particle density, g cm^{-3}	0.285
Conductivity, µS/cm	41.63
Surface area, m^2/g	25.25

2.3 Preparing the Adsorbent

At first, Zizyphus Jujuba seed shell was collected from local area of Thiruvarur district and washed several times by de-ionized water in order to remove the primary impurities. Next, the shell was placed in Con. H_2SO_4 (w/v) for 24 hours for carbonization and increasing the adsorbent's porosity. Afterwards, the prepared sample was washed several times by de-ionized water, ground well to fine powder and sieved by a mesh. Finally, this was activated around 1100 ^{0}C in muffle furnace for 12 hours; the fine micro-porous size of activated nano carbon is 50 nm was utilized as the adsorbent.

2.4 Adsorption Study

To study the effect of important parameters like the pH, contact time and initial dye concentration on the adsorptive removal of BR-111, batch experiments were conducted. For each experimental run, 50 ml of different concentrations of the dye solution (25 - 125 mg/L) was agitated with 0.025 g of the adsorbent at 120 rpm until the equilibrium was achieved. Samples were withdrawn at different time intervals (15, 30, 45 and 60 minutes) and kinetics, isotherm and other parameters of adsorption was determined by analyzing the remaining dye concentration from aqueous solution. In order to evaluate the effect of the initial pH on BR-111 adsorption, the equilibrium study was conducted at different pH levels 2, 3, 4, 5, 6, 7, 8 and 9 and other equilibrium studies were continued at the optimum pH 6.5. The pH of the solutions was adjusted by adding 0.01 N aqueous solutions of NaOH and Hcl.

The percentage removal of dye was calculated using the following equation [18]:

$$\%MB\ Removal = \frac{(C_0 - C_t)}{C_0} \times 100 \quad \text{.....(1)}$$

Where, C_0 (mg/L) and C_t (mg/L) are the initial dye concentration and dye concentration at time t, respectively. When the system reached the equilibrium concentration, the equilibrium adsorption capacity was calculated through the following equation [19]:

$$q_e = \frac{v\,(C_0 - C_e)}{w} \quad \text{.....(2)}$$

In this equation, q_e (mg/g) represents the rate of the adsorbed dye per mass unit of the absorbent, C_o (mg/L) and C_e (mg/L) are initial and equilibrium dye concentrations, respectively, and v (L) and w (g) are the volume of the dye solution and the weight of the adsorbent, respectively.

3. RESULTS AND DISCUSSION

3.1 The Effect of Contact Time

Generally, diffusion of the adsorbate on the used adsorbent and ultimately the adsorption phenomena on the adsorbent are time consuming processes [21]. The adsorption rate, obtained for BR-111 adsorption on AZJ-NC was observed by decrease of the concentration of BR-111 within the adsorption medium with contact time. The time necessary to reach the equilibrium for the removal of the BR-111 molecules at different concentrations (25 - 125 mg/L) by AZJ-NC from aqueous solution was established to be about 60 minutes. As Figure 2 shows, at all the used concentrations, as the contact time between the adsorbent and the adsorbate increased, the adsorption rate increased, as well. According to Figure 2, the highest rate of BR-111 removal took place during the 15 - 30 minute interval. In the remaining concentrations, this reduction continued up to 45 minutes with a lower slope. From this time up to 60 minutes, the system was almost constant and did not have much adsorption. At 25-125 mg/L of BR-111, the removal rate varied from 44.53% to 92.96% of the maximum removal onto AZJ-NC the values are shown in table 2. The surface of AZJ-NC may contain a large number of active sites and the solute uptake can be related to the active sites on equilibrium time. The higher sorption rate at the initial period (first 45 minutes) may be due to an increased number of vacant sites available at the initial stage. As a result there exists increased concentration gradient between adsorbate in solution and adsorbate in adsorbent surface. This increase in the concentration gradients tends to increase in BR-111 sorption at the initial stages.

3.2 The Effect of adsorbent dose

The adsorption of the BR-111 dye on AZJ-NC was studied by varying the adsorbent dose (25–125 mg/50ml) for 50 mg/L of dye concentration. The percentage of adsorption increased with increases in the AZJ-NC dose, which is attributed to increased carbon surface area and the availability of more adsorption sites [6, 7]. Hence, all studies were carried out with 0.025g of adsorbent/50 ml of the varying adsorbate solutions.25, 50, 75, 100 and 125 mg/L. The results obtained from this study are shown in figure 3. The amount of Rh-B adsorbed per gram reduced with increase in the dosage of AZJ-NC. This reveals that the direct and equilibrium capacities of BR-111 are functions of the activated AZJ-NC dosage. [22].

3.3The Effect of pH

Solution pH affects both aqueous chemistry and surface binding sites of the adsorbents. The effect of initial pH on adsorption of BR-111 was studied from pH 2 to 9 at initial BR-111 dye concentration of 25 mg/L, adsorbent dosage of 0.025 g and contact time of 60 min. Two possible mechanisms of adsorption of BR-111 dye on the AZJ-NC adsorbent may be considered include: (a) electrostatic interaction between the adsorbent and the BR-111 molecule, (b) a chemical reaction between the BR-111 and the adsorbent. When pH increases, the concentration of OH^- ions in the desired solution is increased, as well. This causes the surface of the AZJ-NC to become deprotonated and, as a result, the negative charge of the used AZJ-NC surface will be amplified. Therefore, the electrostatic attractive force between the BR-111 dye, which has a positive charge, and the adsorbent surface increases, and consequently, the rate of dye adsorption increases, as well [20] as Figure 4 depicts, as the pH of the solution increased from 2 to 9, the rate of removal also increased up to pH 6.5 then decrease.

