Application of Synthesized Biomass Bamboo Charcoal–Iron Oxide “BC/Fe” Nanocomposite Adsorbents in the Removal of Cationic Methylene Blue Dye Contaminants from Wastewater by Adsorption

Tushar Kanti Sen

Department of Chemical Engineering, College of Engineering, King Faisal University, P.O. Box 380, Al-Ahsa 31982, Saudi Arabia; tsen@kfuf.edu.sa

Abstract: In this work, synthesized, raw-bamboo-biomass-based magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite adsorbents were characterized and tested for their effects on the removal of aqueous-phase cationic methylene blue (MB) dye pollutants from synthetic wastewater through a laboratory batch adsorption study. This batch adsorption study aimed to identify various physico-chemical process parameters such as initial dye concentration, solution pH, adsorbent dose, temperature, and their effects on the adsorption kinetics and adsorption isotherm characteristics. From the kinetic studies, it was found that the amount of MB dye adsorption by synthesized adsorbents $q_e$ (mg/g) increased from 9.50 mg/g to 15.30 mg/g with the increase in the initial dye concentration range of 10 to 30 ppm, as per contact time, but decreased with the increase in the temperature range from 30 to 60 $^\circ$C and the adsorbent doses from 20 to 40 mg, respectively, under specified experimental process conditions. From the kinetic study, it was also found that equilibrium was reached within 120 min, the adsorption kinetics followed three mechanistic steps, and the pseudo-second-order (PSO) kinetic model was applicable to explain the data of the batch adsorption kinetics. The various kinetic model parameters were determined from a fitted model equation. Furthermore, there was an increase in the amount of the MB dye adsorption $q_e$ (mg/g) from 9.87 mg/g to 17.62 mg/g with the increase in the solution pH from 3 to 7, and a reduction in the amount of dye adsorption $q_e$ (mg/g) was found at the solution pH of 10 for a 20 ppm MB dye solution at 30 $^\circ$C. Both the Freundlich and Langmuir isotherm models were applicable to the equilibrium data, and the maximum adsorption capacity from the Langmuir isotherm fitting was 111.11 mg/g, which was comparative to or even better than many other magnetic adsorbents for methylene blue dye adsorption. Finally, the regeneration and reusability of the magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite materials as well as the limitations of these batch adsorption studies are also discussed here.

Keywords: methylene blue dye adsorption; magnetic nanocomposite materials; wastewater treatment; kinetic models; equilibrium isotherm model

1. Introduction

Dyes are one of the potential organic color and toxic pollutants, and methylene blue (MB) (3,7-bis(dimethylamino)-phenazathionium chloride), a thiazine cationic dye, is one of these cationic water-soluble synthetic dye compounds, whose chemical structure is shown in Figure 1 [1]. Over the last few years, the usage of chemical dyes across various industries has increased, resulting in significant environmental threats due to an inevitable release of effluents encompassing toxic dyes into the soil and water ecosystems [2]. Methylene blue (MB) dye is commonly used in the paper, textiles, dyeing leather, printing, tannin, pigment, and food industries to color their products [1,3]. Textile industries are the primary source of MB-dye-bearing effluents. There are more than 100,000 known commercial dyes, with an annual production of over $7 \times 10^5$ tons/year, and approximately 100 tons/year of
dye-bearing effluents are discharged worldwide from the textile industry alone [4,5]. Even at very low dye concentrations, the pollution is highly visible and undesirable.

![Figure 1. Chemical structure of methylene blue (3,7-bis(dimethylamino)-phenazathionium chloride).](image)

Synthetic dyes are stable and possess very complex structures. Therefore, their strong effects on the aquatic environment through the discharging of dye-bearing effluents have created deep concerns for the public and environmentalists [6]. In low amounts, dyes such as MB are not fatal to humans. However, in higher quantities, they can cause eye and/or skin irritations, vomiting, nausea, diarrhea, profuse sweating, dizziness, headaches, stomach pains, and increased heart rate [7,8]. Therefore, treating effluents containing MB before being released into aqueous systems is of environmental significance. Several methods are commonly used for the separation of dyes from wastewater, including coagulation–flocculation, reverse osmosis, membrane filtration, photocatalytic degradation, oxidation, adsorption, ion exchange, chemical precipitation, and biological treatments [1,7,8]. Among them, adsorption has been found to be the preferred separation technique due to its simplicity in design, flexibility, high efficiency of separation, and attentiveness to hazardous pollutants. Currently, most commercial systems use activated carbon (AC) as an adsorbent to remove dyes from wastewater because of its excellent adsorption ability and porous structure. However, the high cost, inapplicability for low-solute concentration removal, strength, regeneration, and separation issues of commercially activated carbon (CAC) remains a challenging problem. Therefore, the use of locally available agricultural solid waste or plant-biomass-based activated carbon or charcoal in the adsorptive separation of inorganics and organics is one of the current research directions for sustainable and cost-effective but efficient and alternative adsorbent options. In this research direction, Jjagwe et al. [9] recently reviewed and compiled a wide range of biomass-based activated carbon synthesis and activation methods and, finally, presented their successful applications in the adsorptive removal of aqueous phase inorganic/organic pollutants. Readers are encouraged to go through this review article. They also critically discussed the synthesis and activation methods of biomass-based adsorbents; the mechanisms of the adsorption, identification, and optimization of various process parameters; and, finally, the limitations and future research directions. Charcoal/carbon from waste biomasses may act as a cost-effective but efficient adsorbent for contaminant remediation due to its low production cost, economic benefits, local availability with throwaway prices, and conducive surface characteristics [10–12]. Nowadays, the application of biochar commonly synthesized from biomasses for wastewater treatment is being explored by different researchers [10,13]. However, adsorptive pollutant removal using a wide range of biomass-based activated carbons or charcoals possesses some kinds of limitations, particularly for the removal of low-solute adsorbate concentrations, adsorbent regeneration, reuse, and post-treatment separation [14]. Therefore, the combination and application of biomass-derived, carbon-based magnetic nanocomposite materials may overcome these limitations and popularize carbon-based magnetic particle adsorption technologies in the water purification process with more efficient and easier separation and recovery processes. The commonly used synthesized method to produce magnetically activated carbon or magnetic biochar is the combination of biomass-based charcoal or activated carbon with magnetic materials. Therefore, carbon-based magnetic nanocomposite material synthesized with high carbon contents, large specific surface areas, high strengths, easy magnetic separations, and other superior properties, including high adsorption capacities, are the present day’s hot research area.
among researchers, scientists, and engineers. Sivashankar et al. [4] concluded in their review article that the application of magnetic composites and magnetic nanocomposites is becoming a promising option in the removal of aqueous phase dyes over conventional adsorbents. They compiled ample references of various synthesized magnetic composite adsorbent materials and their applications in the removal of dyes by batch dye adsorption. On the other hand, the present state of the art in the field of carbon-based magnetic nanocomposite material syntheses and their various applications, including the adsorptive removal of dyes from wastewater as adsorbents, were also recently reviewed and critically discussed by Sharma et al. [15] and Zhao et al. [16], respectively.

