*Desalination and Water Treatment*
www.deswater.com

doi: 10.1080/19443994.2015.1024742

57 (2016) 7345–7357
April

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# *Calligonum polygonoides* biomass as a low-cost adsorbent: surface characterization and methylene blue adsorption characteristics

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Received 1 July 2014; Accepted 2 February 2015

## ABSTRACT

In this present research work, *Calligonum polygonoides* (CP) was used as an effective biosorbent for the methylene blue (MB) removal from aqueous solution. The biosorbent was used without any chemical treatment. The biosorbent was characterized by various techniques, such as Fourier transform infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy (SEM). The particle size and surface area were measured by using particle size analyzer and Brunauer–Emmett–Teller (BET) equation. The SEM and BET results expressed that the adsorbent has porous nature. Effect of various experimental conditions, such as initial concentration of MB, initial pH, contact time, dosage of biosorbent, and stirring rate, were also investigated on adsorption capacity of MB on CP. The contact time experiment indicated that the rate of adsorption of MB is a rapid process and equilibrium is reached in 1 h. The kinetics study expressed that MB adsorption on biosorbent followed the pseudo-second order kinetic equation with correlation coefficient value ($R^2$) of 0.999. The study revealed that CP proved to be an effective, inexpensive, alternative, and environmentally friendly biosorbent for MB from aqueous solution.

*Keywords:* Methylene blue; *Calligonum polygonoides*; Characterization adsorption kinetics

## 1. Introduction

Environmental pollution is a severe and challenging problem all over the world because of the fast growth in population, science, technology, and industries. The effluents coming from industries containing both inorganic and organic toxic substances which are being discharged into the surface water have severely affected the biodiversity and aquatic life [1–3]. Among these pollutants, synthetic dyes are considered to be the most common and toxic water pollutants [4,5].

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Among these dyes, some cause depletion of the dissolved oxygen content of water, severely affecting aquatic life as a result. In addition, some of the textile dyes are carcinogenic and toxic to living organisms and have adverse effect on human health, domestic animals, and wildlife that come into contact with the water containing these dyes [6,7].

Among the dyeing agents, methylene blue (MB),a heterocyclic aromatic chemical compound, is extensively used in textile industries to colorize the products. MB and MB-like other dyes can cause eye burns in humans and animals, skin irritation, dyspnea, convulsions, cyanosis, tachycardia, and if ingested can cause gastrointestinal tract irritation, nausea, vomiting, diarrhea, etc. MB is stable and has large organic molecular structures which show resistance to heat and light, so it does not easily degrade [3,8–12]. Due to these toxicological and hazardous effects of MB on environment and subsequently on living organism, the removal of MB from wastewater is a key challenging task for researchers and an important area of research directed toward a better life.

There are various methods used for removal of dyes from aqueous media, such as flotation, chemical coagulation, membrane filtration, ion exchange, biological and chemical oxidation, and adsorption [13,14]. However, most of these methods have some major shortcomings, such as the high concentration of dye , high cost, insufficient dye removal, and high energy requirement [15].

Presently, the sorption technique is proved to be quite simple, affective, economic, attractive, and most easily available technique for the dye removal from the dye-bearing wastewater [14,16,17]. Activated carbon, most widely and commonly used adsorbent, has a good potential for the removal of organic pollutants because of its surface porous nature [18]. However, activated carbon is both very expensive and its regeneration challenging, which increase the cost of wastewater treatment. Thus, there is a great demand for such type of adsorbents, which are made from low-cost material, are environmentally benign, and have great potential for adsorption without any additional expensive pretreatment [19,20]. Thus, there is a great demand for such type of adsorbents which are cheaper and still have high adsorption capability toward pollutants and dyes without any additional expensive pretreatment. Presently, cellulose and lignocellulosic biomass have got considerable attraction because of their abundance in nature, effectiveness, low cost, and environmentally friendly nature of biopolymers. Thus, biosorption has been proved to be the most effective technique for the removal of MB and metal ions from the aqueous solution [21–26].

In this research work, *Calligonum polygonoides*, which had been used as a fuel for domestic cooking purposes, was collected from district Lakki Marwat, Khyber Pakhtunkhawa, Pakistan, and utilized as biosorbent without any chemical treatment for MB removal from aqueous solution. The utilization of this alternative, abundantly available, and environmentally benign biosorbent will solve both waste discarding problems as well as give access to an inexpensive material for wastewater decontamination.

## 2. Materials and methods

### 2.1. Methylene blue

All the chemicals used in the present research work were of analytical grade and purchased from Sigma–Aldrich, BDH, and Merck. MB with chemical formula: $C_{16}H_{18}ClN_3S_3H_2O$, was used as model adsorbate to study the adsorption capacity of biosorbent (Fig. 1). The stock solution of 1,000 ppm of MB was prepared and subsequently their solutions of desired concentration were prepared by applying the dilution formula ($M_1V_1 = M_2V_2$).