3.4 Adsorption Isotherms

It is important to determine the most appropriate correlation for equilibrium adsorption isotherm, to optimize the design of a sorption system. The Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Hurkins-Jura, Halsay, Radlich-Peterson, Jovanovic and BET isotherm models were used to analyses the adsorption

equilibrium. Experimental isotherm data were obtained at an adsorption time of 60 min at different temperatures.

3.4.1 Freundlich adsorption isotherm

The Freundlich adsorption isotherm is based on the equilibrium sorption on heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to heat of adsorption. The adsorption isotherm is expressed by the following equation

$$q_e = K_F C_e^{1/nF} \quad \text{.....(3)}$$

Which, can be linearized as

$$\ln q_e = \ln K_F + \frac{1}{nF} \ln C_e \text{.....(4)}$$

Where, q_e is the amount of BR-111 dye adsorbed at equilibrium (mg/g) and C_e is the concentration of BR-111 dye in the aqueous phase at equilibrium (ppm). K_F (L/g) and $1/n_F$ are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

The Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$ Vs $\ln C_e$ plot, and the model parameters are shown in Table 3. The magnitude of K_F showed that AZJ-NC had a high capacity for BR-111 dye adsorption from the aqueous solutions studied. The Freundlich exponent, n_F, should have values in the range of 1 and 10 (i.e., $1/n_F < 1$) to be considered as favorable adsorption [23]. A $1/n_F$ value of less than 1 indicated that BR-111 dye is favorably adsorbed by AZJ-NC. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.

3.4.2 Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the assumption that all sorption sites possess equal affinity to the adsorbate. The Langmuir isotherm in a linear form can be represented as [23]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \text{.....(5)}$$

Where, q_e is the amount of BR-111 dye adsorbed at equilibrium (mg/g), C_e is the concentration of BR-111 in the aqueous phase at equilibrium (ppm), q_m is the maximum BR-111 dye uptake (mg/g), and K_L is the Langmuir constant related to adsorption capacity and the energy of adsorption (g/mg).

A linear plot of C_e/q_e Vs C_e was employed to determine the value of q_m and K_L, and the data so obtained were also presented in Table 3. The model predicted a maximum value that could not be reached in the experiments. The value of K_L decreased with an increase in the temperature. A high K_L value indicates a high adsorption affinity. The monolayer saturation capacity, q_m, is shown in table 3. Weber and Chakraborti [24] expressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) defined in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{.....(6)}$$

Where, C_0 is the initial BR-111 dye concentration (ppm). Four scenarios can be distinguished:

The sorption isotherm is unfavorable when $R_L > 1$, the isotherm is linear when $R_L = 1$, The isotherm is favorable when $0 < R_L < 1$ and the isotherm is irreversible when $R_L = 0$. The values of dimensionless separation factor (R_L) for BR-111 dye removal were calculated at different concentrations and temperatures. At all concentrations and temperatures tested the values of R_L for BR-111 dye adsorptions on the AZJ-NC were less than 1 and greater than zero, indicating favorable adsorption. The calculated value as shown in table 4.

The Langmuir isotherm showed a better fit to the adsorption data than the Freundlich isotherm. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the AZJ-NC surface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

3.4.3 Temkin adsorption isotherm

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions [25]. The Temkin isotherm equation is given as:

$$q_e = \frac{RT}{bT} \ln(K_T C_e) \text{.....(7)}$$

Which, can be represented in the following linear form

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \text{.....(8)}$$

Where, K_T (L/g) is the Temkin isotherm constant, b_T (J/mol) is a constant related to heat of sorption, R is the ideal gas constant (8.314 J/mol K), and T is absolute temperature (K). A plot of q_e versus $\ln C_e$ enables the determination of isotherm constants K_T and b_T from the slope and intercept, The model parameters are listed in Table 3. The Temkin isotherm appears to provide a good fit to the BR-111 dye adsorption data.

The adsorption energy in the Temkin model, b_T, is positive for BR-111 dye adsorption from the aqueous solution, which indicates that the adsorption is endothermic. The experimental equilibrium curve is close to that predicted by Temkin model. Consequently, the adsorption isotherm of BR-111 dye on AZJ-NC can be described reasonably well by the Temkin isotherm.

3.4.4 Hurkins-Jura adsorption isotherm

The Hurkins-Jura adsorption isotherm can be expressed as [26]:

$$q_e = \sqrt{\frac{A_H}{B_H + \log C_e}} \text{.....(9)}$$

This can rearranged as follows:

$$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H} \log C_e \text{.....(10)}$$

Where, A_H (g^2/L) and B_H (mg^2/L) are two parameters characterizing the sorption equilibrium.