Bamboo is primarily a grass that comes from plant biomass and is considered a natural renewable resource that can be further converted to valuable energy and materials. It is a versatile material that societies have used for thousands of years [17]. The process of carbonization generates a product with a large surface-area-to-mass ratio as well as an increased ability to absorb and essentially extract a variety of chemicals, minerals, and other harmful substances. This is possible due to the composition of carbonized bamboo [18]. Generating bamboo charcoal (BC) from wood (bamboo) changes the chemical structure of the carbon molecules in such a form that a whole new type of molecule is created [18]. In addition, magnetic nano-iron oxides are successfully used as catalyst materials, effective adsorbents for pollutant removal [19,20], pigments, and flocculants [21]. However, to overcome some challenging problems associated with the use of pure magnetic nano iron oxide particles, such as agglomeration, oxidation in acidic medium, and separation/recycling issues, present-day researchers are developing various magnetic carbon nanocomposite materials through utilizing the synergetic effect of both materials [20,22,23]. Hence, carbon-based magnetic nanocomposite adsorbents have emerged as a new generation of effective adsorbents in the removal of various potential aqueous-phase pollutants. Additionally, the process becomes sustainable and cost-effective whenever these magnetic nanocomposite adsorbent materials are produced from locally available agricultural biomass materials. Basically, the inclusion of magnetism in adsorption technology is an innovative concept, and magnetic composites belong to this newest class [15]. In the past decade, there have been various reported results on aqueous-phase dye removal via magnetic-activated carbon nanocomposite materials as an effective adsorbent [14]. The efficiency of adsorption is also affected or determined by various influencing factors such as the surface area of the adsorbent, the interaction between the adsorbent and adsorbate, the particle size of the adsorbent, adsorbent-to-adsorbate ratio, pH, contact time, temperature, and the concentration of adsorbent. Altingtig et al. [24] reported on the aqueous-phase methylene blue dye removal via synthesized magnetic activated carbon (Fe-AC) adsorbents of BET surface area of 940.1 m²/g under various physico-chemical process conditions, and the obtained maximum adsorption capacities for AC and Fe-AC adsorbents at 298 K were 303 and 357.1 mg/g, respectively [14]. Yadav et al. [25] found that the synthesized magnetic/activated charcoal/alginate polymer nanocomposite effectively removed cationic MB dye from water with 99.53% removal efficiency, and the adsorption reaction was very fast and depended on many influential process parameters such as adsorbate dye concentration, adsorbent density, solution pH, and temperature. Similarly, natural zeolite/Fe₃O₄ magnetic composite materials were an effective adsorbent in removing MB dye from an aqueous solution with an adsorbent capacity of 32.25 mg/g under specified conditions [26]. Adsorbent beds of alginate (A)/magnetic nanoparticle and carbon nanotubes were successfully synthesized and used for aqueous phase methylene blue removal, and equilibrium was achieved by 48 h [27]. Hashem [28] also reported magnetic Fe₃O₄/bentonite nanocomposite material successfully removed MB from water with high removal efficiency under various process conditions, including adsorbate concentration, adsorbent dose, solution pH, and temperature, respectively. Amar et al. [8] reported the results of batch methylene blue adsorption using CoFe₉.₉Mo₀.₁O₄ magnetic nanoparticles under various process conditions such as solution pH, initial dye concentration, adsorbent dose, and contact time to be 95% under optimum process conditions. The fast and effective removal of crystal
violet dye using magnetically activated carbon iron oxide nanocomposite materials with an adsorbent capacity of 16.5 mg/g under specified process conditions was reported by Hamidzadeh et al. [29]. Similarly, Fe₃O₄ NPs (Fe₃O₄/AC nanocomposites) using a polyol-mediated solvothermal reduction method were successfully used to remove methyl orange (MO) dye from aqueous solution under different process conditions [30].

The goals of this research work are mainly threefold: (a) to test the applicability of the author’s previously synthesized magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite adsorbents in the adsorptive removal of cationic (M) dye from synthetic wastewater, which is very much common practice at solid/liquid adsorption areas; (b) to identify the initial various basis process parameters and their effects on dye adsorption kinetics for future continuous column experimental design with real dye-bearing wastewater effluents before piloting a plant-scale design; and (c) to study the MB dye adsorption kinetics and equilibrium under various process conditions for determination of the adsorbent’s capacity and mechanism of adsorption and its re-generation/reusability via a quick desorption study. Finally, the limitations of this present work have also been discussed.