### 2.2. Preparation of biosorbent

The *C. polygonoides* was collected from local areas of District Lakki Marwat, Khyber Pakhtunkhwa, Pakistan. The *C. polygonoides* was dried in sunlight and washed with double-distilled water to remove sand, dust, and other soluble impurities. The sample was dried in oven at 100˚C for 5 h. Biosorbent was prepared by grinding the plant into powder using grinder machine. The powder was dried in oven at 80˚C and then stored in airtight glass bottle.

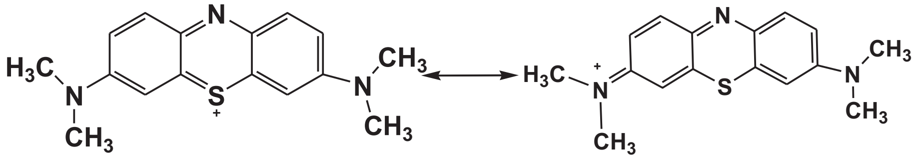

Fig. 1. Resonance structure of MB (3,7-bis(dimethylamino)phenothiazine-5-ium chloride) [27].

### 2.3. Characterization of biosorbent

The surface structure of biosorbent was analyzed using scanning electron microscopy (SEM) (JMT-300, JEOL) and energy dispersive X-ray spectrometry (EDX) was used for elemental analysis. The surface area of *C. polygonoides* was determined using Brunauer–Emmett–Teller (BET) method and the pore size diameter was obtained using adsorption/desorption isotherm of nitrogen gas at 77.0 K employing Micromeritics ASAP 2010 apparatus. The chemical structure and nature of functional groups of *C. polygonoides* were studied using Fourier transform infrared spectroscopy (FTIR) transmission spectra on a Perkin Elmer Spectrum One. For FTIR spectra measurement, sample was mixed with KBr in the ratio of 1/1,000 and pressed into the pellet using a Perkin Elmer hydraulic pump. FTIR spectrum was recorded in the wave number range from 4,000 to 450 $\text{cm}^{-1}$ with resolution of 5 $\text{cm}^{-1}$. The particle size distributions were measured using Mastersizer 2000 Ver. 5.54, Serial number: Mal 18486 (Malvern Ltd., UK). For particle size distribution measurement, 0.5 g of *C. polygonoides* was loaded into the tray and dispersed by compressed air to bring sample into laser beam for measurement of the particle size distributions. To investigate the thermal characteristic or weight loss profiles of *C. polygonoides*, a thermogravimetric analyzer (Pyris-1, Perkin Elmer, Shelton, CT) was used over the temperature range from 50 to 800˚C at heating rate 10˚C/min.

### 2.4. Batch experiments

The pure biosorbent of *C. polygonoides* was prepared and used for removal of MB from aqueous solution. The biosorption experiment of MB was conducted by adding 100 mg of biosorbent to 25 mL of aqueous solution of MB dye (4–10 mg/L) in 50 mL conical flask and shaken at 300 rpm in orbital shaker at 298 K. After a specific interval of time, sample aliquots were withdrawn and centrifuged to separate the dye-loaded biosorbent from the dye solution. The remaining concentration of MB was measured spectrophotometrically by measuring the absorbance of the supernatant (dye solution) left after centrifugation. To find the optimum experimental conditions for MB removal, the effect of time (10–120 min), initial dye concentration (2–10 mg/L), biosorbent loading (20–100 mg), and shaking velocity (100–600 rpm) were thoroughly studied.

The color-removal efficiency ($R$) and adsorption capacity ($q$) of *C. polygonoides* were measured by applying the following Eqs. (1) and (2), respectively.

$$(R\%) = \left(\frac{C_0 - C_t}{C_0}\right)100 \tag{1}$$

$$q_t = (C_0 - C_t)V/m \tag{2}$$

where $q_t$ (mg/g) is the amount of MB adsorbed at time $t$; $C_0$, $C_t$, and $C_e$ (mg/L) are concentrations of MB at initial, time $t$, and equilibrium, respectively; and $V$ is the solution volume and $m$ (g) is the mass of biosorbent.

### 2.5. Optimization of physicochemical parameters

The adsorption capacity of MB on the surface of biosorbent depends upon the chemical structure and properties of MB and also on the chemistry and morphology of biosorbent surface. Various parameters which affect the adsorption capacity of MB dye on biosorbent were studied and optimized as follows.

#### 2.5.1. Effect of biosorbent dose

The effect of biosorbent dose (concentration) on biosorption of MB dye was studied by adding different amounts (0.05–1.50 g) of biosorbent.

#### 2.5.2. Effect of time

To study the equilibrium time required for the biosorbent to bind to the dye molecules, 100 mg of biosorbent and specified concentrations of the dye solution (4, 6, 8, 10, and 20 mg/L) were added into a 50 mL bottle. The solution was shaken for varying periods of time (10, 20, 30, 60, 90, and 120 min) at 150 rpm and 298 K. After incubation for specific contact time, the supernatant was analyzed for the determination of the concentration of MB in the solution.

#### 2.5.3. Effect of initial dye concentration

In order to investigate the effect of the contact time, various experiments were carried out using different initial concentrations of MB dye (2, 4, 6, 8, and 10 mg/L). The dose of adsorbent, contact time, stirring speed, and temperature were maintained constant throughout the experimental work unless otherwise specified.

