

Research Article

Effectiveness of Alkali-Acid Treatment in Enhancement the Adsorption Capacity for Rice Straw: The Removal of Methylene Blue Dye

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The effectiveness of alkali-acid modification in enhancement the adsorption capacity of rice straw (RS) for removing a basic dye was studied. The obtained adsorbents were characterized by slurry pH, pH_{PZC} , iodine number, methylene blue number, FTIR, and SEM analyses. Adsorption of methylene blue (MB) was described by the Langmuir, Freundlich, Tempkin, and Redlich-Peterson isotherm models. Effects of contact time, initial concentration of MB dye, pH of solution, adsorbent dose, salt concentration of NaCl, and desorbing agents on the removal of MB were reported. Kinetic studies were analyzed using the pseudo-first-order, pseudo-second-order, and the intraparticle diffusion models and were found to follow closely the pseudo-second-order model. Equilibrium data were best represented by the Langmuir and Redlich-Peterson isotherms. The adsorption capacities were varied between 32.6 and 131.5 mg/g for untreated and treated RS samples with NaOH-1M citric acid (ARS-1C), respectively. Adsorption behavior of the ARS-1C sample was experimented in a binary mixture containing methylene blue (basic) and reactive blue 19 (acidic) dyes which showed its ability to remove MB higher than RB19. Overall, the results indicate that the alkali-acid treatment proved to be potential modification for producing effective low-cost adsorbents for the removal of the basic dyes from wastewater.

1. Introduction

Nowadays, industrial societies suffer from two main problems with respect to disposal of colored pollutants in wastewater and agroresidues in environment. Thus, with compliance to the decrease in natural water resources and the increase in water pollution, researchers have urged to find appropriate and environmentally friendly treatment techniques. The main sources of wastewater can be attributed to discharge of toxic industrial wastes, dumping of industrial effluents, and runoff from agriculture fields. It is well known that 70%–80% of all illnesses in developing countries are related to water contamination particularly susceptible for women and children [1]. For instance, wastewater contaminated with dyes comes from a wide range of industries such as textile, paper, tannery, food, chemical, pharmaceutical, and many others. Consequently, environmental regulations demand the removal of dyes before discharging industrial effluents into water bodies due to their mutagenic and carcinogenic

impacts to aquatic living organisms, and its presence of even very small amounts in water (less than 1 ppm) is highly visible and undesirable [2–6]. Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood, and silk. It can cause a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, and methemoglobinemia [7, 8]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters. However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat, and oxidizing agents [9, 10]. Amongst various technologies of dyes removal, adsorption process is widely used and recognized for feasible, inexpensive, and easy operation for the removal of different dyes from wastewater [7–11]. The most explored adsorption is activated carbon which is used to remove dyes from wastewater due to its excellent adsorption ability [10]. However, it is restricted due to its high cost; several researchers have studied

the development of cheaper and more effective adsorbents [2–7, 12, 13].

Recently, agricultural byproducts are economic and eco-friendly adsorbents that make them viable option for wastewater remediation [2, 7]. For example, rice is one of the major crops grown throughout the world. World production of rice has risen steadily from about 200 million tonnes of paddy rice in 1960 to 600 million tonnes in 2004 [2]. Rice crop produces several byproducts, for example, rice straw, rice husk/hull, rice husk/hull ash, and rice bran. In Egypt, approximately 16 million tons of agricultural residues are currently disposed of every year, and the annual amount of rice residues is about 3.6 million tonnes [13]. Rice straw is used as ruminant feed as it is rich in carbohydrates, but its potential as an energy source is limited [13]. Hence, the use of rice straw as low-cost adsorbents is very essential in developing countries. Recently, Gong et al. prepared modified rice straw with phosphoric acid [14] and citric acid without base pretreatment [15, 16] to produce potential adsorbents for the removal of dyes from aqueous solutions. Chakraborty et al. [17] developed NaOH-modified rice husk as low-cost adsorbent for adsorption of crystal violet dye and found that the monolayer adsorption capacity increased to be 44.87 mg/g. They found that the treatment of rice husk with sodium hydroxide breaks the covalent association between lignocellulose components, hydrolyzing hemicellulose, and depolymerizing lignin, and, hence, it enhances the adsorption capacity. Also, treatment with NaOH also removes natural fats and waxes from the cellulose fiber surfaces thus revealing chemically reactive functional groups like –OH [18].

Therefore, from the formentioned literature, the main purpose of this paper was to optimize the effectiveness of alkali-acid modification on rice straw for removing methylene blue dye from single and binary solutions. This study will be of added value in the literature with respect to the preparation procedure. In addition, batch studies were performed to evaluate the effects of various parameters such as pH, contact time, initial dye concentration, adsorbent dose, ionic salt concentration, and desorbing agents on the removal of a basic dye from aqueous solution. Langmuir, Freundlich, Tempkin, and Redlich-Peterson isotherms were used to analyze the equilibrium data. Also, the potential adsorption of cationic and anionic dyes from a binary aqueous was determined.

2. Materials and Methods

All chemical reagents were of analytical grade (AR) and purchased from Merck and Sigma Aldrich companies. These chemicals are citric acid, ethylenediaminetetraacetic acid (EDTA), NaOH and HCl, potassium iodide, sodium thiosulphate, methylene blue (MB), and reactive blue 19 (RB19).

2.1. Adsorbates. All adsorption experiments were carried out using an aqueous solution of MB dye at room temperature and the optimum pH. In binary mixture experiment, the RB19 dye was mixed with an MB dye in aqueous solution in order to explore the feasibility of adsorbent to adsorb two dyes. A methylene blue is a basic blue 19 of a thiazine type

($C_{16}H_{18}N_3SCl$, C. I. No. 52015, MW = 319.19 g/mol, molecular diameter = 0.8 nm, λ_{max} = 664 nm) and a reactive blue 19 dye is a Remazol Brilliant Blue ($C_{22}H_{16}O_{11}N_2S_3Na_2$, C. I. No. 61200, MW = 626.5 g/mol, λ_{max} = 592 nm). The dye stock solution was prepared by dissolving accurately weighted dye in distilled water to the concentration of 500 mg/L. The initial concentrations of dye solution were done by diluting the dye stock solutions in appropriate proportions to different initial concentrations.

2.2. Adsorbents. A novel procedure was employed to prepare low-cost adsorbents from rice straw. This byproduct was collected from a local rice field and washed thoroughly with a hot water followed by soaking in 1 L of 0.1 M HCl solution for 48 h then rinsed with distilled water and dried at 50°C overnight. The dried rice straw was ground and placed in 4 L of 0.2 M NaOH with stirring at 150 rpm for 2 h and then left overnight at room temperature (35°C ± 2). The alkali-treated rice straw (ARS) was rinsed for several times with distilled water until the pH ~6, and then dried at 80°C for several hours until constant mass is obtained. The treated alkali rice straw was then subjected to esterification with organic acids (citric acid and/or EDTA). Five adsorbents were prepared as NaOH-citric acid and/or -EDTA from rice straw followed by heating at 150°C for 4 h to ensure that esterification process is completely obtained.

Briefly, ARS was mixed with two concentrations (0.5 M and 1 M) of citric acid (C) in a ratio of 1 g husks to 7 mL citric acid with stirring for 30 min in order to ensure that husks had completely imbedded the liquid as described earlier by Marshall et al. [19]. These samples were dried and labeled as ARS-0.5C and ARS-1C. The EDTA (E) treatment was performed to ARS and citric acid modified rice husks, in order to study the chemical changes on their surfaces which would affect on their adsorption capacities. A low concentration of EDTA solution (1.34×10^{-4} M) was prepared in 100 mL of 0.1 M NaOH. The EDTA solution mixed with the previous samples under stirring for 1 h then rinsed with distilled water and dried overnight at 50°C. The modified samples were labeled as ARS-E, ARS-0.5C-E, and ARS-1C-E. The produced adsorbents were thoroughly washed with a hot water and distilled water to remove excess of organic acids completely. This can be confirmed by 10 mL of 0.1 M lead nitrate into the liquid, and no turbidity was observed from the mixture. Finally, the produced modified RS samples were dried overnight at 50°C and then kept in glass bottles for further use.

2.3. Characteristics of Adsorbents. Some physicochemical characteristics were run for the obtained adsorbents as shown in Table 1. Slurry pH and point of zero charge (pH_{PZC}) were measured according to the following procedure. (i) For pH, 0.1 g of the dry, grinded adsorbent was mixed with 25 mL of distilled water and allowed to boiling for 30 min in stoppered glass bottle. After cooling, the slurry pH of the adsorbents was measured using a digital pH meter (HANNA, Model HI1110), allowing 5 min for the pH probe to equilibrate, while for (ii) the point of zero charge (pH_{PZC}), 200 mL of deionized

TABLE I: Physicochemical characteristics of the native rice straw and their modified rice straw adsorbents.