2. Materials and Methods

2.1. Chemicals

All chemicals used were of analytical grade. The cationic MB dye organic colour contaminant was used to prepare synthetic wastewater for this experiment. The MB dye powder chemical was procured from Sigma Aldrich (St. Louis, MO, USA) with 99.9% purity, and it was used to prepare a 1000 ppm stock solution with the specified amount in distilled water. The various experimental dye solutions were prepared via dilution of stock solution with distilled water. The pH of the medium was adjusted by dropwise addition of 0.1 M HCl or 0.1 M NaOH solution to decrease or increase the solution pH, respectively, which was measured using an Adwa pH meter. A UV/VIS (V-670) spectrophotometer (Perkin Elmer, Waltham, MA, USA) was used to measure MB dye concentration at λ_max = 665 nm. Previously known calibration plots between the obtained absorbance and known dye solution concentration were used to determine unknown dye concentration.

2.2. Adsorbent Magnetic “BC/Fe” Bamboo Charcoal–Iron Oxide Nanocomposite Materials Synthesis and Characterization

The adsorbent magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposites from locally obtained raw bamboo (Phyllostachys pubescens) were prepared using the solvothermal process as per Nishioka and Sen [20] in the chemistry laboratory of University of Hyogo, Japan. The detailed synthesis methods and characterization of this said magnetic “BC/Fe” nanocomposite adsorbent material are available in the author’s previous publication [20]. First, bamboo charcoal was prepared from raw bamboo biomass through a pyrolysis reaction. Generally, biomass-based charcoal/activated carbon is produced via pyrolysis at different temperatures and contact times. The characteristics of pyrolysis-based biochar production strongly depend on pyrolysis time, temperature, and rate of temperature [10,31,32]. Briefly, clean and dry raw bamboo slice biomass was placed in a temperature-controlled muffle furnace (ADVANTEC, KM-160), and a slow pyrolysis reaction was carried out at 800 °C in the presence of N₂ for 3 h at a rate of 2.5 °C per min. The obtained bamboo charcoal was ground in a mill (Osaka Chemical Co., Ltd., Osaka, Japan, New Power Mill PM-2005) to fine powder and sieved through 150 μm mesh screen. The resultant 150 μm size powders were collected and kept in an airtight sample bottle and were used for magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposites synthesis. Similarly, the charcoal powder which passed through the 150 μm mesh screen was also collected and was used in magnetic “BC/Fe” bamboo charcoal iron-oxide nanocomposites [20]. Secondly, a carbon matrix of magnetic and nonmagnetic iron oxide nanoparticles was prepared by the following solvothermal process.

Briefly, a solution mixture of 15 mL of ethylene glycol and 10 mL of water sample was taken in a 50 mL glass beaker and then 2.5 g of synthesized bamboo charcoal and ferric
nitrate (Fe(NO$_3$)$_3$ 9H$_2$O) with different carbon/Fe molar ratios of 35, 40, and 80 were added. Finally, the whole solution mixture was stirred and was kept in a vacuum degassing system for an hour before being transferred to a Teflon-coated autoclave reactor. The reaction was carried out in the sealed Teflon-coated autoclave at 180 ºC and for a period of 2 h reaction time. At the end of the vacuum degassing period the whole mixture was cooled and filtered, and the product was oven dried at 70 ºC for 12 h. The same synthesis procedures were followed with varying reaction times, different solvents, and with different reaction temperatures. Readers are encouraged to go through the author’s previous publication to know the detailed methods and detailed characterization of magnetic “BC/Fe” nanocomposite materials [20]. The synthesized materials were characterized via X-ray diffraction (XRD) using a diffractometer (Rigaku, Tokyo, Japan, Ultima IV) equipped with a Cu Kα radiation source. The phases were identified using files acquired from the Joint Committee on Powder Diffraction Standards (JCPDS), and crystal sizes were determined using Scherrer’s Equation. A scanning electron microscope (JEOL, Tokyo, Japan, JSM-7001F) equipped with an energy-dispersive X-ray microanalysis system was used to examine the morphology and the shape of BC and BC/Fe nanocomposites for which detailed characterization results are presented and discussed elsewhere [20]. Charcoal particle size was measured using a Malvern Hydro 2000S Master Sizer, Malvern Instruments Ltd. (Malvern, UK). In this work, the author just utilized the prepared sample magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite adsorbent materials and tested their applicability in cationic MB dye color removal from synthetic water solution via adsorption with different process conditions.

2.3. Batch Kinetics and Equilibrium Adsorption Experimental Procedure

Batch adsorption kinetics experiments were carried out through shaking a 50 mL reaction mixture solution of a specified amount of adsorbate methylene blue dye concentration and adsorbent materials in several 100 mL plastic bottles placed in a constant-temperature shaker. The kinetic experimental reaction was conducted for a period of 120 min and at 120 rpm. The experimental runs were conducted by varying the initial solution pH, adsorbent dose, initial dye concentration, and temperature at a predetermined time interval. These adsorption batch experiments were carried out as per the method reported by Abuzerr et al. [33], Ahmed and Almaruzzaman [34], and Dawood and Sen [35]. During these kinetic batch adsorption experiments, the sample bottles were periodically taken out at a fixed time interval and the mixture was centrifuged. Finally, residual dye solution concentration at a particular time was determined using a UV spectrophotometer from the supernatant. Equilibrium isotherm adsorption experiments were performed with the wide ranges of initial MB concentration, for period of 2 h (more than equilibrium time) and all other parameters were kept constant during the reaction period. After equilibrium time, the residual dye concentrations were measured. The following Equations (1) and (2) were used to calculate the amount of MB dye adsorption at time t, $q_t$ (mg/g) and % of adsorption, respectively.