The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution. The Harkins–Jura isotherm parameters are obtained from the plots of of $1/q_e^2$ versus log C_e enables the determination of model parameters A_H and B_H from the slope and intercept.

3.4.5 Halsay adsorption isotherm

The Halsay adsorption isotherm can be given as [27]:

$$q_e = \exp\left(\frac{\ln K_{Ha} - \ln C_e}{n_{Ha}}\right) \text{.....(11)}$$

And, a linear form of the isotherm can be expressed as follows:

$$\ln q_e = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_e}{n_{Ha}} \text{.....(12)}$$

Where, K_{Ha} (mg/L) and n_{Ha} are the Halsay isotherm constants.

A plot of $\ln q_e$ Vs $\ln C_e$, enables the determination of n_{Ha} and K_{Ha} from the slope and intercept. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of adsorbent. The experimental

data and the model predictions based on the non-linear form of the Halsay models. The model parameters are listed in Table 3. This result also shows that the adsorption of BR-111 dye on AZJ-NC was not based on significant multilayer adsorption. The Halsay model is also not suitable to describe the adsorption of BR-111 dye on AZJ-NC, because this model also assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent.

3.4.6 Radlich-Peterson adsorption isotherm

The Radlich-Peterson adsorption isotherm contains three parameters and incorporates the features of Langmuir and Freundlich isotherms into a single equation. The general isotherm equation can be described as follows [28]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad \text{.....(13)}$$

The linear form of the isotherm can be expressed as follows:

$$\ln \frac{C_e}{q_e} = g \ln C_e - \ln K_R \quad \text{.....(14)}$$

Where, K_R (L/g) and a_R (L/mg) are the Radlich-Peterson isotherm constants and g is the exponent between 0 and 1. There are two limiting cases: Langmuir form for g = 1 and Henry's law for g = 0.

A plot of ln C_e/q_e versus ln C_e enables the determination of isotherm constants g and K_R from the slope and intercept. The values of K_R, presented in Table 3, indicate that the adsorption capacity of the AZJ-NC decreased with an increase temperature. Furthermore, the value of g lies between 0 and 1, indicating favorable adsorption.

3.4.7 Dubinin-Radushkevich adsorption isotherm

The Dubinin-Radushkevich adsorption isotherm is another isotherm equation [32]. It is assumed that the characteristic of the sorption curve is related to the porosity of the adsorbent. The linear form of the isotherm can be expressed as follows [29]:

$$\ln q_e = \ln Q_D - B_D \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2 \quad \text{.....(15)}$$

Where, Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol^2/kJ^2). A plot of $\ln q_e$ Vs $R_t \ln(1+1/C_e)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept.

3.4.8 Jovanovic adsorption isotherm

The model of an adsorption surface considered by Jovanovic [30] is essentially the same as that considered by Langmuir. The Jovanovic model leads to the following relationship [29]:

$$q_e = q_{max}\left(1 - e^{K_J C_e}\right)$$

The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln q_{max} - K_J C_e$$

Where, K_J (L/g) is a parameter. q_{max} (mg/g) is the maximum Copper (II) uptake.

The q_{max} is obtained from a plot of ln q_e and C_e. Their related parameters are listed in Table 3.

By comparing the values of the error functions, it was found the Langmuir and Temkin models are best to fit the BR-111 adsorption on the AASCA. Both models show a high degree of correlation. This is clearly confirming the good fit of Langmuir and Temkin models with the experimental data for removal of BR-111 dye from the solution.

3.4.9 The Brunauer–Emmett–Teller (BET) isotherm model

Brunauer–Emmett–Teller (BET) [31] isotherm is a theoretical equation, most widely applied in the gas–solid equilibrium systems. It was developed to derive multilayer adsorption systems with relative pressure ranges from 0.05 to 0.30 corresponding to a monolayer coverage lying between 0.50 and 1.50. Its extinction model related to liquid–solid interface is exhibited as:

$$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)(C_e/C_s)]} \quad \text{.....(16)}$$

Where, CBET, Cs, qs and qe are the BET adsorption isotherm (L/mg), adsorbate monolayer saturation concentration (mg/L), theoretical isotherm saturation capacity (mg/g) and equilibrium adsorption capacity (mg/g), respectively. As C_{BET} and C_{BET} (C_e/C_s) is much greater than 1,

In the linear form as used is represented as;

$$\frac{C_e}{q(C_s - C_e)} = \frac{1}{q_s C_{BET}} + \left(\frac{C_{BET} - 1}{q_s C_{BET}}\right)\left(\frac{C_e}{C_s}\right) \quad \text{.....(17)}$$

Where, C_e is equilibrium Concentration (mg/l), C_s is adsorbate monolayer saturation concentration (mg/l) and C_{BET} is BET adsorption relating to the energy of surface interaction (l/mg).

3.5 Adsorption Kinetics

The rate and mechanism of the adsorption process can be elucidated based on kinetic studies. Dye adsorption on solid surface may be explained by two distinct mechanisms: (1) An initial rapid binding of dye molecules on the adsorbent surface; (2) relatively slow intra-particle diffusion. To analyze the adsorption kinetics of the dye, the pseudo-first-order, the pseudo-second-order, and intra-particle diffusion models were applied [32]. Each of these models and their linear modes of them equations presented in below.