Characteristics	RS	ARS	ARS-0.5C-E	ARS-1C-E	ARS-0.5C	ARS-1C	ARS-E
Slurry pH	4.65	6.50	7.86	7.92	5.21	5.55	7.85
pH _{ZPC}	4.68	6.33	7.09	7.29	4.22	4.52	7.75
Bulk density (g/cm ³)	0.3989	0.3605	0.2949	0.3440	0.3861	0.3713	0.2601
Moisture, %	1.008	0.1834	0.0202	0.0064	0.0082	0.0131	0.0252
Methylene blue number (mg/g)	28.9	55.2	72.0	61.0	80.0	116.0	102.0
Iodine number (mg/g)	56.8	243.8	284.8	308.4	244.9	311.3	261.9

water was added to an Erlenmeyer flask, which was then capped with stoppered glass. The deionized water was heated until boiling for 20 min to eliminate the CO₂ dissolved in the water. The CO₂-free water was cooled down as soon as possible and the flask was immediately capped. On the other hand, 0.5 g of each sample was weighed and placed in a 25 mL Erlenmeyer flask to which 20 mL of CO₂-free water was added. The flask was sealed with a rubber stopper and left in continuous agitation for 72 h at room temperature. Then, the solution pH was measured and this value is the point of zero charge. This method has been reported by Leon y Leon and Radovic [20]. The bulk density was estimated by a standard procedure by weighing a known volume of gently tapped adsorbent granules. The apparent density was calculated from the volume of the graduated cylinder closely packed with the powdered sample and from the sample weight in triplicate. For moisture measurement, about 0.5 g of powdered air-dried adsorbent sample was weighed and taken in a crucible. The crucible was placed inside an electric hot-air oven and heated at 150°C for 3 hour. It was then taken out, cooled in a desiccator and weighed. From this, the percentage of moisture can be calculated as follows: *Percentage of moisture* = *(loss in weight of adsorbent/weight of air dried adsorbent taken)* × 100.

Iodine and methylene blue numbers were performed to determine the capability of prepared adsorbents in removing dyes from aqueous media according to NORIT [21]. The surface morphology of the developed samples was characterized by scanning electron microscopy (SEM-JEOL, JXA-840A Electron Probe Micro-Analyzer, Japan). The oxygen-containing functional groups presented in these samples were characterized qualitatively by a Fourier transform infrared spectroscopy (FTIR-6100 JASCO) in the range 4000–400 cm⁻¹.

2.4. Adsorption Studies. All batch adsorption experiments were performed in conical flasks stirred on a shaker (150 rpm) at 35°C ± 2. Adsorption isotherm experiments were carried out by shaking 0.15 g of adsorbents in 25 mL of methylene blue solutions with initial concentrations ranging from 20 to 200 mg/L (at pH 6), shaking for 2 h to ensure equilibrium adsorption and then kept overnight at room temperature. Kinetic experiments were conducted by using 0.15 g of adsorbent and employing 20–100 mg/L of MB dye concentration. The mixture was magnetically stirred at 35°C for 2 h to ensure equilibrium is attained, and suitable aliquots were drawn at different intervals of time (5–90 min).

The effects of contact time (5–90 min), initial concentration of dye (20–100 mg/L), solution pH (2–10), adsorbents dose (0.05–0.2 g), and salt concentration of NaCl (0.01–0.2 M) on the adsorption of MB were studied with an initial concentration 100 mg/L of MB dye. The pH value was adjusted by 0.1 M HCL or NaOH solution. Also, a binary mixture of cationic MB and anionic reactive blue 19 dye with initial concentration (10–100 mg/L) conducted with 0.15 g of adsorbent (ARS-1C), which had the highest adsorption capacity (135.1 mg/g) towards MB in a single system, was examined.

For all the previously mentioned batch studies, the mixture of adsorbent and dye solution in a single or a binary system was magnetically stirred at 150 rpm for 2 h as determined from kinetic testes. Absorbance measurements were performed on MB and RB19 dye solutions at λ_{max} = 664 and 592 nm, respectively, using a UV-Vis spectrophotometer (2401 PC Shimadzu model, Germany) to measure the residual concentration of dye solutions and diluted as required to obtain absorbance within the linear calibration range. The amount of dye adsorbed per unit adsorbent (mg dye/g adsorbent) was calculated according to a mass balance on the dye concentration using

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where C₀ and C_e are the initial and equilibrium liquid-phase concentrations of dye in aqueous solution (mg/L), respectively, V the volume of the solution (L), and m is the mass of the adsorbent used (g).

The removal efficiency (% R_E) of the dye was calculated using the following equation:

$$\% R_E = \frac{(C_0 - C_e)100}{C_0}. \quad (2)$$

In order to ensure the reproducibility of the obtained results, all the adsorption experiments were performed in triplicate and the average values were used in data analysis. Relative standard deviations were found to be ±3%. Linear regression analysis (R²) was applied to determine the best fitted isotherm model with experimental data obtained in this study.

2.5. Adsorption Isotherm Models. The adsorption isotherm shows the equilibrium relationship of concentration in the adsorbate-adsorbent system at constant temperature [22–24].

The shape of the equilibrium adsorption isotherm provides us information about the adsorbent surface, whether it is homogeneous or heterogeneous, and its study is helpful in evaluating the maximum adsorption capacity of adsorbate for the given adsorbent [24]. Four adsorption isotherms models: Langmuir, Freundlich, Tempkin, and Redlich-Peterson isotherms, were used in this work. They differ in their assumption, shape of the isotherm, and nature of the adsorbent surface [25].

2.5.1. Langmuir Isotherm Model. It assumes that adsorption occurs on a homogeneous surface containing sites with equal energy and that are equally available for adsorption. This model can be described by the linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e, \quad (3)$$

where Q_m is the maximum adsorption capacity (mg/g), and K_L is the Langmuir constant (g/L). A linear plot of C_e/q_e versus C_e confirms the validity of the Langmuir giving correlation coefficients (R^2) close to unity, and K_L is a constant related to the free energy of adsorption as expressed ($K_L \propto e^{-\Delta G/RT}$). The free energy of adsorption ΔG can also be evaluated from the parameter K_L according to the expression $\Delta G = -RT \ln K_L$. Values of Q_m and K_L are obtained from slope and intercept of C_e/q_e versus C_e plot, respectively.

Also, the influence of the isotherm shape on whether the adsorption is "favorable" or "unfavorable" at highest initial concentration of the dye, C_0 , can be described by a term " R_L ", a dimensionless constant separation factor in equation:

$$R_L = \frac{1}{1 + K_L C_0}. \quad (4)$$

The calculated value for R_L indicates the nature of adsorption process as given: irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), and unfavorable ($R_L > 1$).

2.5.2. Freundlich Isotherm Model. It is an empirical equation that can be described the reversible adsorption onto heterogeneous surface at sites with different energy of adsorption and is not restricted to the formation of the monolayer of adsorbate. The linear form of this model is expressed as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (5)$$

where K_F is the Freundlich constant (mg/g)/(L/mg) $^{1/n}$, also referred to as adsorption capacity, while n is the heterogeneity factor and related to adsorption intensity. The value of n can be used also to describe the adsorption whether linear ($n = 1$) or a physical process ($n > 1$) is favorable, or a chemical process ($n < 1$). On the other hand, the value of $1/n < 1$ or $1/n > 1$ indicates a normal Langmuir isotherm and cooperative adsorption, respectively. The values of K_F and $1/n$ are determined from the intercept and slope of the plot $\ln q_e$ versus $\ln C_e$, respectively.

2.5.3. Tempkin Isotherm Model. Like the Freundlich isotherm, it assumes that the adsorption heat of all molecules decreases linearly when the layer is covered and that the adsorption has a maximum energy distribution of a uniform bond. The linearized form of Tempkin equation can be given as

$$q_e = B \ln K_T + B \ln C_e, \quad (6)$$

where b_T and K_T are the Tempkin constants, R the universal gas constant (8.314 J/mol K), and T is the absolute solution temperature in Kelvin. K_T is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy, and b_T is the variation of adsorption energy (J/mol), and also it is related to the heat of adsorption process, where the positive or negative value of b_T shows that the adsorption process is exothermic or endothermic process, respectively. B is related to the heat of adsorption and equals RT/b_T . A linear plot of q_e versus $\ln C_e$ gives the value of constants B and K_T from the slope and intercept, respectively.

2.5.4. Redlich-Peterson Isotherm Model. It incorporated the features of the Langmuir and Freundlich isotherms into a single equation and presented in the linear equation

$$\log \left(\frac{K_R C_e}{q_e} - 1 \right) = \beta \log C_e + \log A_R, \quad (7)$$

where K_R is the modified Langmuir constant (L/g), and A_R (L/mg) and β are constants. The parameter β lies between 0 (Henry's law) and 1 (Langmuir equation). Moreover, Redlich-Peterson isotherm was developed to improve the fitting between the Langmuir and Freundlich models. The value of the parameter β shows whether the Langmuir isotherm ($\beta = 1$) or Freundlich isotherm ($\beta = 0$) is preferable for the adsorption data. For simplicity, $K_R = K_L$. This model can describe the adsorption process over a wide range of concentrations. A_R and B can be estimated from the slope and intercept of linearized form of Redlich-Peterson, respectively.