$$Q_t = \frac{(C_o - C_t)V}{m}$$  \hspace{1cm} (1)

Additionally,

$$\text{Percentage of adsorption, } \% = \frac{(C_o - C_t)}{C_o} \times 100$$  \hspace{1cm} (2)

where $C_o$ is the initial dye concentration in mg/L, $C_t$ is the dye concentration at time t (min), $V$ is the volume of dye reaction mixture solution in (L), and $m$ is the mass of adsorbent added in solution in (g). Experiments were performed in replicates and hence included error bars in all of my adsorption kinetics results. Here, error bars were standard deviations with custom-specified trial run data.
2.4. Adsorption Kinetics and Equilibrium Adsorption Isotherm Data Analysis

To know the adsorption reaction rate and mechanism of adsorption, the following two well-known linearized kinetic models, pseudo-first-order (PFO) model equation (Equation (3)) and pseudo-second-order (PSO) model equation (Equation (4)), were used to determine their applicability and to determine various kinetic parameter and adsorption mechanism by fitting with the batch adsorption experimental data set. This information is essential to design an adsorber for commercial use.

In the following two linearized kinetic model equations, Equation (3) represents the pseudo-first-order (PFO) and Equation (4) represents the pseudo-second order (PSO) kinetic model equation [35].

\[
\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]

Similarly, the linearized form of the pseudo-second-order kinetic model is presented as Equation (4) [15,35]:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]

where \(q_e\) is the amount of dye adsorption by magnetic bamboo charcoal nanocomposite materials at equilibrium (mg/g) and \(q_t\) is the same but at time \(t\) (mg/g); \(k_1\) represents the pseudo-first-order adsorption rate constant (min\(^{-1}\)), \(k_2\) represents the pseudo-second-order rate constant [g/(mg min)], and \(t\) represents the contact time (min).

The value of pseudo-first-order reaction rate constant, \(k_1\) (min\(^{-1}\)), and the value of \(q_e\) (mg/g) can be obtained from the slope and intercept of a linear plot between \(\log (q_e - q_t)\) vs. time, \(t\) as per Equation (3).

Similarly, the value of pseudo-second-order reaction rate constant \(k_2\) [g/(mg min)] and the equilibrium dye adsorption \(q_e\) (mg/g) can be found from the slope and intercept of a linear plot \(\frac{t}{q_t}\) against time, \(t\), as per Equation (4).

An adsorbent’s capacity, effectiveness, and mechanism of adsorption are commonly determined via the application of the following two traditional but well-known isotherm model equations: one called the Freundlich isotherm model [36] (Equation (5)) and the second one Langmuir isotherm model equation [37] (Equation (6)), which are fitted with the equilibrium isotherm experimental data set.

The linearized Freundlich model isotherm is presented by Equation (5) shown below [35]:

\[
\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e
\]

where:
- \(q_e\): amount of dye adsorbed \((\text{mg g}^{-1})\) at equilibrium.
- \(K_f\): Freundlich adsorption constant \((\text{mg g}^{-1})\).
- \(C_e\): Concentration of dye in solution at equilibrium \((\text{mg L}^{-1})\).
- \(n\): intensity of adsorption constant.

The obtained value of slope and intercept of a linear plot between \(\ln q_e\) against \(\ln C_e\) will give the value of the Freundlich constant, \(n\), rate of adsorption, and \(K_f\) from the intercept of the plot.

The linear form of the Langmuir isotherm model-II equation is shown below [35]:

\[
\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right) \left(\frac{1}{C_e}\right) + \left(\frac{1}{q_m}\right)
\]

where:
- \(q_m\): Maximum adsorption capacity of adsorbent \((\text{mg g}^{-1})\).
- \(K_a\): Langmuir isotherm constant \((\text{L mg}^{-1})\).
The feasibility of the adsorption reaction can be determined from the obtained dimensionless separation factor ($R_L$) calculations as per following Equation (7) at different initial dye concentration, $C_0$ (mg/L).

$$R_L = \frac{1}{1 + (K_a C_0)}$$

where $K_a$ is the Langmuir isotherm constant ($\frac{L}{mg}$) and the $R_L$ values in the range of $0 < R_L < 1$ indicates favorable adsorption [38].

3. Results and Discussion

3.1. Characteristics of Synthesized Adsorbent Magnetic “BC/Fe” Bamboo Charcoal–Iron Oxide Nanocomposite Materials

The influences of various synthesized system parameters, including reaction time, temperature, BC/Fe molar ratio, and types of solvents on the amount of magnetic magnetite particles, along with nonmagnetic humboldtine production, shapes, and sizes were analysed via XRD and SEM analyses for which detailed data analysis was reported in the author’s own earlier publication [20]. For example, Figure 2 (adapted from Nishioka and Sen [20] with written permission) presents the XRD pattern of synthesized magnetic bamboo charcoal–iron oxide nano particles via solvothermal process at different reaction times. The BC/Fe molar ratio was 35, and the reaction temperature was 180 °C. The production of nano-sized iron-oxide particles in the range of 13.1 nm to 15.6 nm was obtained with the changes in solvothermal reaction times. Most of the obtained peaks at 2θ values of 18.48°, 18.89°, 22.92°, and 29.76° correspond to the (−202), (200), (002), and (−402) crystal planes, respectively. This indicates the presence of humboldtine (H), whose empirical formula is Fe(C₂O₄)₂H₂O (Figure 2a). The presence of magnetite of Fe₃O₄ (M), which is shown in Figure 2b,c, was confirmed by observed peaks at 2θ values of 30.11°, 35.46°, 43.45°, and 58.76° that correspond to the (220), (311), (400), and (511) planes as per JCPDS#1309-1 at reaction times of 1.5 h and 2 h, respectively. These magnetic properties are due to the presence of magnetic magnetite along with nonmagnetic humboldtine iron oxide particles embedded within a bamboo charcoal surface matrix which was also supported via SEM analysis [20]. The corresponding surface morphology and texture of synthesized magnetic bamboo charcoal–iron oxide nanocomposite materials at different BC/Fe molar ratios according to SEM studies were reported elsewhere [20]. SEM studies also clearly indicate the distribution of magnetic magnetite and nonmagnetic humboldtine iron-oxide particles on the surface of bamboo charcoal (BC) [20]. The particle size distribution of bamboo charcoal (BC) composite was also determined using a Malvern MasterSizer 2000S with the Hydro 2000S (A), and the results are presented in Figure 3. It can be seen from the graph above that the most common sample particle size is 0.182 μm, which is evident at the highest volume percent (6.34%) of the particle size distribution (Figure 3). The adsorbent material’s specific surface area was 0.192 m²/g.