Kinetic Models and Their Linear Forms

Model	Nonlinear Form	Linear Form	Number of Equation
Pseudo-first-order	$dq_t/d_t = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	(18)
Pseudo-second-order	$dq_t/d_t = k_2(q_e - q_t)^2$	$t/q_t = \frac{1}{k^2 q_e^2 + (1/q_e)t}$	(19)

Pseudo-second-orde (19)

Where, q_e and q_t refer to the amount of BR-111 dye adsorbed (mg/g) at equilibrium and at any time, t (min), respectively and k_1 (1/min), k_2 (g/mg.min) are the equilibrium rate constants of pseudo-first order and pseudo-second order models, respectively. Pseudo-first order model is a simple kinetic model, which was proposed by Lagergren [33] during 1898 and is used for estimation of the surface adsorption reaction rate. The values of ln (q_e - q_t) were linearly correlated with t. The plot of ln (q_e - q_t) Vs t should give a linear relationship from which the values of k_1 were determined from the slope of the plot. In many cases, the first-order equation of Lagergren does not fit well with the entire range of contact time and is generally applicable over the initial stage of the adsorption processes [34].

In the pseudo-second order model [35], the slope and intercept of the t/q_t Vs t plot were used to calculate the second-order rate constant, k_2. The values of equilibrium rate constant (k_2) are presented in Table 6. According to Table 6, the value of R^2 (0.999) related to the pseudo-second order model revealed that BR-111 dye adsorption followed this model, which is in agreement with the results obtained by Karagoz et al. [36] and Hameed et al. [37], Nevertheless, pseudo-first order and pseudo-second order kinetic models cannot identify the mechanism of diffusion of dye into the adsorbent pores.

3.5.1 Error analysis

The traditional methods of determining the isotherm parameters by linear regression appear to give a good fit to experimental data. However, the R^2 is based on the linear forms of the isotherm equations, but does not represent the errors in the isotherm curves. To evaluate the fit of the isotherm equations to the experimental data, different error functions of non-linear regression were used here to determine the constants model parameters, and they were

compared with those determined from the less accurate linearized data fitting. The Sum of Square Error (SSE) and chi-square test were used. SSE can be defined as [36, 37]

$$SSE=\sqrt{\Sigma\left(q_{e,exp}-q_{e,cal}\right)^2/N} \quad \text{.....(20)}$$

Where, $q_{e,cal}$ is the amount of sorbate adsorbed at equilibrium calculated from the model (mg g^{-1}), $q_{e,exp}$ is the equilibrium value obtained from experiment (mg g^{-1}) and N is the number of data points.

The chi-square test (χ^2) is basically the sum of the squared error of the differences between the experimental data and data obtained by calculating using the models, with each squared difference divided by the corresponding data obtained by calculating from models. This can be represented by Equation 20 [17]. If experimental data is fitted to the model, χ^2 should give a small number [18].

Nonlinear chi-square test (χ^2)

$$\chi^2=\Sigma\frac{\left(q_{e,cal}-q_e\right)^2}{q_{e,Cal}} \quad \text{.....(21)}$$

Nonlinear chi-square test is a statistical tool necessary for the best fit of an adsorption system, obtained by judging the sum squares differences between the experimental and the calculated data, with each squared difference is divided by its corresponding value (calculated from the models). Small χ^2 value indicates its similarities while a larger number represents the variation of the experimental data.

$$\chi^2=\Sigma\frac{\left(q_{e,cal}-q_e\right)^2}{q_{e,Cal}} \quad \text{.....(22)}$$

3.5.2 Simple Elovich Model

The simple Elovich model is expressed in the form,

$$q_t=\alpha+\beta \ln t \quad \text{.....(23)}$$

Where, q_t is the amount adsorbed at time t, α and β are the constants obtained from the experiment. A plot of q_t against ln t should give a linear relationship for the applicability of the simple Elovich kinetic model. The figure shows the simple Elovich kinetics of BR-111 dye on to AZJ-NC for various initial concentrations (25, 50, 75, 100 and 125 mg/L) of volume 50 mL (each), adsorbent dose 0.025g, temperature 30 °C and pH 6.5. Their related parameters are listed in Table 6.

3.5.3 Intra-Particle Diffusion Model

The adsorption process on a porous adsorbent is generally a multi-step process. In order to analyse the mechanism of the adsorption of BR-111 dye by AZJ-NC, the experimental data were tested against the intra-particle diffusion model. The adsorption mechanism of the adsorbate on to the adsorbent follows three consecutive steps: mass transfer across the external film of liquid surrounding the particle, adsorption at the surface of pores and the intra-particle diffusion. The slowest of these steps determines the overall rate of the process. The possibility of intraparticle diffusion resistance which could affect the adsorption is explored by using the intra-particle diffusion model given in the equation,

$$q_t=K\,t^{1/2}+I \quad \text{.....(24)}$$

Where, K is the intra-particle diffusion rate constant and I is the intercept. A plot of q_t against $t^{1/2}$ is drawn to analyse the possibility of intra-particle diffusion as the rate determining step. A two stage adsorption mechanism with first was rapid and second was slow has been observed from the experimental data. The plot of q_t against $t^{1/2}$ is multi-linear and deviating from the origin, indicating more than one process has affected the adsorption [18]. Hence, the first portion of the plot indicates the external mass transfer and the second portion is due to intra-particle or pore diffusion.