### 2.6. Kinetics study

To study the adsorption mechanism of MB on biosorbent, pseudo-first- and pseudo-second-order kinetic models were used.

### 2.6.1. The pseudo-first-order equation

The pseudo-first-order kinetic model or Lagergren kinetic equation is generally expressed as follows:

$$\log(q_e - q_t) = \log q_1 - \frac{k_1\ t}{2.303} \quad (3)$$

where $q_e$ is the amount adsorbed (mg/g) at equilibrium, $q_t$ is the amount adsorbed (mg/g) at any time, and $k_1$ is the adsorption rate constant for pseudo-first-order ($s^{-1}$).

### 2.6.2. The pseudo-second-order model

If the rate of sorption is a second-order mechanism, the pseudo-second-order kinetic rate equation is used and it is expressed as:

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \quad (4)$$

$$\frac{dq_t}{(q_2 - q_t)^2} = k_2 dt \quad (5)$$

By integration of Eq. (5) for the boundary conditions when $t = 0$ and $q_t = q_i$

$$\frac{1}{(q_2 - q_t)} = \frac{1}{q_2} + k_2 dt \quad (6)$$

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \quad (7)$$

If $\frac{t}{q_t}$ is plotted against $t$, it gives a straight line, which means that the adsorption follows pseudo-second-order kinetics. This model is based upon the assumption that if the rate-limiting step may be chemisorption, which involves valence forces resulting from electron sharing or electron exchange between the adsorbent and adsorbate.

## 3. Results and discussion

### 3.1. Effect of particle size

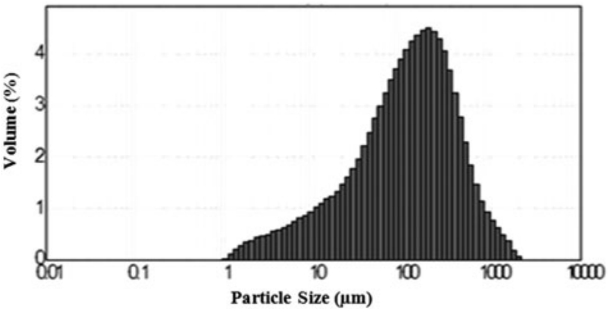

Fig. 2. Particle size distributions of biosorbent.

Fig. 2 shows the particle size distributions of biosorbent after grinding with grinding machine. The result shows that the biosorbent particles have various diameter particles. Commonly, by decreasing the particle size of biosorbent, the adsorption of dye is increased because of the availability of more and more surface area.

In other words, we can say that the adsorption capacity of dye on the adsorbent surface is directly proportional to the exposed surface and inversely related to the particle diameter of non-porous material. By increasing the particle size, the number of particles decreases, and hence surface area starts decreasing and ultimately the adsorption capacity is decreased [28,29].

### 3.2. Effect of surface area

The process of adsorption is a multistep complex phenomenon and therefore many factors affect the phenomenon. Among these factors, the pore size of adsorbent significantly affects the adsorption process. Pore size is generally classified into various groups such as micropores (<2 nm diameter), mesopores (2–50 nm), and macropores (>50 nm). The surface chemistry of adsorbent and its pore structure considerably affects the adsorption of big molecules like MB into its structure [30]. MB has a molecular cross-sectional diameter of about 0.8 nm and cannot easily penetrate materials with pores smaller than 1.3 nm [31]. The surface area of *C. polygonoides* ash depends on the amorphous carbon content. During the dye adsorption process, the diffusion of dye molecules to the active sites takes place first, which is followed by attachment of these dye molecules to the active sites. The pore size and total pore volume thus play a decisive role in the adsorption process [32].

Fig. 3 and Table 1 show that adsorbent has a significant surface area and wide pore size distributions. The BET surface area of adsorbent is 16.933 $m^2/g$, whereas adsorption/desorption surface area of pores of *C. polygonides* is 13.843/9.026 $m^2/g$. For *C. polygonides*, the single point total pore volume of pores ($d < 1098$Å

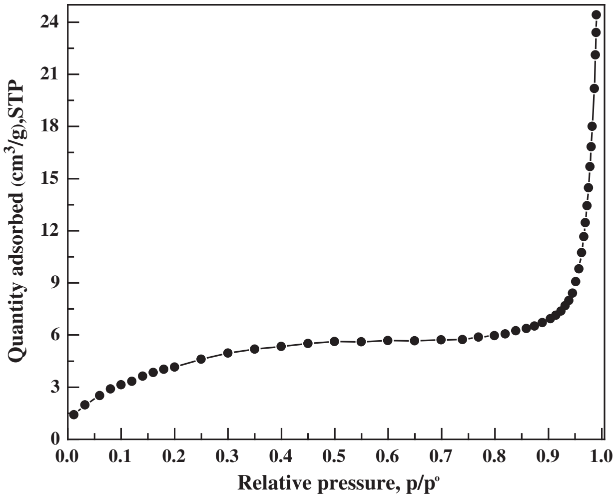

Fig. 3. $N_2$ adsorption isotherm of biosorbent.

and $d < 3166$Å) is found to be 0.02785 $cm^3/g$. The cumulative adsorption/desorption pore volume of the pores (17Å $< d <$ 3000Å) of adsorbent is 0.037677/ 0.035357 $cm^3/g$. The biosorbent, thus, is found to consist of mesopores predominantly. This is desirable for the liquid-phase adsorptive removal of dyes and metal ions [33,34]. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the isotherm represents micropore and mesopore surface area [35].