Figure 2. XRD patterns of magnetic “BC/Fe” bamboo charcoal nanocomposites at different reaction periods (adopted from [20] with written permission).
3.2. Studies on MB Dye Adsorption Kinetics by Magnetic “BC/Fe” Bamboo Charcoal–Iron Oxide (BC/Fe) under Different Process Conditions

3.2.1. Effect of Solution pH

The initial pH of the solution is one of the most important factors which strongly influences the amount of contaminant adsorbed by adsorbent from the bulk fluid medium. This is because of changes in adsorbent surface charges and surface chemistry as well as changes in adsorbate chemistry with the change in solution pH. There are a number of review articles, including the author’s review articles, where a large number of information on MB dye adsorption at different influential process parameters such as adsorbate dye concentration, adsorbent dose, solution pH, temperature, etc., has been compiled [7,33], which also supports the results of this current research work. Therefore, each batch of kinetic experiments was carried out at three different pH values covering acidic, neutral, and basic ranges, as the pH of real textile effluents varies from acidic medium to basic medium and depends on the type of cloth processed as well [7,25,32,33]. Figure 4 presents the effect of solution pH on MB dye adsorption kinetics, for which other experimental conditions were as follows: initial dye concentration ($C_0$) = 20 ppm, adsorbent “BC/Fe” bamboo charcoal–iron oxide nanocomposite dose = 20 mg, and temperature = 30 °C. The solution pH was adjusted using 0.1 M HCl or 0.1 M NaOH solutions. From Figure 4, there was an increase in the amount of methylene blue (MB) dye adsorption, $q_e$ (mg/g), from 9.87 mg/g to 17.62 mg/g with the increase in solution pH from 3 to 7, and then a reduction in the amount of dye adsorption, $q_e$ (mg/g), was found at a solution pH of 10 for a 20 ppm MB dye solution. The maximum amount of MB dye adsorbed was 24.12 mg/g at a solution pH of 7 after 10 min reaction time. At high solution pH greater than 3, the adsorbent surface becomes more and more negatively charged and hence more cationic dye MB molecules areadsorbed, mainly due to the presence of a strong electrostatic force of attraction between the cationic adsorbate and the negatively charged adsorbent surface. In addition, at high solution pH, there is also less competitive adsorption between the lower presence of H$^+$ ions and major cationic MB adsorbate. For lower acidic solution pH, less MB dye adsorption onto magnetic “BC/Fe” nanocomposite adsorbent is due to the presence of competitive adsorption between hydronium (H$_3$O$^+$) ions and MB dye molecules for the same available adsorption sites [25,38–40].
neutral, and basic ranges, as the pH of real textile effluents varies from acidic medium to basic medium and depends on the type of cloth processed as well [7,25,32,33]. Figure 4 presents the effect of solution pH on MB dye adsorption kinetics, for which other experimental conditions were as follows: initial dye concentration (C₀) = 20 ppm, adsorbent "BC/Fe" bamboo charcoal–iron oxide nanocomposite dose = 20 mg, and temperature = 30 °C. The solution pH was adjusted using 0.1 M HCl or 0.1 M NaOH solutions. From Figure 4, there was an increase in the amount of methylene blue (MB) dye adsorption, qₑ (mg/g), from 9.87 mg/g to 17.62 mg/g with the increase in solution pH from 3 to 7, and then a reduction in the amount of dye adsorption, qₑ (mg/g), was found at a solution pH of 10 for a 20 ppm MB dye solution. The maximum amount of MB dye adsorbed was 24.12 mg/g at a solution pH of 7 after 10 min reaction time. At high solution pH greater than 3, the adsorbent surface becomes more and more negatively charged and hence more cationic dye MB molecules are adsorbed, mainly due to the presence of a strong electrostatic force of attraction between the cationic adsorbate and the negatively charged adsorbent surface. In addition, at high solution pH, there is also less competitive adsorption between the lower presence of H⁺ ions and major cationic MB adsorbate. For lower acidic solution pH, less MB dye adsorption onto magnetic "BC/Fe" nanocomposite adsorbent is due to the presence of competitive adsorption between hydronium (H₃O⁺) ions and MB dye molecules for the same available adsorption sites [25,38–40].

Figure 4. Effect of solution pH on MB dye adsorption kinetics by magnetic “BC/Fe” nanocomposite adsorbent. The condition of all experiments was initial MB dye concentration (C₀) = 20 ppm, adsorbent dose (m) = 20 mg, temperature = 30 °C, rpm = 120, and reaction volume (V) = 50 mL.