3.6 Thermodynamic treatment of the sorption process

In order to study the feasibility of the adsorption process, the thermodynamic parameters such as free energy, enthalpy and entropy changes can be estimated from the following equations.

$$K_c=C_{Ae}/C_e \quad \text{..... (25)}$$

$$\Delta G^0=-RT \ln K_c \quad \text{..... (26)}$$

$$\text{Log } K_c=\Delta S^0/2.303R-\Delta H^0/2.303RT \quad \text{..... (27)}$$

Where C_e is the equilibrium concentration in solution in mg/L and C_{Ae} is the equilibrium concentration on the sorbent in mg/L and K_c is the equilibrium constant. The Gibbs free energy (ΔG^0) for the adsorption of BR-111 onto biomass at all temperatures was obtained from Eq.26 and is presented in Table 5. The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot log K_c against 1/T. Their related parameters are also listed in Table 5.

In order to support that physical adsorption is the predominant mechanism, the values of activation energy (Ea) and sticking probability (S*) were calculated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows:

$$\theta=\left(1-\frac{C_e}{C_i}\right) \quad \text{..... (28)}$$

$$S^*=(1-\theta)_e\,\frac{-E_a}{RT} \quad \text{..... (29)}$$

The sticking probability, S*, is a function of the adsorbate/adsorbent system under consideration but must satisfy the condition $0 < S^* < 1$ and is dependent on the temperature of the system. The values of Ea and S* can be calculated from slope and intercept of the plot of ln(1-θ) versus 1/T respectively and are listed in Table 5.

From Table 5 it is clear that the reaction is spontaneous in nature as ΔG^0 values are negative at all the temperature studied. Again positive ΔH^0 value confirms that the sorption is endothermic in nature. The positive value of ΔS^0reflects the affinities of the adsorbents for the BR-111 dye. The result as shown in Table 5 indicate that the probability of the BR-111 dye to stick on surface of biomass is very high as $S^* << 1$, these values confirm that, the sorption process is physisorption.

3.7 Evidence of Adsorption

The FT-IR spectra of the raw AZJ-NC carbon and after adsorption of BR-111 dyes have shown in Figure 14a and 14b. It could be seen that the slight reduction of stretching vibration adsorption bands. This clearly indicates the adsorption of BR-111 dyes on the adsorbent by physical forces not by chemical combination. The XRD diagrams of AZJ-NC carbon and BR-111 dyes -adsorbed carbon have shown in Figure 15a and 15b. The intense main peak shows the presence of highly organized crystalline structure of raw AZJ-NC carbon, after the adsorption of BR-111 dyes, the intensity of the highly organized peaks is slightly diminished. This has attributed to the adsorption of BR-111 dyes on the upper layer of the crystalline structure of the carbon surface by means of physisorption.

4. Discussion

The present study investigated the efficiency of AZJ-NC as a cheap adsorbent and the results revealed that AZJ-NC was an appropriate adsorbent for removing BR-111 from the aquatic environments. pH also plays a major role in removing the BR-111. The findings of the present study also showed that as the contact time increased, the dye's primary concentration as well as the dose of the intended adsorbate of the adsorption efficiency increased, as well. Adsorption equilibrium data follows Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Hurkins-Jura, Halsay, Radlich-Peterson, Jovanovic and BET isotherm models. The equilibrium data fitted very well in the Langmuir and BET isotherm equation. The kinetic

study of BR-111 on to AZJ-NC was performed based on pseudo-first-order, pseudo-second-order and intra-particle diffusion equations. The data indicate that the adsorption kinetics follow the pseudo-second-order rate. This study concludes that the AZJ-NC could be employed as an appropriate, inexpensive, accessible and low-cost adsorbent for the removal of BR-111 from aquatic environments.

Author's Contribution

The overall implementation of this study including design, experiments and data analysis, and manuscript preparation was the results of joint efforts by individuals who are listed as coauthors of this paper. All authors have made extensive contributions to the review and finalization of this manuscript.

Funding/Support

The project has been supported financially by the University Grants Commission, New Delhi for providing the fund from Major Research Project.