### 3.3. Fourier transform infrared spectroscopy

The FTIR spectrum of *C. polygonoides* is shown in Fig. 4. The broad band around 3,400 $cm^{-1}$ can be assigned to the stretching vibration of O–H and N–H groups. This peak is broad because of the complex vibrational modes due to participation of –OH group in hydrogen bonding. This peak represents the presence of hydroxyl group and chemisorbed water in the adsorbent [31,36]. Besides this, the vibrational modes in this area also correspond to inter- and intramolecular hydrogen bonding. The presence of peak at 2,910 $cm^{-1}$ shows the symmetric and asymmetric C–H stretching due to the existence of methyl and/or methylene groups. The sharp intense peak at about 1,637 $cm^{-1}$ corresponds to O–H bending vibration of secondary adsorbed water molecules. The bands at 1,528 and 1,445 $cm^{-1}$ confirm the presence of C=C bond of alkenes and aromatic ring [37–39]. The FTIR spectra showed the presence of another peak at 1,100 $cm^{-1}$, which tentatively could be assigned to –OH deformation. The absorption peaks in region 1,000 to 1,200 $cm^{-1}$ represented the main skeleton of cellulose. The presence of peak at 1,035 $cm^{-1}$ represents stretching vibration of cellulose/hemicellulose and ary-OH group in lignin. The occurrence of peaks at about 793 shows the existence of Si–H [40]. The presence of adsorption band in region from 1,300 to 900 $cm^{-1}$ represents the carbonyl component (i.e. alcohols, esters, carboxylic acid, or ethers). The presence of absorbance peaks in region from 900 $cm^{-1}$ shows O–H stretching vibrations, indicative of aromatic groups. The absorption peak 874.69 is the prominent peak for β-glucosidic linkage of cellulose in biosorbent [23]. The presence of nucleophile groups, such asOH$^-$, COO$^-$, and $NH_2^-$, on the surface of biomass gives considerable cation exchange/adsorption capacity to the adsorbents.

Table 1
Surface properties of *C. polygonoides*

| Surface properties | Values |
|---|---|
| BET surface area | 16.933 $m^2\ g^{-1}$ |
| Average pores volume | 0.0278 $cm^3\ g^{-1}$ |

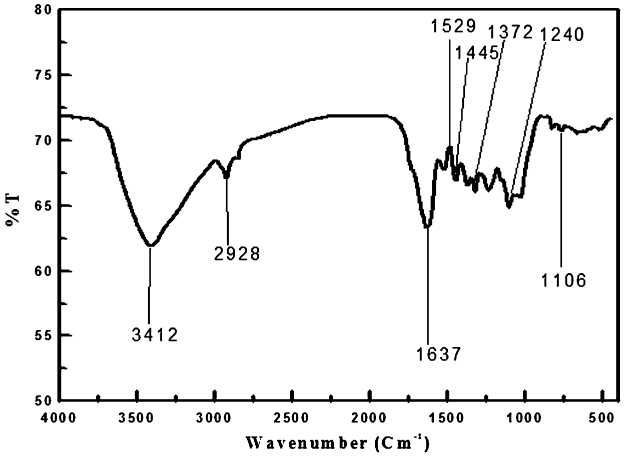

Fig. 4. FTIR spectra of biosorbent.

### 3.4. Study of morphology of adsorbent

SEM study is one the most popular, primary, and widely used characterization techniques applied for the study of surface properties and morphology of biosorbent material. Moreover, SEM study also tells about porosity and texture of biosorbent material [41–44]. Fig. 5 shows that biosorbent has small cavities on surface and has porous texture that provides large surface for the adsorption of the MB molecules. The

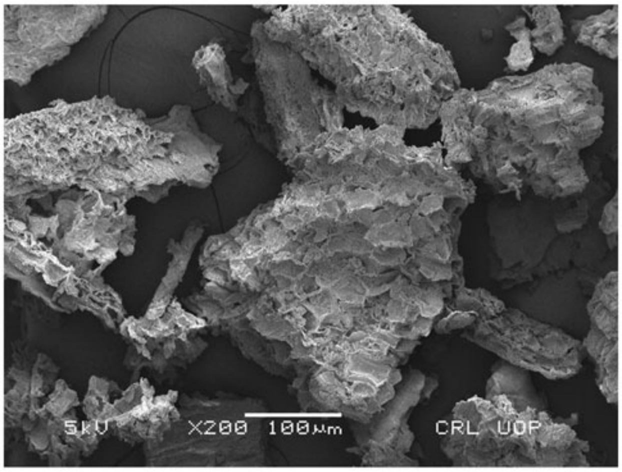

Fig. 5. SEM image of biosorbent.

EDX analysis has been provided in Table 2 and also depicted in Fig. 6.