2.6. Kinetic Models. The kinetic tests were carried out following the same procedure used for the previous equilibrium tests. Aqueous samples were taken at different intervals of time and the concentrations of MB were measured at the same intervals. The amount of MB absorbed onto the developed adsorbents at time t (min); q_t (mg/g) was calculated by means of the expression

$$q_t = \frac{(C_0 - C_t)V}{m}, \quad (8)$$

where C_0 and C_t are the liquid-phase concentrations (mg/L) at an initial and predetermined time t (min), respectively, V the volume of solution (L), and m is the dry weight of the added adsorbent (g). In addition, the kinetic data were then fitted into the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

2.6.1. Pseudo-First-Order Kinetic Model. The rate constant of adsorption was determined from the pseudo-first-order equation proposed by Langergren [26]

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}, \quad (9)$$

where q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the adsorption rate constant (min^{-1}).

2.6.2. Pseudo-Second-Order Kinetic Model. The pseudo-second-order equation based on the equilibrium adsorption is expressed as [27]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (10)$$

where k_2 (g/mg·min) is the rate constant of second-order adsorption.

2.6.3. Intraparticle Diffusion Model. The adsorbate species are most probably transported from the bulk of the solution into the solid phase through intraparticle diffusion/transport process, which is often the rate limiting step in many adsorption processes, especially in a rapidly stirred batch reactor [28]. This model was employed to identify the diffusion mechanism. This theory assumes an empirically based functional relationship, common to most adsorption processes, where uptake varies almost proportionally to $t^{1/2}$ rather than to the contact time t . According to this theory,

$$q_t = K_{id} t^{1/2} + C_i, \quad (11)$$

where k_{id} , $t^{1/2}$, and C_i are the intraparticle diffusion rate constant ($\text{mg/g}\cdot\text{min}^{1/2}$), square root of the time ($\text{min}^{1/2}$), and intercept at stage i , respectively. Values of k_{id} and C_i are calculated from the slope and intercept of linear portion of $q_t - t^{1/2}$ plot. The value of C_i is related to the thickness of boundary layer. The extrapolation of the linear straight lines to the time axis gives intercepts C_i . If C_i is equal to zero, the only controlling step is intraparticle diffusion. However, if $C_i \neq 0$, this indicates that the adsorption process is rather complex and involves more than one diffusive resistance.

2.7. Desorption Studies. Regeneration of adsorbent and recovery of adsorbate are important aspects to minimize the waste and reuse of adsorbent. In this study, some desorbing mediums were used (0.1 M of HCl and NaOH solutions and deionized H_2O at pH ~ 6) in order to investigate the leaching (or desorption) of MB dye in both single and binary aqueous solutions from the adsorbent use. Prior to the desorption process, 0.1 g of either ARS-1C or ARS-E was conducted with 50 mL of 100 mg/L MB dye solution. Also, 0.1 g of ARS-1C contacted with 100 mg/L of a binary mixture (MB and RB19). The adsorbate-adsorbent mixture was agitated at 35°C for 2 h to allow equilibrium. The sample adsorbed MB (or RB19) was separated using Whatman filter paper and washed gently with water to remove any unadsorbed dye followed by drying at

60°C until constant weight is obtained. Afterwards, a 0.02 g of dried sample-adsorbed dye was treated with 20 mL of different mediums under stirring for 30 min. The amount of MB adsorbed was measured spectrophotometrically and calculated using the equation

$$\begin{aligned} \text{Amount of dye desorbed (\%)} \\ = \frac{\text{Concentration of desorbed dye (mg/g)}}{\text{Concentration of adsorbed dye (mg/g)}} \times 100. \end{aligned} \quad (12)$$

3. Results and Discussion

3.1. Physicochemical Characteristics of the Adsorbents. Rice straw has a fibrous structure and composed of cellulose (37.4%), hemicellulose (44.9%), lignin (4.9%), and ash content (13.1%) [29]. Table 1 lists the physicochemical characteristics for the hereby prepared adsorbents from rice straw (RS) as follows: slurry pH, point of zero charge (pH_{PZC}), bulk density, moisture, iodine number, and methylene number. It can be deduced from Table 1 that the chemical treatment using NaOH and NaOH-citric acid and/or -EDTA had a remarkable effect on the physicochemical properties of the produced RS adsorbents. Hence, the mentioned chemical modification procedure caused a great enhancement on the adsorption capacity of developed rice straw adsorbents. Wing [30] developed a method to modify corn fiber thermochemically with citric acid. Upon heating, citric acid is dehydrated to yield a reactive anhydride which can react with the starch or cellulosic hydroxyl groups resulting in an ester-linkage and introduce free carboxyl groups to starch or corn fiber surface. Thus, citric acid increases the net negative charge on the corn fiber, thereby enhancing its binding potential for cationic dye.

The pH of the slurry and PZC of adsorbents may give a good indication about the surface oxygen complexes and the electronic surface charges of adsorbents. This surface charge arises from the interaction between adsorbent surface and the aqueous solution. The complexes on adsorbent surface are generally classified as acidic, basic, or neutral. Carboxylic, anhydride, and lactone are acidic groups, while phenolic, carbonyl, quinone, and ether groups are neutral or weakly acidic. Basic complexes are mainly pyrone and chromene groups. Based on the slurry pH values, the nature of surface oxygen groups on the adsorbents can be deduced. It is clear that the slurry pH and PZC of each adsorbent are very similar and between 4.22 and 7.92, which verifies the conclusion by Noh and Schwarz [31], in which slurry pH can be taken as equivalent to the PZC of adsorbent. Samples such as untreated RS, ARS-0.5C, and ARS-1C are acidic (pH = 4.22–5.55), whereas other adsorbents are found to be slightly acidic or neutral (pH = 6.33–7.92). Furthermore, when the solution pH is higher than the pH_{PZC} , the surface of the adsorbent is negatively charged, favoring the adsorption of cationic species, while for a solution pH is lower than the pH_{PZC} , the surface is positively charged, preferring the adsorption of anionic species [32]. Table 1 shows that the slurry pH $>$ pH_{PZC} , and, hence, the adsorbents are negatively charged and would be effective for removing cationic dyes.

The bulk density and moisture of the untreated rice straw were decreased from 0.3989 to 0.2601 g/cm³ and from 1.008 to 0.0064% for the produced modified rice straw, respectively. This result might be due to the base treatment and water washing resulting in removal of brown straw pigments [32]. Therefore, after alkali treatment, the citric acid and/or EDTA-modified rice straw seems to be low density materials based on the bulk density of the modified product. A similar result was also observed by Wartelle and Marshall [33]. Furthermore, the methylene blue number and iodine number increased from 28.9 to 116 mg/g and from 56.8 to 311.3 mg/g, respectively. This finding referred to the formation of porous structure, and, hence, there is an increase in surface area as detected by iodine number and in binding sites after chemical modification.

The surface morphology of adsorbent was characterized by scanning electron microscopy (SEM) of rice straw raw (RS), ARS, ARS-E, ARS-IC-E, and ARS-IC loaded dye samples (see Figure 1). The SEM images show progressive changes in the surface of particles. The shape of raw RS is mainly smooth and nonporous surface composed of fibrous rods with some bright needles refer to amorphous silica on the surface. After alkali treatment, its fibrous structure was altered and resulted in surface roughness with developing porous structure due to the elimination of silica, hemicellulose, and lignin from interfibrillar region [34]. Thus, it affirmed that NaOH pretreatment has a substantial influence on morphological, molecular, and supramolecular properties of cellulose causing changes in crystallinity, pore structure, accessibility, stiffness, unit cell structure, and orientation of fibrils in cellulosic fibers, and also it is similar to reported results on NaOH-modified rice husk [17]. Esterification of alkali rice straw with citric acid and/or EDTA causes also considerable changes within adsorbent surface. The SEM images clearly show the generation of porous structure after alkali-acid treatment. After adsorption, the caves and pores in SEM photograph of ARS-IC are more densely packed with MB and RB19 dyes as compared to the vacant pores present on surface of ARS-IC. It can be concluded that the adsorption of dye by the present samples correlated with due to the presence of pores as well as surface functional groups also.