TABLE: 3. EQUILIBRIUM PARAMETERS FOR THE ADSORPTION OF BR-111 DYE ONTO AZJ-NC

M_0	C_e (Mg / L)				Q_e (Mg / L)				Removal %			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
25	1.92 31	1.15 38	0.77 02	0.73 08	46.1 53	47.6 92	48.4 59	48.5 38	92.3 07	95.3 84	96.9 19	97.0 76
50	4.23 08	3.84 79	3.47 77	2.69 32	91.5 38	92.3 04	93.0 44	94.6 13	91.5 38	92.3 04	93.0 44	94.6 13
75	9.26 25	8.38 62	7.30 78	6.77 09	131. 47	133. 22	135. 38	136. 45	87.6 50	88.8 18	90.2 56	90.9 72
100	13.4 93	12.3 40	11.7 05	10.9 79	173. 01	175. 31	176. 58	178. 04	86.5 06	87.6 59	88.2 94	89.0 20
125	20.0 00	19.3 06	18.8 80	17.7 59	210. 00	211. 38	212. 23	214. 48	84.0 00	84.5 55	84.8 95	85.7 92

TABLE: 4. LANGMUIR AND FREUNDLICH ISOTHERM PARAMETER FOR THE ADSORPTION OF BR-111 DYE ONTO AZJ-NC

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_f (mg/g) (L/mg)$^{1/n}$	32.784	44.407	53.831	57.312
	n	1.5800	1.8800	2.1335	2.1507
Langmuir	Q_m (mg/g)	328.71	281.55	262.11	258.54
	b (L/mg)	0.0832	0.1359	0.1875	0.2222
Temkin	b_T (J/mol)	68.118	57.243	50.597	51.038
	K_T (L/mg)	0.8803	1.8477	2.4900	2.7143
Hurkins-Jura	A_H (g^2/L)	-2425.5	-2936.6	-3375.0	-3500.2
	B_H (mg^2/L)	-1.2025	-1.1820	-1.1660	-1.1331
Halsay	K_{Ha} (mg/L)	248.26	1251.34	4933.8	6046.7
	n_{Ha}	1.5800	1.8800	2.1335	2.1507
Radlich-Peterson	g	0.3671	0.4681	0.5312	0.5350
	K_R (L/g)	0.0305	0.0225	0.0185	0.0174
Dubinin-Radushkevich	q_s (mg/g)	165.98	156.99	154.63	159.13
	$K_D \times 10^{-4}$ mol^2 kJ^{-2}	1.6344	1.6144	1.6054	1.6107
Jovanovic	K_J (L/g)	0.0760	0.0759	0.0748	0.0778
	q_{max} (mg/g)	54.710	58.943	62.804	64.924
BET	C_{BET} (L/mg)	11.848	21.268	32.662	38.523
	qs (mg/g)	0.0843	0.0470	0.0306	0.0259

TABLE: 5. DIMENSIONLESS SEPERATION FACTOR (R_L) FOR THE ADSORPTION OF BR-111 DYE ONTO AZJ-NC

(C_i)	Temperature C			
	30°C	40°C	50°C	60°C
25	0.3246	0.2272	0.1757	0.1525
50	0.1937	0.1282	0.0963	0.0825
75	0.1380	0.0892	0.0663	0.0566
100	0.1072	0.0685	0.0506	0.0430
125	0.0876	0.0555	0.0409	0.03474

TABLE: 6. THERMODYNAMIC PARAMETER FOR THE ADSORPTION OF BR-111 DYE ONTO AZJ-NC

(C_0)	ΔG°				ΔH°	ΔS°	E_a	S^*
	30°C	40°C	50°C	60°C				
25	-6259.83	-7881.07	-9261.35	-9697.6	-29.380	118.41	27963.2	2×10^{-6}
50	-5998.65	-6465.13	-6964.81	-7934.45	-13.017	62.445	12123.3	5×10^{-5}
75	-4936.76	-5392.76	-5977.84	-6396.05	-10.119	49.671	9046.6	4×10^{-4}
100	-4680.52	-5102.03	-5426.22	-5794.05	-6.4255	36.717	5641.8	3×10^{-3}
125	-4177.31	-4424.2	-4636.26	-4978.39	-3.7254	26.036	3162.6	4×10^{-2}

TABLE: 7. THE KINETIC PARAMETERS FOR THE ADSORPTION OF BR-111 DYE ONTO AZJ-NC

C_0	Temp C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
25	30	49.422	0.0038	0.992	9.5085	43.770	0.1866	0.993	0.1276	0.999	1.7321
	40	49.436	0.0074	0.992	18.129	120.66	0.3111	0.996	0.0710	0.995	1.8493
	50	49.564	0.0117	0.990	28.927	153.70	0.4661	0.997	0.0458	0.994	1.9024
	60	49.581	0.0124	0.992	30.676	967.44	0.4912	0.991	0.0433	0.995	1.9077
50	30	95.842	0.0027	0.993	25.336	257.28	0.1301	0.993	0.0900	0.991	1.7939
	40	96.363	0.0030	0.991	27.947	189.6.8	0.1363	0.994	0.0848	0.995	1.8081
	50	97.026	0.0033	0.991	31.691	423.13	0.1429	0.993	0.0796	0.994	1.8237
	60	97.955	0.0036	0.992	35.381	105.97	0.1577	0.994	0.0707	0.996	1.8453
75	30	135.56	0.0027	0.993	51.169	110.89	0.1297	0.995	0.0615	0.997	1.8264
	40	138.18	0.0030	0.994	57.995	142.92	0.1193	0.991	0.0656	0.998	1.8312
	50	141.10	0.0026	0.995	52.094	458.09	0.1024	0.993	0.0759	0.992	1.8202
	60	140.83	0.0036	0.996	72.474	913.59	0.1206	0.996	0.0634	0.993	1.8482
100	30	179.14	0.0027	0.990	88.502	103.98	0.0885	0.997	0.0682	0.993	1.8191
	40	181.41	0.0025	0.991	85.078	108.67	0.0868	0.992	0.0688	0.992	1.8223
	50	182.40	0.0027	0.994	91.303	125.46	0.0889	0.992	0.0665	0.992	1.8301
	60	183.97	0.0027	0.995	92.534	123.16	0.0890	0.996	0.0659	0.990	1.8347
125	30	216.55	0.0016	0.996	77.278	737.21	0.0759	0.999	0.0665	0.992	1.7983
	40	218.14	0.0016	0.997	77.020	115.51	0.0744	0.992	0.0671	0.993	1.8001
	50	218.55	0.0017	0.998	82.086	114.51	0.0787	0.993	0.0629	0.991	1.8096
	60	221.13	0.0015	0.999	77.589	114.06	0.0736	0.991	0.0669	0.991	1.8063