### 3.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is an important analytical technique used to study the thermal characteristics of materials. By placing a sample to TGA, the loss in weight of sample which occurred is the function of temperature and time is also measured to know the thermal characteristics of material. The TGA provides information on the degradation process of material occurring at different temperatures and under different atmospheres [45].

The TGA curve of biosorbent is shown in Fig. 7a. TGA and differential thermal analysis (DTA) of biosorbent show (Fig. 7b) a typical three-stage mass loss:

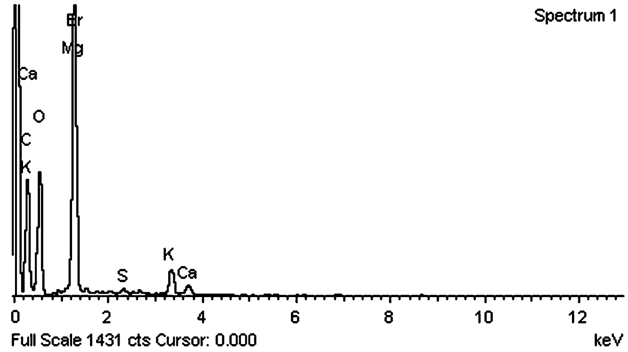

Fig. 6. EDX analysis of biosorbent.

(1) the first mass decomposition occurred below 100˚C, which could be attributed to water elimination/desorption which was physically adsorbed in biosorbent. The DTA graph also shows an endothermic peak at 100˚C. In this region, the loss of very small amounts of volatile compounds may also contribute to weight loss [38,45];

(2) the second mass loss appeared around 300˚C due to the thermal decomposition of cellulose/hemicellulose/lignin degradation; and

(3) the third mass decomposition occurred between 350 and 550˚C, corresponding to the burning of carbonaceous residues [46–48].

Table 2
Elemental analysis of *C. polygonoides*

| Element | Weight (%) | Atomic (%) |
|---|---|---|
| C K | 29.24 | 39.47 |
| O K | 42.74 | 43.30 |
| Mg K | 23.06 | 15.37 |
| S K | 0.37 | 0.19 |
| K K | 2.57 | 1.06 |
| Ca K | 0.97 | 0.39 |
| Br L | 1.06 | 0.21 |
| Totals | 100.00 | |

### 3.6. Optimizations of parameters

#### 3.6.1. Effect of contact time and initial concentration

The time of contact between the dye and adsorbent and also initial concentration of dye can affect the adsorption process. Fig. 8a shows that adsorption of various initial concentrations of MB on the surface of biosorbent is the function of contact time and initial

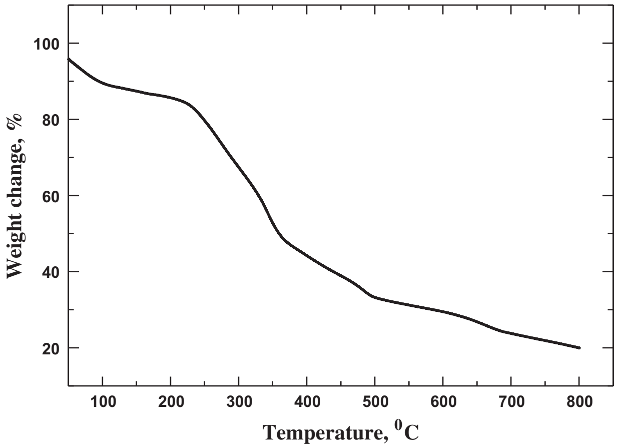

Fig. 7a. TGA of biosorbent in N2 atmosphere at 10˚C/min.

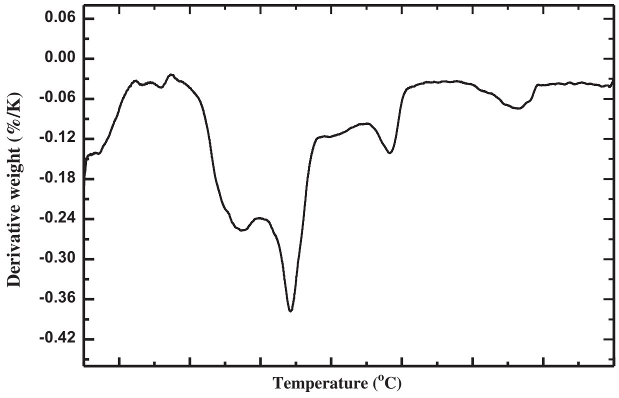

Fig. 7b. Derivative thermogravimetric curves of biosorbent.

concentration of MB. Both the percentage removal and adsorption capacity of MB increased with increase in contact time and reached equilibrium after 60 min. Increase in contact time after 60 min cannot enhance the adsorption of MB. In the beginning stage, the percentage removal of dye is very rapid due to the adsorption of more molecules of dye on the external surface of adsorbent. Increase in contact time after 60 min cannot enhance the adsorption of MB on *C. Polygonoids*. After 60 min, the surface pores of adsorbent are covered and it becomes difficult for dye molecules to enter into the interior surface of adsorbent and be adsorbed. The initial rapid removal of dye may be due to the presence of more and more binding sites for the adsorption of dye molecules and the slow removal of dye in the last stages may be due to the occupation/saturation of these binding sites with dye molecules. The equilibrium time required for adsorption of various types of dye concentrations is independent of their initial concentration [49,50].