3.2.2. Effect of Contact Time and Adsorbate MB Dye Concentration and Adsorption Kinetics

Figure 5 shows that the amount of dye adsorption, qₜ (mg/g), by magnetic “BC/Fe” bamboo-charcoal–iron oxide increases with the variations in dye concentration of 10, 20, and 30 ppm. There were two reasons behind the selection of dye concentration ranges of 10, 20, and 30 ppm for this batch adsorption kinetics: (a) to test the adsorbent’s effectiveness in the removal of low contaminant adsorbate concentration and (b) the dye concentration in textile industry effluents ranges from 0.01 g/L to 0.25 g/L depending on the process and type of dyes [33]. From Figure 5, the amount of dye adsorption, qₑ (mg/g), also increases with time and an equilibrium is reached within 120 min. Interestingly, the whole adsorption kinetics at the solid/liquid interface can be considered as more or less three mechanistic steps: (i) a rapid movement of dye solutes from the bulk liquid phase to the surface of the solid adsorbent, (ii) a slow intraparticle transition stage, and (iii) slow intramolecular diffusional mass transport through the porous adsorbent until an equilibrium adsorption stage is attained [7,35]. The initial fast adsorption was due to the existence of a large concentration difference driving force for mass transfer between bulk phase adsorbate solute and available active sites on the adsorbent surface, and adsorbate solute molecules quickly occupied the adsorbent surface via diffusional and convection mass transfer mechanisms. Then, after some time, there was a shortage of available active sites as well as lower adsorbate concentration; hence, slow mass transfer took place, and equilibrium adsorption was reached. At this stage, the adsorbent surface may become saturated with adsorbate molecules, and no more adsorption takes place.
To know the adsorption reaction kinetics and to determine the various reaction kinetic parameters, two commonly used kinetic model equations, pseudo-first-order (PFO) and pseudo-second-order (PSO), were applied with the batch adsorption kinetic experimental data set at various initial dye concentrations as per Equations (3) and (4). The PFO model fitted plots are not presented here because of poor linear regression coefficient ($R^2$) values (70%) for the fitted PFO model. Equation (3) indicated the inapplicability of this PFO kinetic model. Additionally, the pseudo-first-order (PFO) model predicted a significantly lower amount of dye adsorbed at equilibrium, $q_e$ (mg/g), from the experimental value. However, using the PSO model Equation (4) with the experimental results fitted well, which is shown in Figure 6, with significantly high linear regression coefficient ($R^2$) values of greater than 99% at different initial dye concentrations.

**Figure 5.** Effect of adsorbate initial MB dye solution concentrations on adsorption kinetics using magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite adsorbent. Other experimental conditions were as follows: pH = 3, adsorbent dose (m) = 20 mg, temperature = 30 °C, rpm = 120, and reaction volume (V) = 50 mL.
and pseudo-second-order (PSO), were applied with the batch adsorption kinetic experimental data set at various initial dye concentrations as per Equations (3) and (4). The PFO model fitted plots are not presented here because of poor linear regression coefficient ($R^2$) values (70%) for the fitted PFO model. Equation (3) indicated the inapplicability of this PFO kinetic model. Additionally, the pseudo-first-order (PFO) model predicted a significantly lower amount of dye adsorbed at equilibrium, $q_e$ (mg/g), from the experimental value. However, using the PSO model Equation (4) with the experimental results fitted well, which is shown in Figure 6, with significantly high linear regression coefficient ($R^2$) values of greater than 99% at different initial dye concentrations.

Figure 6. The linear fitting of pseudo-second-order (PSO) kinetic model equation (Equation (4)) with the batch experimental MB dye adsorption kinetics data at different initial dye concentrations.

From Figure 6, the amount of adsorption at equilibrium ($q_e$), pseudo-second-order rate constant ($K_2$), and value of linear regression coefficient ($R^2$) are determined and tabulated in Table 1.

Table 1. Various kinetic model fitting parameter values.

<table>
<thead>
<tr>
<th>Initial Dye Concentration in ppm</th>
<th>Pseudo-Second-Order Rate Constant, $K_2$ (g/mg-min)</th>
<th>Calculated Amount of Dye Adsorption at Equilibrium, $q_e$ (mg/g)</th>
<th>Experimental Amount of Dye Adsorption at Equilibrium, $q_e$ (mg/g)</th>
<th>Linear Regression Coefficient, $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1945</td>
<td>9.53</td>
<td>9.50</td>
<td>0.995</td>
</tr>
<tr>
<td>20</td>
<td>0.0799</td>
<td>13.36</td>
<td>14.25</td>
<td>0.994</td>
</tr>
<tr>
<td>30</td>
<td>0.0835</td>
<td>13.48</td>
<td>15.12</td>
<td>0.9965</td>
</tr>
</tbody>
</table>

From Table 1, the amount of MB dye adsorption using magnetic “BC/Fe” bamboo-charcoal–iron oxide nanocomposite adsorbent increased with the increase in dye concentration, but the rate constant, $K_2$, decreased with the increase in dye concentration. Furthermore, it can be noticed from Table 1 that the calculated amount of dye adsorption at equilibrium ($q_e$) from model fitting data and the experimental amount of adsorption at equilibrium ($q_e$) are very close to each other, and low error function gives additional confirmation for the applicability of this PSO model, which is also further confirmed by high linear regression coefficient values of $R^2$ (>99%). This PSO model applicability and variation in rate constant with methylene blue (MB) dye concentration indicate the nonexistence of diffusional adsorption rate limitations, that a covalent bond may be formed during adsorption between adsorbate and adsorbent, and that the adsorption mechanism is mainly governed by multistep. The overall process does not depend on internal or external mass transfer resistances [41,42].
3.2.3. MB Dye Adsorption Kinetics under Varying Adsorbent Doses

Here, MB dye batch adsorption kinetics were carried out through varying adsorbent dosages of 0.04, 0.06, and 0.08 g/100, which were within the range of activated carbon adsorbent dosages of 0.01 to 0.3 g/100 mL for spent textile dyeing wastewater treatment [43]. The variation in the amount of MB dye with the adsorbent is shown in Figure 7. All other experimental conditions remained constant, with $C_0 = 10$ ppm, temperature $T = 30^\circ$C, and solution $pH = 3$, respectively. It was observed that with the increase in adsorbent dosages, the amount of MB dye adsorption, $q_t$ (mg/g), decreased from 7.02 mg/g to 2.1 mg/g at 80 min for an initial dye concentration of 10 ppm (Figure 7) while the percentage dye removal was increased, for which a plot is not presented here. This may be due to division on flux or the concentration gradient between bulk solute concentration and adsorbent surface [40] and, therefore, the amount of dye per unit weight of adsorbent, $q_t$ (mg/g), was decreased with an increase in adsorbent mass. Similar behavior was reported by various researchers [6,25,39,40].