Furthermore, FTIR technique is an interesting application for studying the interaction between an adsorbate and the active groups on the surface of adsorbent. Consequently, in order to get some insight into the nature of the mechanism of dye adsorption onto prepared RS-adsorbents, the infrared spectra of ARS, ARS-IC, ARS-E, ARS-IC-E, and ARS-IC-loaded dye samples were recorded in the range 4000–400 cm⁻¹ (Figure 2). Three characteristic absorption bands are clearly shown at regions: 3780–3400 cm⁻¹, two bands at 2922 and 2855 cm⁻¹, and also two bands at 1724 and 1620 cm⁻¹, in addition to shoulder bands between 1600 and 500 cm⁻¹. The first region between 3780 and 3600 cm⁻¹ has been assigned to stretching of free O–H groups on the surface, and broad peak in the 3350–3446 cm⁻¹ is ascribed to hydrogen bonded OH groups and chemisorbed water. In the FTIR spectra of ARS-E and ARS-IC-E adsorbents, the absorption band at around 3400 cm⁻¹ becomes very broad

due to the existence of N–H stretching. The absorption peak at 3446 cm⁻¹ was shifted to low transmittance as a result of interaction between MB molecules and –OH groups on ARS-IC surface. The band at 2925 cm⁻¹ and its shoulder at 2855 cm⁻¹ were ascribed to C–H asymmetric and symmetric stretching of residual methylene groups on the surface. A strong absorption band at 1724 cm⁻¹ and conjugated to 1620 cm⁻¹ in all FTIR spectra is attributed to stretching vibration of carboxyl groups on the edges of layer planes or to conjugated carbonyl groups (C=O stretching in carboxylic and lactone) [35, 36]. It was observed that the intensity of this peak increased during citric acid or/and EDTA modification which has a maximum at 1005 cm⁻¹ for ARS-IC-E adsorbent, meaning introduction of new carboxyl groups to adsorbent surface. The bands near 1600 cm⁻¹ are due to C=C stretching vibration in the aromatic ring. The appearance of broad bands between 1300 and 900 cm⁻¹ could be assigned to C–O stretching vibrations in carboxylic acids, alcohols, phenols, ethers, and esters. Also, shoulder absorption bands that occurred between 770 and 520 cm⁻¹ are ascribed to C–H and O–H bending in aromatics, respectively. In conclusion, the FTIR spectra in this investigation showed occurrence differences in intensities of the observed peaks during modification of alkali rice straw with citric acid and/or EDTA.

3.2. Effect of Contact Time and Initial MB Concentration.

The effects of contact time (5–90 min) and initial MB concentrations (20–100 mg/L) on the removal efficiency (% R_E) of MB by ARS and ARS-IC as representative samples are shown in Figure 3. It was observed that the percent removal of MB dye increased progressively with the time. The rate of adsorption was rapid at the initial stages and gradually decreased with increasing contact time until equilibrium was attained at 60 min and 30 min for adsorption onto ARS and ARS-IC, respectively. Furthermore, the equilibrium time for removal of MB dye by untreated RS (not shown here) was attained at nearly 300 min. On the other hand, Gong et al. [16] found that the adsorption equilibrium time for removal of MB by both native and modified rice straw using 0.5 M citric acid reached at about 600 min within three phases which could be attributed to boundary layer, intraparticle diffusion, and sorption equilibrium. Generally speaking, the fast removal at the beginning may be attributed to (i) the rapid attachment of dye molecules to the surface of the adsorbent and also (ii) the increased number of binding sites available, consequently leading to an increase in driving force of the concentration gradient between adsorbate in solution and adsorbate-adsorbent interaction. The following slower adsorption process with increasing contact time may be owing to intraparticle diffusion [37].

Regarding the effect of the initial dye concentration, it was found that increasing the concentration from 20 to 100 mg/L led to a decrease in the percent removal from 97.1 to 92.9% and 99.9 to 93.3% for ARS and ARS-IC, respectively. Thereby the dye removal by adsorption of modified rice straw was concentration dependent. This finding was attributed to the saturation and quick exhaustion of the binding sites on the adsorbents as the number of dye molecules per unit

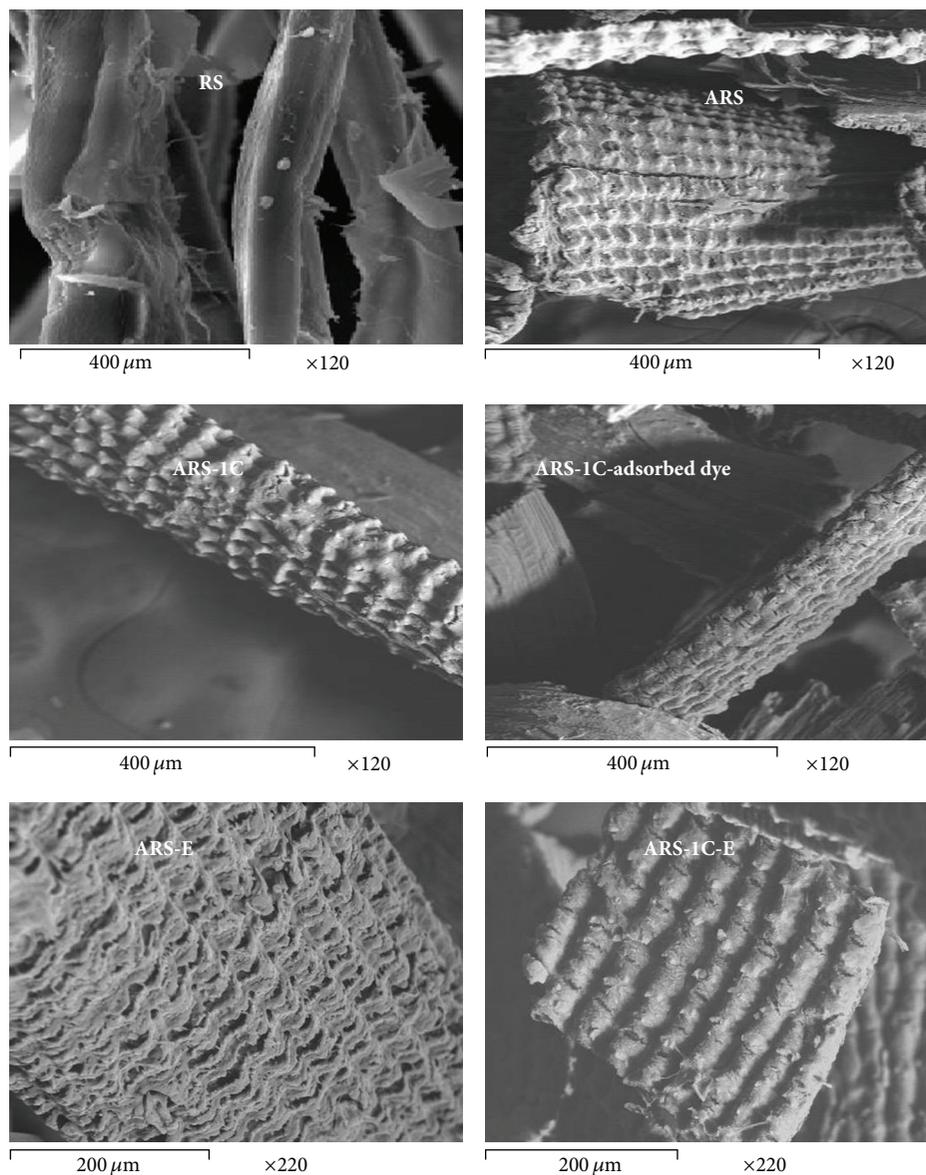


FIGURE 1: SEM photographs of the raw rice straw and its treated alkali-acid adsorbents.

volume increased [38]. A similar trend was also observed for adsorption of MB by EDTA-modified rice husk [38]. Finally, the removal of MB dye by ARS-1C and ARS-E is highly efficient. In case of ARS treated with mixture of citric acid and EDTA, the removal of dye slightly decreased as compared to ARS treated with either citric acid or EDTA. It was concluded that this treatment may be due to the reduction in active sites on the surface (as shown in Figure 1).

3.3. Effect of Solution pH on Dye Adsorption. It is well known that pH of solution influences the adsorption of dyes on adsorbent. Most of the dyes are ionic and upon dissociation release conferred dye ions into solution. The degree of adsorption of these ions onto the adsorbent surface is primarily influenced by the solution pH. The effect of pH on the adsorption of MB by the prepared samples was

investigated in the range of 2–10 as shown in Figure 4. It can be seen that there is an irregular change in the adsorbed amount of MB (mg/g) with increasing pH from 2 to 10. Lower amount of MB dye was adsorbed onto the prepared adsorbents at acidic pH 2–6 and then increased sharply as pH reached to 10. Above pH 6, for both samples of ARS-treated with citric acid, the amount of MB adsorbed is decreased significantly at pH 8 and then increased slightly up to pH 10. The reduction in adsorbed amount of MB at pH 8 may be ascribed to the increasing repulsive forces between surface functional groups of adsorbent and cationic MB dye that mainly exists as anion form [38]. Basically, methylene blue and other cationic dyes produce an intense molecular cation (C^+) and reduced ions (CH^+), and, hence, at higher pH, the adsorbent surface will be negatively charged and result in higher adsorption capacity. This behavior of the removal