Fig. 8a and 8b show that the capacity and rate of MB adsorption is dependent of initial concentration of the dye. It was found that with increase of the concentration of dye from 4 to 10 mg/L, the rate of adsorption and thus percentage removal and adsorption capacity increased. It is very common in the adsorption of dye molecules that with increase of initial concentration of dyes, the capacity of adsorption increases because of strong driving force and transfer of more dye molecules from aqueous phase to solid phase increase. The adsorption capacity of *C. polygonoides* along with other reported adsorbents has been given in Table 3.

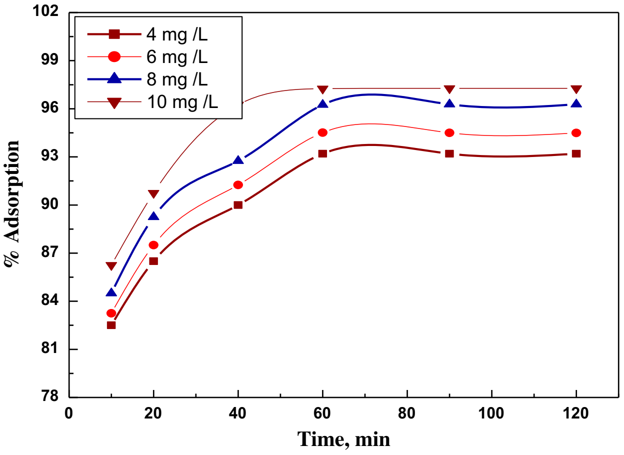

Fig. 8a. Effect of contact time and concentration on adsorption of MB on biosorbent.

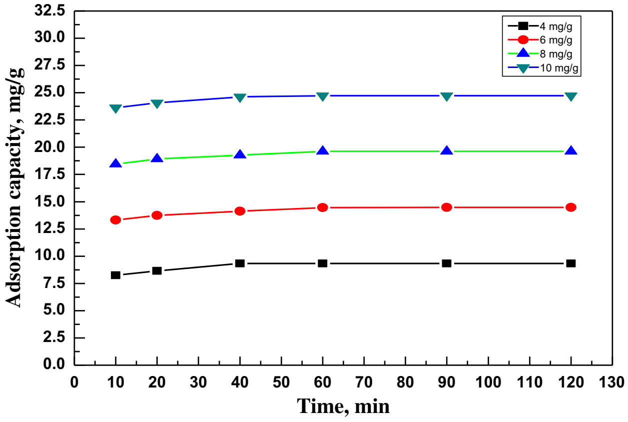

Fig. 8b. Effect of contact time and concentration on adsorption capacity of MB on biosorbent.

### 3.6.2. Effect of stirring speed/rate

To investigate the effect of stirring speed on the adsorption of MB on *C. polygonoides*, the experiment was carried out by increasing stirring speed from 100 to 600 with 100 interval increase at dye concentration 10 mg/L, contact time 60 min, and temperature 298 K. Fig. 9 shows the effect of stirring speed on the MB adsorption; with increase of shaking speed the adsorption of MB from aqueous solution was increased. This increase in adsorption reached a maximum at 300 rpm and after this, there is no such considerable increase in the adsorption of dyes. This increase in adsorption reached a maximum at 300 rpm, and further increase in speed had no significant effect on the adsorption of the dye. The increase in adsorption of MB may be due to the decrease in the thickness of diffuse layer around the surface of adsorbent with increasing the stirring speed [56].

Table 3
Comparison of adsorption capacity of *C. polygonoides* with other reported adsorbents [20]

| Adsorbent | Adsorption capacity (mg/g) | References |
|---|---|---|
| *C. polygonoides* | 25.20 | This work |
| NaOH-treated raw koalin | 16.34 | [15] |
| NaOH-treated pure koalin | 20.49 | [15] |
| Beech sawdust pretreated with $CaCl_2$ | 13.02 | [51] |
| Calotropisprocera leaf | 4.17 | [52] |
| Orange peel | 14.3 | [53] |
| Jute fiber carbon | 27.99 | [54] |
| Sawdust | 37.83 | [55] |

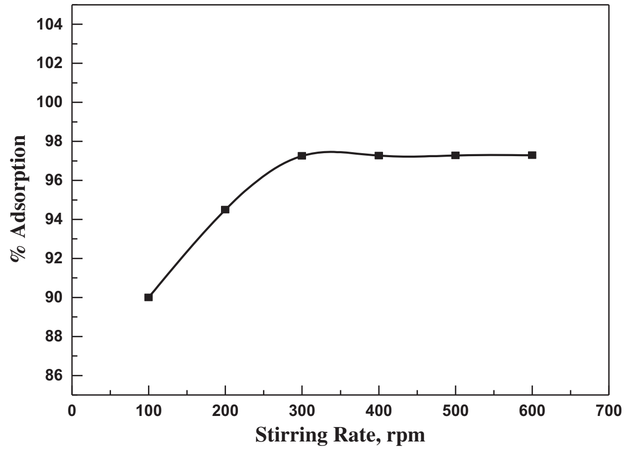

Fig. 9. Effect of stirring rate on adsorption of MB on biosorbent.