![Figure 7](image-url)

**Figure 7.** Effect of adsorbent dosages on MB dye adsorption kinetics by magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite materials. Experimental conditions were: $C_0 = 10$ ppm, temperature $T = 30^\circ$C, rpm = 120, $V = 50$ mL, and solution $pH = 3$.

3.2.4. Effect of Solution Temperature

One of the crucial physiochemical process parameters is the temperature, which determines whether the adsorption reaction is exothermic or endothermic in nature. Various thermodynamic parameters can be estimated from temperature-effect batch adsorption results. Therefore, system temperature affects MB dye batch adsorption kinetic results using magnetic nanocomposite adsorbents, which are presented in Figure 8 at three different temperatures of 30, 45, and 60 $^\circ$C, respectively. All other experimental conditions were initial dye concentration $C_0 = 20$ ppm, $pH = 7$, adsorbent mass $m = 20$ mg, $V = 50$ mL, $m = 20$ mg, and rpm = 120, remaining constant during the adsorption reaction. The maximum amount of adsorption, $q_t$ (mg/g), was 24.45 mg/g that occurred at a temperature of 30 $^\circ$C and the lowest amount of adsorption of 7.05 mg/g occurred at a temperature of 60 $^\circ$C; hence, adsorption density, $q_t$ (mg/g), as well as the percentage of MB dye removal, decreased with the increase in temperature. This effect indicates that the adsorption reaction
is exothermic in nature, and this may be due to an increase in the kinetic energy of dye molecules with the increase in solution temperature, which ultimately reduces the strength of interaction between adsorbate dye molecules and the active sites of adsorbent magnetic “BC/Fe” nanocomposite materials with the temperature rise [8]. Similar temperature effects on MB dye adsorption by nanomagnetic adsorbents were observed by various investigators [8,44].

Figure 8. Effect of temperature of methylene blue (MB) dye adsorption kinetics using magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite adsorbent materials.

3.3. Mechanism of Adsorption and Isotherm Studies

The adsorption isotherm is important for describing how the adsorbate will interact with the adsorbent and gives an idea of the adsorption capacity of the adsorbent [35]. The MB dye adsorption equilibrium experiments were carried out with the range of initial dye concentrations of 20, 40, 60, and 80 ppm for a period of 2.5 h, which is more than the equilibrium time. The other experimental parameters were adsorbent dose = 40 mg, solution pH = 10, temperature = 30 °C, and rpm = 120. The two most used equilibrium models, Freundlich isotherm and Langmuir isotherms model Equations (5) and (6), were fitted with the experimental equilibrium results and isotherm model parameters were determined. The Freundlich model is developed based on multi-layer adsorption, assuming a heterogeneous adsorbent surface [3]. On the other hand, the Langmuir isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical adsorption sites [38]. The Freundlich isotherm model (Equation (5)) was found to be fitted well with a high linear regression coefficient, $R^2$, value of 0.986, which is presented in Figure 9. From Figure 9 (a linear plot of ln $q_e$ vs. ln $C_e$ as per Equation (5)), the Freundlich constant, $K_f$ (adsorption capacity), was determined from the intercept of the linear plot, which is equal to 3.205 mg/g, and the rate of adsorption, $n$, was obtained from slope of the linear plot with a value of 1.30, which is greater than 1, indicating a physical and favorable adsorption process [35].
Similarly, a linear plot of Langmuir-II as per Equation (6) was plotted between $1/q_e$ vs. $1/C_e$, which is presented in Figure 10. The very high fitted linear regression coefficient ($R^2$) values of 0.9861 to 0.9918 obtained strongly indicate the applicability of both Freundlich and Langmuir isotherm models within the current experimental equilibrium study data. The values for $K_f$ and $q_m$ for Langmuir isotherm model II are 0.0207 L/g and 111.11 mg/g, respectively. The obtained adsorption capacity, $q_m$ (mg/g), of 111.1 in this current study on magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite adsorbents for MB dye, is comparable with other cost-effective biomass- and clay-mineral-based adsorbents, including magnetic nanomaterials adsorbents such as $q_m$ (200 mg/g) for magnetic charcoal composite [1], (60.4 mg/g) of magnetic chitosan [45], (25.25 mg/g) of activated charcoal [46], (142 mg/g) of Chitosan clay [47], (17–51 mg/g) for G-Fe₃O₄/CA nanocomposite [48], (147.71 mg/g) for activated charcoal–magnetic nanocomposite [34], and (396.7 mg/g) of magnetic nanocomposite [27], respectively.

![Figure 9](image9.png)

**Figure 9.** A linear plot for Freundlich isotherm model.

![Figure 10](image10.png)

**Figure 10.** A linear plot for Langmuir-II isotherm model.
The obtained dimensionless separation factors ($R_L$) using Equation (7) at different initial dye concentrations were 0.7072, 0.5470, 0.3816, and 0.3164, which confirmed the favorable adsorption of methylene blue (MB) dye onto magnetic bamboo charcoal–iron oxide (BC/Fe) nanocomposite adsorbents as all are in the range the values of 0 to 1. Many researchers also reported similar results on methylene blue dye removal using various adsorbents including magnetic nanomaterial adsorbents [7,8,28,39].