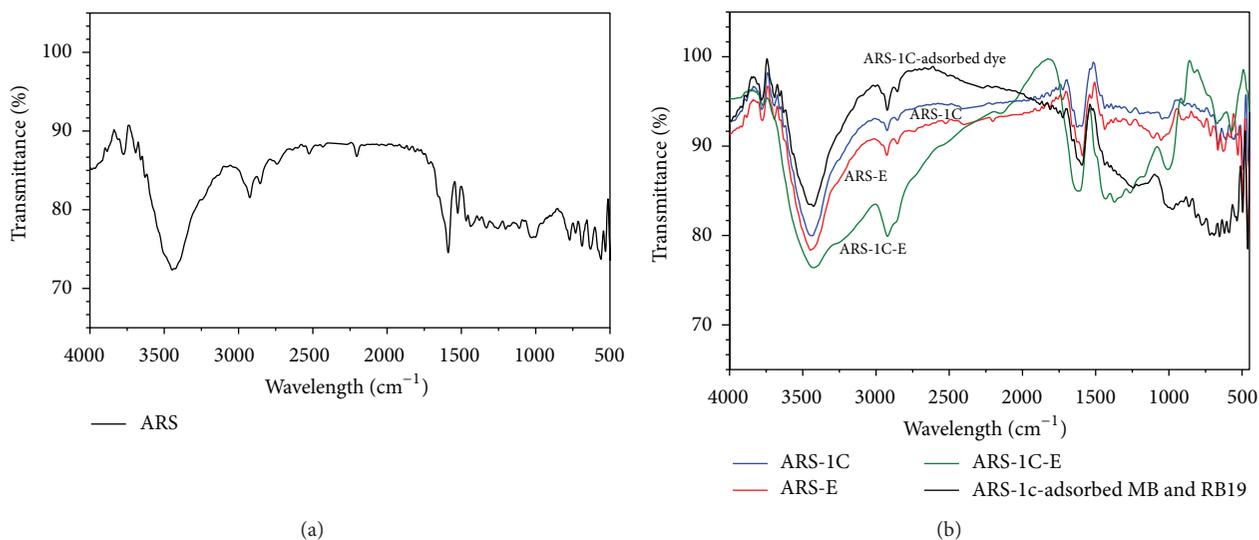


FIGURE 2: FTIR spectra of the developed adsorbents and ARS-1C-adsorbed MB and RB19 dyes.

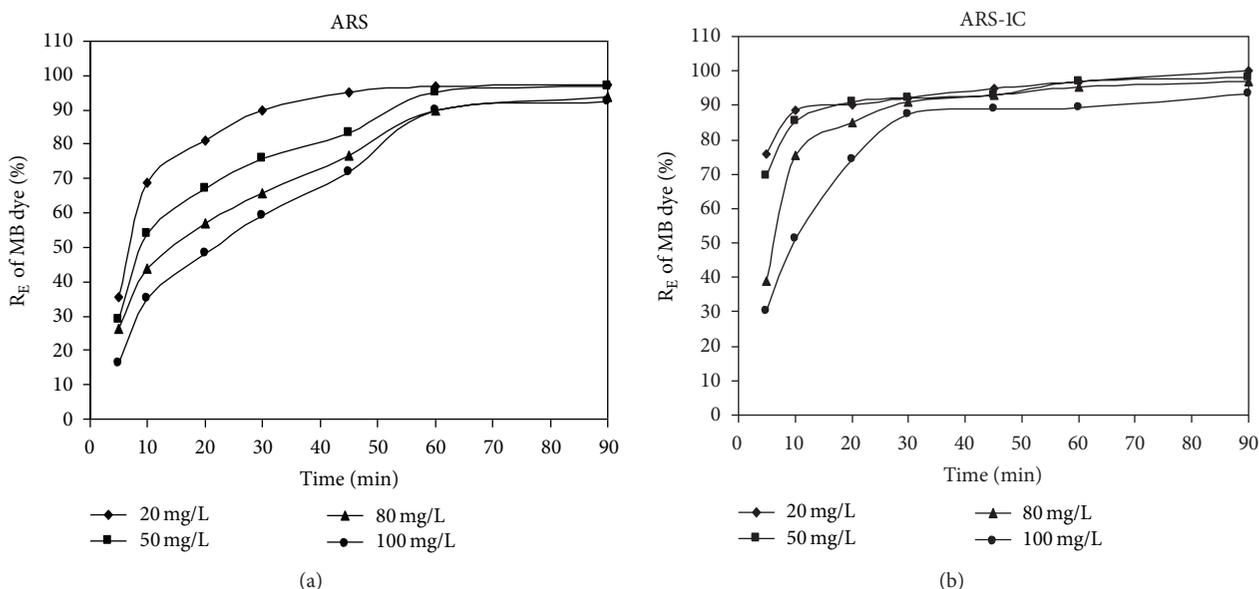


FIGURE 3: Effect of contact time and initial MB concentrations on the removal efficiency of MB by ARS and ARS-1C at pH 6 ($35^{\circ}\text{C} \pm 2$) and adsorbent dose = 0.15 g/25 mL.

of MB dye using activated carbon treated with HCl and HNO₃ was also reported by Wang and Zhu [39]. Although the adsorption of MB by these adsorbents was found to be enhanced slightly at pH 10, further adsorption equilibrium experiments were carried out at the pH 6, because the pH 6 is favored in wastewater treatment. Therefore, it can be interpreted the aforementioned findings are the following: (i) the lower adsorbed amount of MB at acidic pH is probably due to the presence of excess H⁺ ions competing with the cation groups on MB dye molecules (MB)⁺ and preferably combining with active functional group sites like -OH, C=O, -HN- of adsorbent surface, and thus reduction in adsorption of cationic MB dye could be due to repulsive forces, and (ii) as surface density decreases with an increase in the solution pH, the electrostatic repulsion force between the positively

charged dye, MB, and the adsorbent surface is lowered, and the carboxyl groups are predominantly deprotonated which may result in enhanced sorption sites available for binding MB adsorbate. For example, -OH⁻ ions neutralize the functional groups of adsorbents like -OH and -COOH, and formation of anionic active sites on adsorbents increased the adsorption of cationic dye due to increase in attractive forces. Also the -OH, C=O, -HN- of the surface of sorbent are set free due to deprotonation by base and are then available for adsorption.

3.4. Effect of Adsorbent Dose on Dye Adsorption. The effect of adsorbent dose on the removal efficiency of a basic MB dye on the produced samples is shown in Figure 5. It is obvious that the removal efficiency for MB dye was increased with

TABLE 2: The parameters of Langmuir, Freundlich, Tempkin, and Redlich-Peterson isotherms for MB adsorption.

Parameters	RS	ARS	ARS-0.5C-E	ARS-1C-E	ARS-0.5C	ARS-1C	ARS-E
Langmuir							
Q_m (mg/g)	32.6	62.9	69.0	74.6	95.2	135.1	107.5
K_L (L/g)	0.4453	0.3804	0.2231	0.4012	0.2425	0.1407	0.3432
R_L	0.0994	0.0129	0.0219	0.0123	0.0202	0.0343	0.0143
ΔG (J/mol)	-24.6	-30.0	-28.6	-30.1	-28.8	-27.4	-29.7
R^2	0.9980	0.9895	0.9984	0.9997	0.9946	0.9966	0.9991
Freundlich							
K_F (mg/g)/(L/mg) ^{1/n}	2.7	27.1	27.8	35.6	27.2	31.8	45.2
1/n	0.568	0.215	0.233	0.176	0.387	0.358	0.227
R^2	0.9821	0.9925	0.9706	0.8641	0.9547	0.9919	0.9722
Tempkin							
B	—*	10.3	9.9	10.9	22.9	27.5	17.0
K_T (L/mol)	—	8.6	25.6	8.8	1.9	1.7	10.5
b_T (J/mol)	—	248.1	257.8	234.5	111.9	93.2	151.0
R^2	—	0.9921	0.9074	0.9358	0.9800	0.9986	0.9943
Redlich-Peterson							
β	—	0.7806	0.8215	0.8744	0.6306	0.6421	0.7650
K_R (L/g)	—	0.1364	0.5951	0.0628	0.0129	0.0163	0.0616
A_R (L/mg)	—	8.37×10^{-3}	0.0113	9.95×10^{-3}	8.63×10^{-3}	4.41×10^{-3}	7.60×10^{-3}
R^2	—	0.9993	0.9938	0.9909	0.9762	0.9973	0.9947

—*: not detected.