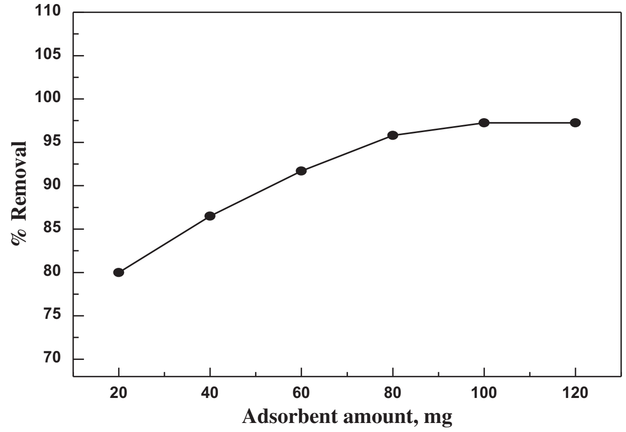

Fig. 10. Effect of adsorption amount on MB adsorption on biosorbent.

### 3.6.3. Effect of adsorbent dose

The effect of *C. polygonoides* amount on MB adsorption was investigated in the range from 20 to 100 mg. Fig. 10 shows that with increase in *C. polygonides* amount, the removal efficiency of MB increased [57]. This increase in adsorption of MB with the increase in *C. polygonides* amount is due to increase in the availability of more and more surface area and active sites for adsorption. Similarly, by increasing surface area, more and more adsorption pores are available for MB adsorption [58–60]. Further increase in concentration of *C. polygonides* over 100 mg does not increase the adsorption of MB, this may be due to saturation of vacant spaces or the aggregation/agglomeration of biosorbent particles with each others. The other possible reason for the decrease in the adsorption of MB molecules may be due to increase in the path length of diffusion for dye molecules to reach the surface of the adsorbent. In the present study therefore 100 mg of *C. polygonides* was optimized [61,62].

## 3.7. Kinetic studies and model fittings

### 3.7.1. Pseudo-first- and pseudo-second-order kinetic models

The adsorption mechanism process of MB on biosorbent was evaluated using pseudo-first-order and pseudo-second-order kinetic models [63–65]. The result in Table 4 shows that adsorption of MB on *C. polygonoides* does not follow pseudo-first-order kinetic model. However, Table 5 shows that the experimental data follow pseudo-second-order kinetics. From Fig. 11, it is clear that the adsorption of MB on *C. polygonoides* can be fitted in the pseudo-second-order kinetics with regression coefficient ($R^2$) 0.999. This suggested that this sorption system is not a first-order reaction and that the pseudo-second-order model, based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate, provides the best correlation of the data or chemical sorption can occur

Table 4
Pseudo-second-order kinetics plot for adsorption of MB on biosorbent

| Conc: mg/L | Intercept | Slope | $R^2$ |
|---|---|---|---|
| 4 | 1.867 | 1.074 | 0.99992 |
| 6 | 1.754 | 1.051 | 0.99991 |
| 8 | 1.736 | 1.032 | 0.99989 |
| 10 | 1.673 | 1.013 | 0.99992 |

Table 5
Pseudo-first-order kinetics plots for adsorption of MB on biosorbent

| Concentration (mg/L) | Intercept | Slope | $R^2$ |
|---|---|---|---|
| 4 | −0.6556 | −0.0269 | 0.96505 |
| 6 | −0.2732 | −0.0547 | 0.79183 |
| 8 | −0.3379 | −0.0522 | 0.80871 |
| 10 | −0.6876 | −0.0262 | 0.9627 |

by the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers as chemical bonding agents [66–72]. Various kinetic parameters obtained from pseudo-second-order kinetics model are listed in Table 6.

### 3.7.2. Adsorption mechanism of the dye

Understanding the mechanism of adsorption of the dye on the adsorbent is the major and key challenge. The major challenge in an adsorption study is to elucidate the adsorption mechanism. To study and understand the mechanism of adsorption, it is necessary and important to know the structure of dye molecule and also the surface of adsorbent. In this regard, it is pointed out that the MB is a cationic dye having an amine group in its structure formula. On dissolution in water, MB dissociated into $MB^+$ and $Cl^{-1}$ [73]. The FTIR and SEM results show that the biosorbent has –OH group which is more exposed and has strong chemical interaction between dye ions and adsorbent, and mechanical interaction because of easy penetration of dye ions into the microstructure of the adsorbent [74]. In this study, it is also found that the initial contact time on the adsorption of MB onto the adsorbent is fast and then becomes slow with the contact time and at last becomes linear.