4. Recovery, Regeneration by Desorption, Reusability, and Limitations of This Present Work

To reduce waste production and secondary pollution, if any, and to reduce operating costs and to make the overall technology cost-effective for further reuse, the regeneration of loaded adsorbents is an essential process. In this research direction, different regeneration methods, process optimization, and their advantages/disadvantages have been compiled and reported by various investigators [4,14,15,33,34]. For cyclic operation, the regeneration of the material can be achieved either through thermal treatment or chemical treatment using desorbing solvents such as NaOH, HCl, acetone, methanol, ethanol, acetonitrile, acetic acid, etc.

In this present study, after attaining adsorption equilibrium, the MB-dye-loaded magnetic “BC/Fe” nanocomposite adsorbent materials were separated from the aqueous phase through applying a strong external magnet. After that, the loaded adsorbent material was oven-dried at 383 K for 40 min and used for the desorption experiment. The desorption experiment was carried out in a 250 mL conical flask with 0.1 g of dye-loaded “BC/Fe” adsorbent, subsequently followed by the addition of 10 mL 0.1 M HCl/methanol (1:9, v/v) desorbing solvent placed in a constant temperature shaker. The experimental desorption reaction was conducted for a period of 120 min and at 120 rpm. It showed a desorption efficiency of 80.25% for these experimental conditions. However, a detailed desorption study with various desorbing solvents, various heating options, and process optimization must be conducted in a future study before applying them in real field wastewater treatment systems. Thus far, we have not undertaken any reusability tests and performances with this regenerated adsorbent due to limited time and limited resources for which future studies are required. In actual wastewater treatment plants, usual practice is to treat with an adsorptive separation column integrated with an adsorbent regeneration unit with an additional standby treatment system for continuous operation. Therefore, this laboratory-based batch adsorption study has been carried out with different objectives and certainly not for large-scale industrial applications, for which continuous column operation under different process conditions must be studied. The primary purpose of this commonly practiced laboratory-based batch methylene blue dye adsorption study using synthesized magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite materials with a synthetic dye-bearing wastewater system are of three folds: (a) to test the effectiveness of prepared magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite adsorbent materials in the adsorptive removal of cationic MB dye from synthetic wastewater, and particularly how effective it is in low contaminant dye concentration removal; (b) to identify the initial various basis process parameters and their effects on dye adsorption kinetics for future continuous column experimental designs with real dye-bearing wastewater effluents before piloting a plant-scale study; and (c) to study the MB dye adsorption kinetics and equilibrium adsorption under various process conditions for the determination of the adsorbent’s capacity and mechanism of adsorption and its re-generation ability through a quick desorption study.

5. Conclusions

In this study, previously prepared new raw bamboo biomass-based magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite materials were used as an effective adsorbent in the removal of methylene blue dye from synthetic dye-bearing effluents, which is highly comparable and sometimes even better to many costly alternative magnetic adsorbents. Different influential process parameters, including adsorbate dye concentration, adsorbent
dose, solution pH, and temperature, have been identified and optimized via laboratory-based batch adsorption kinetic and equilibrium studies. The mechanism of adsorption was also identified and analyzed here. The kinetic study found that the amount of adsorption increased with contact time and equilibrium was reached within 120 min. A pseudo-second-order kinetic model was fitted well with the experimental kinetics data under different process conditions, and kinetic model parameters were determined from the fitted model equation, which is essential for a continuous adsorber design column operation. The kinetic experiments further demonstrated that the adsorption of methylene blue dye onto magnetic “BC/Fe” bamboo charcoal–iron oxide nanocomposite were multi-step processes: quick external film diffusional mass transfer from the bulk phase to the surface of magnetic composite adsorbent, followed by intra-particle diffusional mass transport through the interior of the adsorbent material. Isotherm studies confirmed the applicability of both Freundlich and Langmuir isotherm models to explain the experimental isotherm data. The maximum monolayer adsorption capacity was found to be 111.11 mg/g towards MB dye at a solution pH of 10, which is comparable to other magnetic adsorbents. The dimensionless separation factor, \( R_L \), also indicates favorable adsorption. The effective regeneration of the methylene blue dye-loaded magnetic “BC/Fe” bamboo charcoal nanocomposite with a desorption efficiency of 80.25% confirmed its potential application in industrial dye-bearing effluent treatment, for which detailed future continuous column experiments with more reusability tests and process optimization studies are required.

**Funding:** This work was funded by the Deputyship for Research and Innovation, Ministry of Education in Saudi Arabia (Project number—INST 167).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** All experimental data and model fitting data are presented, analyzed, discussed, and properly cited in this publication.

**Acknowledgments:** The authors extend their appreciation to the Deputyship for Research and Innovation, Ministry of Education in Saudi Arabia, for funding this research work (Project number—INST 167).

**Conflicts of Interest:** The author declares that he has no conflict of interest.

**References**


31. Bai, B.; Sun, G.; Cao, Q.; Cao, Q.; Chen, J.; Tian, S.R.; Cao, Q.; Cao, Q.; Cao, Q. Bioremediation of congo red dye in immobilized batch and continuous packed bed bioreactor by brevibacillus parabreviss using coconut shell biochar. *Bioresour. Technol.* 2018, 252, 37–43. [CrossRef]


41. Diez, E.; Redondo, C.; Gomez, J.M.; Miranda, R.; Rodriguez, A. Zeolite adsorbents for selective removal of Co(II) and Li (II) from aqueous solution. Water 2023, 15, 270. [CrossRef]


Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.