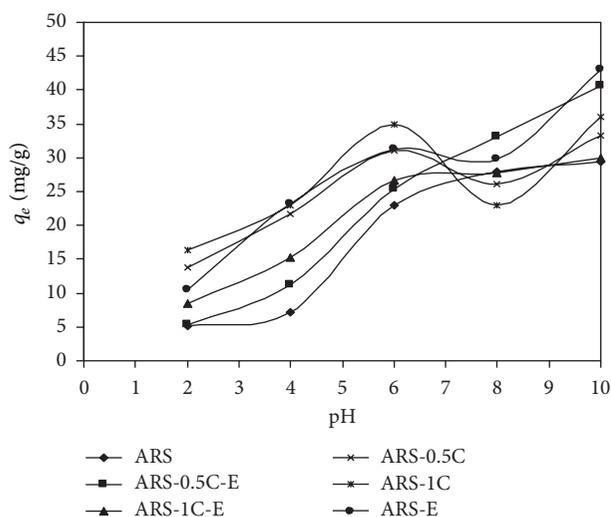


FIGURE 4: Effect of solution pH on the adsorption of MB dye onto the prepared adsorbents at pH 6 ($35^\circ\text{C} \pm 2$), adsorbent dose = 0.15 g/25 mL, and initial MB concentration = 100 mg/L.

increasing amount of adsorbent. This result may be due to the introduction of more binding adsorption sites revealing from the increased dose and adsorbent conglomeration. The increase in the extent of removal of MB is found to be insignificant after a dose 0.15 g/25 mL for various adsorbents which is fixed as the optimum dose of adsorbents (equals to 6 g/L). Such study is useful in establishing the optimum amount of adsorbent to be used in the dye removal.

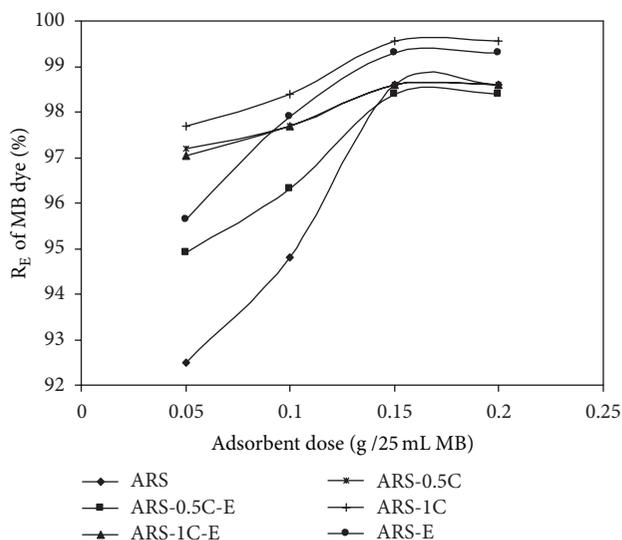


FIGURE 5: Effect of adsorbent dose on removal efficiency of MB dye onto the prepared adsorbents at pH 6 ($35^\circ\text{C} \pm 2$), initial MB concentration = 100 mg/L, and volume = 25 mL.

3.5. Effect of Ionic Strength on Dye Adsorption. Figure 6 depicts the effect of sodium chloride molar concentrations (0.01–0.2 M) on the adsorption of MB dye on ARS-1C and ARS-E samples. As shown in this figure, the existence of salt in solution resulted in steeper decrease in the removal efficiency of MB from 82.2% to 77.4% and from 90.2% to 82.8% using ARS-1C and ARS-E, respectively. The reason

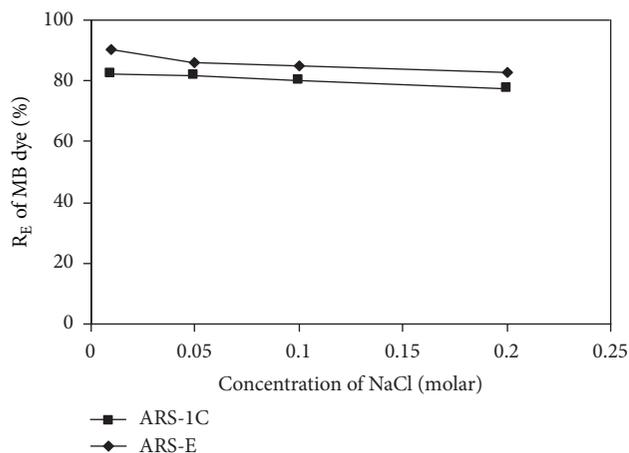


FIGURE 6: Effect of sodium chloride concentration on the adsorption of MB dye onto ARS-1C-E and ARS-E adsorbents at pH 6 ($35^\circ\text{C} \pm 2$), adsorbent dose = 0.15 g/25 mL, and initial MB concentration = 100 mg/L.

could be attributed to the competitive effect between MB ions and metal ions from the salt on the active sites that are available for the adsorption process. Another reason is that the increase in ionic strength leads to the decrease in activity of MB and the active sites, and, hence, the adsorptive capacity of MB decreases. By comparing the removal efficiency of MB from aqueous solution by ARS-1C and ARS-E in absence of sodium salt, it was found that the maximum removal efficiency decreased slightly from 93.3% to 77.4% and from 91% to 82.8% in presence of sodium salt, respectively. From this observation, it can be concluded that modified rice straws still had higher capacity of MB binding in salt-existed solution. Thus, the obtained modified rice straws can be used to remove MB dye from aqueous solution with higher salt concentration.

3.6. Evaluation the Adsorption Isotherm Behavior of the Adsorbents.

The isotherm results were carried out by containing MB dye with 0.15 g of adsorbent for 24 h at different initial concentrations ranged from 20 to 200 mg/L. Figure 7 shows the adsorption isotherms for MB by various adsorbents, but the plots of models are not shown here. The relative parameters of each isotherm were obtained according to the intercept and slope from the plots as mentioned earlier between C_e/q_e versus C_e , $\ln q_e$ versus $\ln C_e$, q_e versus $\ln C_e$, and $\log(K_R C_e/q_e - 1)$ versus $\log C_e$, respectively, and their correlation coefficients (R^2) from the linear isotherm model are given in Table 2.

The monolayer adsorption capacities (Q_m , mg/g) of the adsorbents are found to increase in the order: RS raw < ARS < ARS-0.5C-E < ARS-1C-E < ARS-0.5C < ARS-E < ARS-1C. Among them, ARS-1C and ARS-E adsorbents have the highest adsorption capacity. Moreover, a comparison of maximum monolayer adsorption capacity of MB on untreated and treated various low-cost adsorbents is collected in Table 3. The value of Q_m (mg/g) for modified alkali-acid rice straw samples in this study showed more or less adsorption

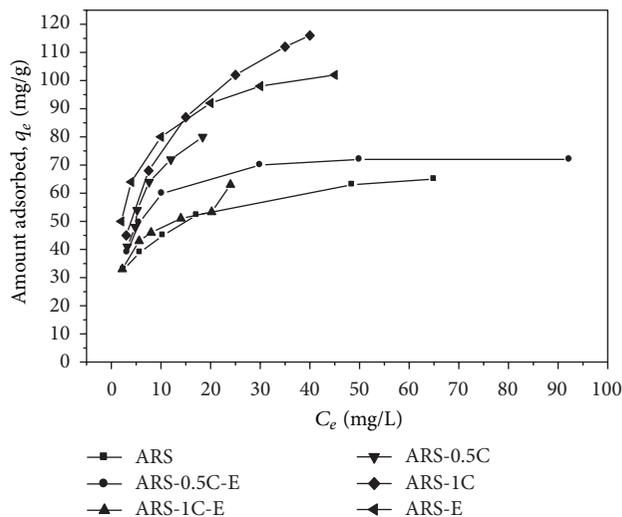


FIGURE 7: Equilibrium adsorption isotherms of MB dye by various prepared adsorbents at pH 6 ($35^\circ\text{C} \pm 2$), adsorbent dose = 0.15 g/25 mL, and initial MB concentrations = 20–200 mg/L.

capacity than of other adsorbents reported in the literature [40–47]. This indicated that the ARS-modified adsorbents from RS could be used to remove MB dye as low-cost adsorbent, and the price is attractive as compared with other adsorbents or activated carbons as shown in Table 3.

The results indicate that the application of Langmuir and Redlich-Peterson isotherm models exhibits satisfactory straight lines with correlation coefficients ≥ 0.99 as compared to other isotherm models. Conformation of the experimental data to the Langmuir isotherm model means the homogeneous nature of adsorbent surface; that is, each dye molecule/adsorbent surface adsorption sites has equal adsorption activation energy. The results also demonstrate the formation of monolayer coverage of dye molecules at the outer surface of the hereby rice straw adsorbents from either NaOH- or NaOH-acids treatment.

The values of K_L are found to be in the range 0.1407 to 0.4453 L/g for the prepared adsorbents, where the lower K_L value is the higher Q_m value (cf. Table 2). The values of R_L for the uptake of MB molecules on the obtained adsorbents were found to be in the range of 0.0129 to 0.0994 confirming that the adsorption of MB was highly favorable onto the prepared adsorbents under the experimental conditions used in this study. Moreover, adsorption of MB onto the developed RS adsorbents exhibited negative values of free energy ($\Delta G = -24.6$ to -30.1) which indicates the feasibility and spontaneous nature of physical adsorption process and confirmed good affinity of treated RS-adsorbents for the uptake of MB basic dye.