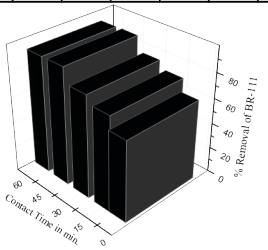
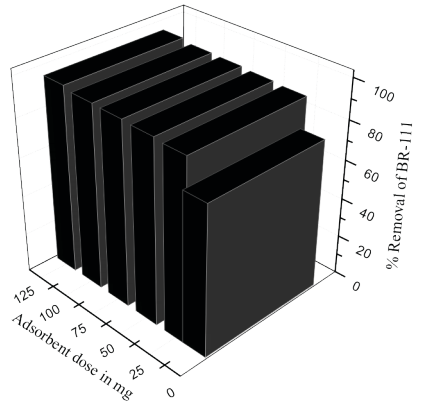
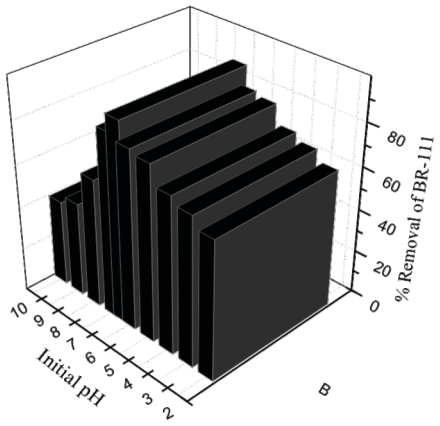


Fig:2- Effect of Contact Time on the Removal of BR-111 Dye
[BR-111]=50 mg/L; Temprature=30°C; Adsorbent dose=0.025g/50ml



Fig;3- Effect of Adsorbent dose on the removal of BR-111 Dye
[BR-111]=50mg/L;Contact Time 45 min;Temprature 30^{0}C



Fig;4- Effect of Initial pH on the removal of BR-111 Dye
[BR-111]=50 mg/L;Temprature 30^{0}C;Adsorbent dose=0.025g/50ml

References:

1. Sapci Z, Ustun B. The removal of color and COD from textile wastewater by using waste pumice. Elec J Environ Agric Food Chem. 2003; 2(2):286–90.
2. Samarghandi MR, Zarrabi M, Sepehr MN, Amrane A, Safari GH, Bashiri S. Application of acidic treated pumice as an adsorbent for the removal of azo dye from aqueous solutions: kinetic, equilibrium and thermodynamic studies. Iranian J Environ Health Sci Eng. 2012;9(1):9.
3. Iqbal MJ, Ashiq MN. Adsorption of dyes from aqueous solutions on activated charcoal. J Hazard Mater. 2007;139 (1):57–66.
4. Yang J, Qiu K. Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for Basic Red 111 removal. Chem Eng J. 2010;165 (1):209–17.
5. Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol. 2001;77(3):247–55.
6. Santhy K, Selvapathy P. Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon. Bioresour Technol. 2006;97(11):1329–36.
7. McKay G, Porter JF, Prasad GR. The removal of dye colours from aqueous solutions by adsorption on low-cost materials. Water Air Soil Pollut. 1999;114(3-4):423–38.
8. Doğan M, Alkan M, Onganer Y. Adsorption of Basic Red 111 from aqueous solution onto perlite. Water Air Soil Pollut. 2000;120(3-4):229–48.
9. Bereket G, Aro AZ, ozel MZ. Removal of Pb(II), Cd(II), Cu(II), and Zn(II) from Aqueous Solutions by Adsorption on Bentonite. J Colloid Interface Sci. 1997;187(2):338–43.
10. Mohamed MM. Adsorption properties of ionic surfactants on molybdenum-modified silica gels. Colloids Surf A: Physicochem Eng Aspect. 1996;108(1):39–48.
11. Mohan D, Singh KP, Singh G, Kumar K. Removal of dyes from wastewater using flyash, a low-cost adsorbent. Indust Eng chem Res. 2002;41(15):3688–95.
12. Ho Y, McKay G. Sorption of dye from aqueous solution by peat. Chem Eng J. 1998;70(2):115–24.
13. McKay G, Otterburn MS, Sweeney AG. Surface mass transfer processes during colour removal from effluent using silica. Water Res. 1981;15(3):327–31.
14. Panuccio MR, Sorgona A, Rizzo M, Cacco G. Cadmium adsorption on vermiculite, zeolite and pumice: batch experimental studies. J Environ Manage. 2009;90(1): 364–74.
15. Kaplan Bekaroglu SS, Yigit NO, Karanfil T, Kitis M. The adsorptive removal of disinfection by-product precursors in a high-SUVA water using iron oxide-coated pumice and volcanic slag particles. J Hazard Mater. 2010;183(1-3):389–94.
16. Moraci N, Calabro PS. Heavy metals removal and hydraulic performance in zero-valent iron/pumice permeable reactive barriers. J Environ Manage. 2010;91 (11): 2336–41.
17. Ozturk B, Yildirim Y. Investigation of sorption capacity of pumice for SO 2 capture. Process Safety Environ Protec. 2008;86(1):31–6.
18. Yavuz Ö, Aydin AH. Removal of direct dyes from aqueous solution using various adsorbents. Polish J Environ Studies. 2006;15(1):155– 61.
19. Alkan M, Doğan M. Adsorption of copper (II) onto perlite. J Colloid Interface Sci. 2001;243(2):280–91.
20. Han R, Wang Y, Han P, Shi J, Yang J, Lu Y. Removal of Basic Red 111 from aqueous solution by chaff in batch mode. J Hazard Mater. 2006;137(1):550–7.
21. El Qada EN, Allen SJ, Walker GM. Adsorption of Basic Red 111 onto activated carbon produced from steam activated bituminous coal: a study of equilibrium adsorption isotherm. Chem Eng J. 2006;124(1):103–10.
22. Chen H, Zhao J, Dai G. Silkworm exuviae--a new non-conventional and low-cost adsorbent for removal of Basic Red 111 from aqueous solutions. J Hazard Mater. 2011;186(2-3):1320–7.
23. Karagoz S, Tay T, Ucar S, Erdem M. Activated carbons from waste biomass by sulfuric acid activation and their use on Basic Red 111 adsorption. Bioresour Technol. 2008;99(14):6214–22.
24. Hameed BH, Din AT, Ahmad AL. Adsorption of Basic Red 111 onto bamboo-based activated carbon: kinetics and equilibrium studies. J Hazard Mater. 2007;141 (3): 819–25.
25. Rao GB, Kalyani G, Saradhi BV, Kumar YP. Removal of Fluoride from Aqueous Solution Using a Waste Material. Nature Environ Pollut Tech. 2009;8(2):231–6.
26. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J American Chem Soc. 1918;40(9):1361–403.
27. Abdelwahab O. Evaluation of the use of loofa activated carbons as potential adsorbents for aqueous solutions containing dye. Desal. 2008;222(1):357–67.
28. Ng C, Losso JN, Marshall WE, Rao RM. Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin-water system. Bioresour Technol. 2002;85(2):131–5.
29. Akbal F. Adsorption of basic dyes from aqueous solution onto pumice powder. J Colloid Interface Sci. 2005;286(2):455–8.
30. Asgari G, Roshani B, Ghanizadeh G. The investigation of kinetic and isotherm of fluoride adsorption onto functionalize pumice stone. J Hazard Mater. 2012;217-218:123–32.
31. Mahvi AH, Heibati B, Mesdaghinia A, Yari AR. Fluoride Adsorption by Pumice from Aqueous Solutions. J Chem. 2012;9(4):1843–53.
32. Veliev EV, Ozturk T, Veli S, Fatullayev AG. Application of diffusion model for adsorption of azo reactive dye on pumice. Polish J Environ Studies. 2006;15 (2):347–53.
33. Freundlich H. Über die adsorption in lösungen. Engelmann, Leipzig. 1906;57(A): 385–470.
34. Temkin MJ, Pyzhev V. Recent modifications to Langmuir isotherms. Acta Physiochim USSR. 1940;12:217–22.
35. Dubinin MM, Zaverina ED, Radushkevich LV. Sorption and structure of active carbons. I. Adsorption of organic vapors. Zhurnal Fizicheskoi Khimii. 1947;21: 1351–62.
36. Rieman W, Walton H. Ion Exchange in Analytical Chemistry, International Series of Monographs in Analytical Chemistry. Pergamon Press, Oxford; 1970.
37. Altenor S, Carene B, Emmanuel E, Lambert J, Ehrhardt JJ, Gaspard S. Adsorption studies of Basic Red 111 and phenol onto vetiver roots activated carbon prepared by chemical activation. J Hazard Mater. 2009;165(1-3):1029–39.
38. Çolak F, Atar N, Olgun A. Biosorption of acidic dyes from aqueous solution by Paenibacillus macerans: Kinetic, thermodynamic and equilibrium studies. Chem Eng J. 2009;150(1):122–30.
39. Murugan T, Ganapathi A, Valliappan R. Removal of dyes from aqueous solution by adsorption on biomass of mango (Mangifera indica) leaves. J Chem. 2010;7(3): 669–76.
40. Lagergren S. Zur theorie der sogenannten adsorption geloster stoffe. Kungliga Svenska Vetenskapsakademiens. Handlingar. 1898;24:1–39.