The Freundlich constants K_F and $1/n$ calculated from the intercept and slope values of the linear plot $\ln q_e$ versus $\ln C_e$, respectively, are given in Table 2. The values of $1/n$ were found to be less than one, indicating a normal Langmuir isotherm. The calculated values of B , K_T , and b_T from Tempkin model are listed also in Table 2. The positive value of b_T indicates that the adsorption of MB dye is exothermic process. Regarding

TABLE 3: Comparison of maximum monolayer capacity (Q_m , mg/g) of MB adsorbed by various adsorbents.

Adsorbents	Q_m , (mg/g)	Reference
Citric acid modified rice straw	270.30	[16]
EDTA-modified rice husk	46.30	[40]
Sulfuric acid treated Pearl millet husk	82.37	[41]
Pineapple stem	119.05	[42]
Sulfuric acid treated Parthenium	88.29	[43]
Rice husk	40.60	[44]
Citric acid modified kenaf core fibers	131.60	[45]
Activated carbon from apricot	136.98	[46]
Oak sawdust	29.94	[47]
Cherry sawdust	39.84	[47]
Hazelnut	76.90	[47]
Rice straw	32.60	This study
Citric and/or EDTA-modified alkali rice straw	62.90–135.10	This study

to the Redlich-Peterson model, the values of β are ranging between 0.6306 and 0.8744 confirming the adsorption of MB dye by prepared samples following the Langmuir isotherm. Mall et al. [48] studied also the previous four isotherm models for the adsorption of congo red dye onto bagasse fly ash and activated carbon and found that their adsorption data have been described well by the Redlich-Peterson and Freundlich models.

3.7. Evaluation of the Kinetic Behavior of the Prepared Adsorbents. In order to investigate the adsorption kinetics of MB dye on the prepared RS adsorbents, three kinetic models have been tested: pseudo-first-order, pseudo-second-order, and intraparticle diffusion models [26–28]. The amount of MB dye adsorbed q_t at time (t) was calculated from (8). The calculated parameters from pseudo-first-order, pseudo-second-order, and intraparticle diffusion models are summarized in Table 4.

According to the pseudo-first-order model, the values of k_1 and q_e were calculated from the slope and intercept from the plots of $\log(q_e - q_t)$ versus t . It was found that the experimental q_e values did not adequate with the calculated ones (Table 4), indicating that the first-order model does not reproduce the adsorption kinetic of MB on the prepared adsorbents. In case of the pseudo-second-order model, the calculated values of q_e fitted well with the experimental data, and, hence, this model is more likely to predict the behaviour over whole the experimental range of MB adsorption more than pseudo-first-order model. Also, the values of correlation coefficients (R^2) are close to unity for pseudo-second-order rather than the pseudo-first-order one; that is, the kinetic removal of MB is quit described by pseudo-second-order model.

By applying the intraparticle diffusion model, the plots of q_t versus $t^{1/2}$ at the different initial concentrations are presented in Figure 8. The $k_{i,d}$ and C_i values can be determined from the slope and the intercept of the linear plots, respectively, and are given in Table 4. The intercept value reflects the importance of the boundary layer thickness; that is, the larger the intercept, the greater the thickness

of the boundary layer. The plots also present multilinearity, indicating that two or more steps have taken place. The first stage (up to 30 min) is the instantaneous or external surface adsorption, that is, the diffusion of the adsorbate through the solution to the external surface of the adsorbent [41, 48]. The second stage (over 30 min) is the phase of gradual adsorption where intraparticle diffusion is the rate-controlling step. In some cases, there is a third phase, as initial concentration increased from 20 to 50, 80, and 100 mg/L (as shown in Figure 8), which is the final equilibrium stage when intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations left in the solutions. As can be seen from Figure 8, the linear line did not pass through the origin, and this deviation from the origin (or near to saturation) might be due to the difference in the mass transfer rate in the initial and final stages of adsorption [41, 48].

3.8. Adsorption Behavior of ARS-1C in a Binary Aqueous Solution. In particular, this study was carried out to explore the adsorption behavior of ARS-1C adsorbent towards removal of both basic and acidic dyes from a binary mixture solution, that is, methylene blue and reactive blue19 dyes, respectively. This adsorbent showed good adsorption capacity as detected previously. It was shown that ARS-1C adsorbent has the ability to remove MB higher than RB19 from both single and binary solutions as shown in Figure 9. This behavior could be attributed to the presence of negative charges that resulted in acidic surface functional groups such as carboxyl groups, preferring adsorption of cationic dye.

3.9. Desorption Studies. Desorption studies assist to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye [41]. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dye of the adsorbent is by weak bonds. If mineral acid or alkaline water can desorb the dye, then the adsorption is by ion exchange. If organic acids, like acetic acid, can desorb the dye, then the dye is held by the adsorbent through chemisorption. The effect of neutral water 0.1M HCl and 0.1M NaOH reagents used

TABLE 4: Kinetic model constants and correlation coefficients for adsorption of MB dye using various adsorbents at different initial concentrations.

Adsorbents	C_0 , (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
			k_1	$q_{e,cal}$ (mg/g)	R^2	k^2	$q_{e,cal}$ (mg/g)	R^2	K_{id}	C_i	R^2
ARS	20	11.6	0.035	8.40	0.9642	6.66×10^{-3}	13.9	0.9923	1.43	2.02	0.9440
	50	29.5	0.040	15.70	0.9799	5.77×10^{-3}	34.5	0.9987	2.67	19.1	0.9620
	80	46.4	0.033	65.70	0.9795	4.96×10^{-4}	48.8	0.9771	6.55	14.6	0.9881
	100	55.3	0.026	54.10	0.9727	1.70×10^{-3}	53.5	0.9908	8.01	3.41	0.9811
ARS-0.5C-E	20	11.2	0.028	6.44	0.8891	9.92×10^{-3}	12.8	0.9959	1.09	3.54	0.9173
	50	31.7	0.032	14.50	0.9536	6.54×10^{-3}	33.0	0.9924	1.86	17.1	0.9340
	80	49.5	0.033	29.30	0.8219	2.29×10^{-3}	54.9	0.9923	5.08	13.2	0.8512
	100	59.8	0.034	47.00	0.9518	1.28×10^{-3}	70.4	0.9969	6.35	13.1	0.9747
ARS-1C-E	20	11.8	0.020	3.96	0.6787	0.0336	12.4	0.9986	0.309	9.63	0.8864
	50	29.6	0.026	12.80	0.9028	8.47×10^{-3}	31.8	0.9984	1.63	18.5	0.9212
	80	47.9	0.038	30.40	0.9539	2.47×10^{-3}	46.1	0.9946	4.52	17.4	0.9177
	100	53.1	0.024	48.40	0.9801	4.36×10^{-3}	55.6	0.8868	5.76	10.6	0.9842
ARS-0.5C	20	11.2	0.047	2.40	0.9338	0.0581	13.4	0.9994	0.263	11.2	0.9453
	50	30.1	0.023	7.75	0.8985	0.0179	31.9	0.9997	1.08	23.4	0.8993
	80	49.8	0.026	18.5	0.8461	6.08×10^{-3}	51.3	0.9990	2.95	28.3	0.7549
	100	61.7	0.037	49.1	0.9137	1.27×10^{-3}	55.5	0.9840	8.32	2.37	0.8711
ARS-1C	20	11.7	0.029	3.35	0.8207	0.0326	13.9	0.9997	0.582	8.61	0.8296
	50	31	0.037	7.78	0.9556	0.0165	33.1	0.9998	1.21	23.7	0.8914
	80	47.3	0.038	29.9	0.8345	2.23×10^{-3}	55.2	0.9941	5.14	12.6	0.8685
	100	62.8	0.029	77.1	0.8919	8.01×10^{-3}	66.6	0.9999	2.35	47.1	0.8290
ARS-E	20	10.4	0.019	8.39	0.9844	9.57×10^{-3}	11.8	0.9835	0.912	3.59	0.9853
	50	26.1	0.018	20.2	0.8696	4.24×10^{-3}	29.0	0.9982	1.59	10.2	0.9399
	80	51.7	0.015	24.1	0.8912	0.0321	50.8	1	2.11	41.1	0.8060
	100	64	0.025	43.8	0.9465	5.83×10^{-3}	63.3	0.9997	3.63	35.3	0.8518

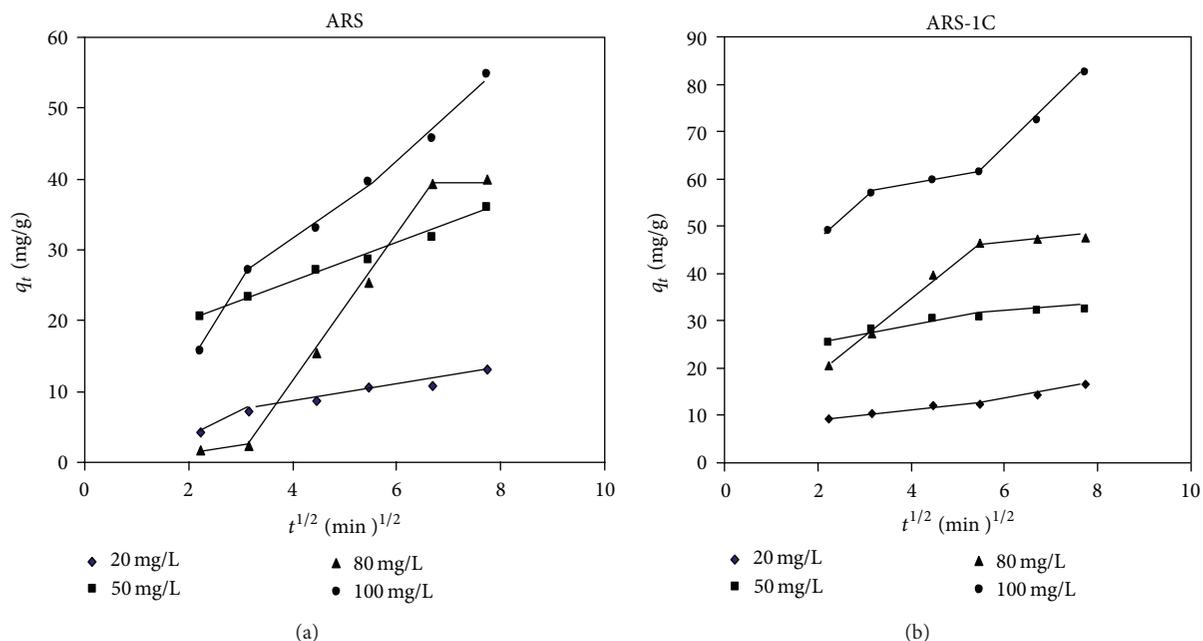


FIGURE 8: Intraparticle diffusion plots for the adsorption of MB onto ARS and ARS-1C.

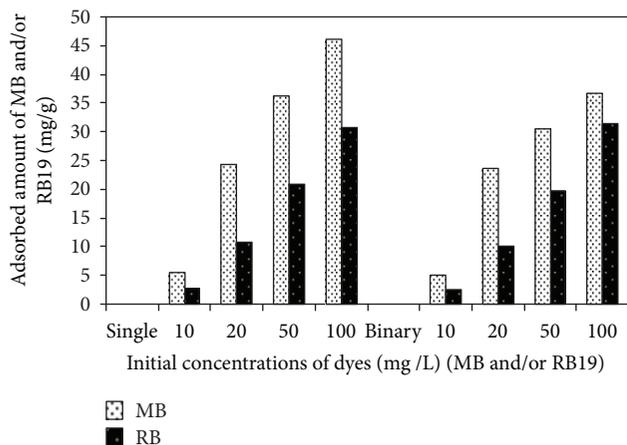


FIGURE 9: Adsorption of basic MB and acidic RB19 on ARS-1C from either a single or a binary mixture solution.

as desorbing agents is shown in Figure 10. It was observed that the hydrochloric acid is a better reagent for desorption of MB and/or RB19 dyes, as it can desorb 100% of the adsorbed MB dye onto ARS-1C and ARS-E adsorbents in a single system while 37.8% and 60.8% of MB and RB19 dyes in a binary solution by ARS-1C, respectively. Lower significant desorption with neutral water and NaOH reagents was obtained as follows: 10.9% and 26.9% of MB adsorbed on ARS-1C and 40.1% and 6.5% of MB adsorbed on ARS-E, respectively. Based on these findings, the desorption of MB and/or RB19 by 0.1M HCl solution indicated that the dye is adsorbed onto both adsorbents by strong forces through chemisorption mechanism [41].

4. Conclusions

The following conclusions are based on the aforementioned findings.

- (i) In our study, we found out that alkali-acid pre-treatment of the rice straw adsorbent improved its adsorption efficiency. Rice straw has low removal efficiency and adsorption capacity for MB removal, but, on the other hand, chemical treatment of ARS with citric acid and EDTA significantly improves its adsorption potential.
- (ii) Adsorption of MB dye was influenced by various parameters such as contact time, initial dye concentration, solution pH, adsorbent dose, and NaCl salt concentration. Adsorption was increased with increasing pH and adsorbent dose and decreased with increasing initial dye concentration. The increase in salt concentration decreased slightly the MB adsorption.
- (iii) The adsorption isotherm data for MB were fitted well to the Langmuir and Redlich-Peterson isotherms, and the maximum monolayer adsorption capacity was found to increase in the order: RS raw < ARS < ARS-0.5C-E < ARS-1C-E < ARS-0.5C < ARS-E < ARS-1C. The experimental data estimated by kinetic

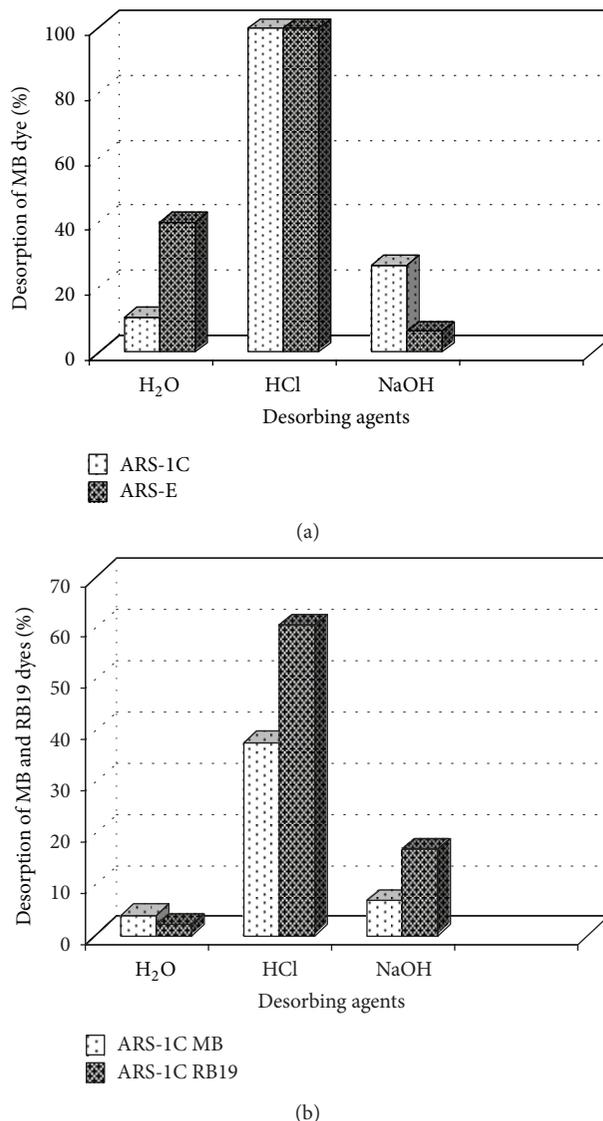


FIGURE 10: Desorption of single MB onto ARS-1C and ARS-E and desorption of both MB and RB19 mixture on ARS-1C.

order models obeys pseudo-second-order model with higher correlation coefficients $R^2 \geq 0.99$.

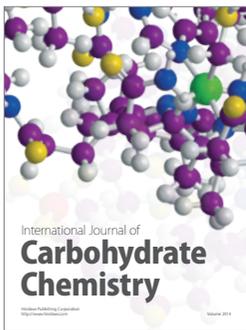
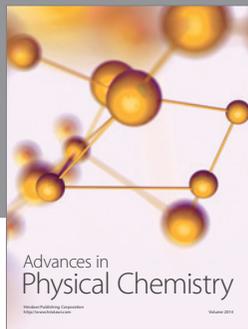
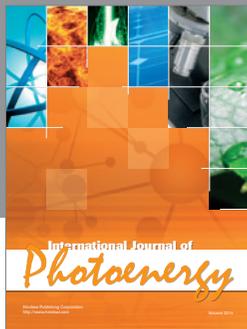
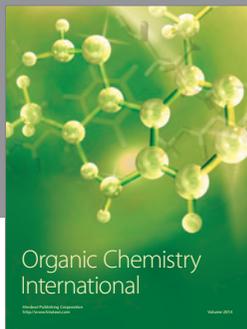
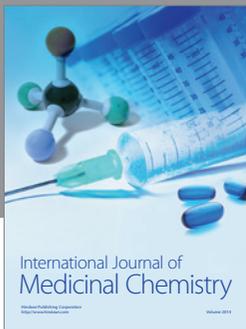
- (iv) The kinetic studies showed that the methylene blue adsorption process follows the pseudo-second-order kinetic model. The adsorption of MB dye was carried out by chemisorption and controlled by film and intraparticle diffusions.
- (v) The present investigation proved that ARS-1C and ARS-E can be employed effectively for the treatment of dyeing effluents containing methylene blue dye. The waste RS is abundantly available, and, hence, its application to the treatment of dyeing wastewater is expected to be economically feasible.

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