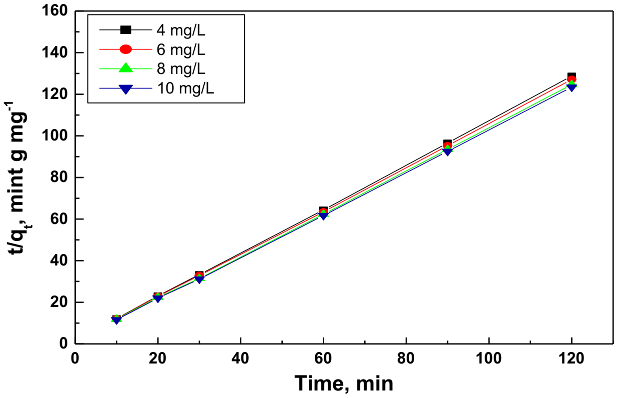

Fig. 11. Pseudo-second-order kinetics plot for adsorption of MB on biosorbent.

### 3.8. Intraparticle and liquid film diffusion model

The diffusivity of the solute molecules plays an important role in the determination of overall rate of an adsorption process. Although the pseudo-second-order equation was found to the best-fitted order for present experimental data, the results obtained from this model are not sufficient to predict the diffusion mechanism. During a solid/liquid adsorption process, adsorbate transfer was usually governed by liquid-phase mass transport (boundary-layer diffusion), or intraparticle mass diffusion, or both. The slowest step, which might be either film diffusion or pore diffusion, would obviously be the overall rate-controlling step of the adsorption process. The intraparticle and liquid film diffusion models are represented by Eq. (8).

$$q_t = K_i \cdot dt^{0.5} \tag{8}$$

Table 6
Various kinetic parameters for the adsorption of MB on *C. polygonoides* at different initial dye concentrations using pseudo-second-order kinetic model

| Conc. (mg/L) | $q_2$ (mg g$^{-1}$) | $k_2$ (g mg$^{-1}$ min$^{-1}$) | $h$ (mg g$^{-1}$ min$^{-1}$) | $R^2$ |
|---|---|---|---|---|
| 4 | 0.931 | 0.464 | 0.402 | 0.999 |
| 6 | 0.951 | 0.516 | 0.467 | 0.999 |
| 8 | 0.968 | 0.540 | 0.507 | 0.999 |
| 10 | 0.987 | 0.582 | 0.567 | 0.999 |

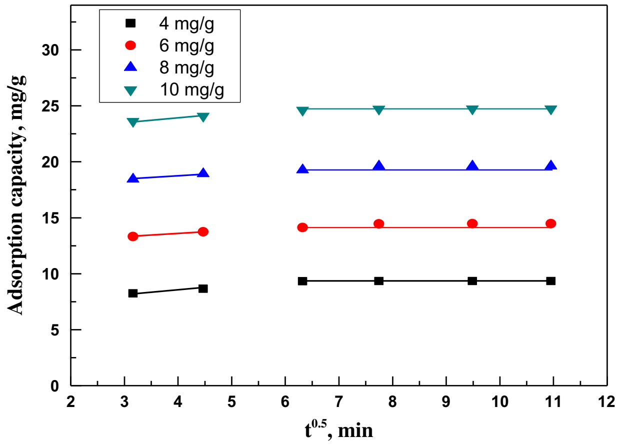

Fig. 12. Plot of intraparticle diffusion model for MB adsorption by *C. polygonoides* at different initial dye concentrations.

Fig. 12 shows the intraparticle diffusion model fitting for the adsorption of various concentrations of MB. The result shows that the plot of $q_t$ vs. $t^{0.5}$ is not very linear for whole time and can be divided into two regions. The multilinearity of the plot for MB adsorption shows the multistage adsorption of MB on the *C. polygonoides*. Normally, if the plot of $q_t$ vs. $t^{0.5}$ passes through the origin, it then indicates the intraparticle diffusion to be only a rate-limiting step. However, in this study, it is clear that the plot of $q_t$ vs. $t^{0.5}$ is not passing through the origin, which shows that the intraparticle diffusion is not involved in the adsorption process; therefore, it is not a sole rate-controlling step [75,76]. This result confirms that the adsorption process is followed by two or more than two phases [23,77].

### 3.9. Desorption study

To make the process of adsorption more economical, the desorption and regeneration study of adsorbent is very important and useful. It was found from the desorption study that 85% of MB was desorbed from biosorbent. The biosorbent was stable up to four cycles; after this the MB dye removal was found to decrease significantly. The desorption process and recycling of *C. polygonoides*-based biosorbent was found similar as reported in the literature [78].

## 4. Conclusions

This present research work demonstrated that *C. polygonoides* can be used as an economical, environmentally friendly, and an effective biosorbent for the removal of MB from aqueous solution. The percentage removal and adsorption capacity of the dye on biosorbent is fast and the adsorption equilibrium is achieved in about 60 min. It has been observed that more than 97.27% removal of MB was achieved in the first 60 min, after that no such increase in adsorption took place. The adsorption of MB on adsorbent follows the pseudo-second-order kinetics model, indicated by the correlation coefficient ($R^2 = 0.99$) values. A comparison of adsorption capacity and percentage removal of *C. polygonoides* with many other biosorbents reported in literature indicated that *C. polygonoides* has better performance. Due to its low cost, high adsorption capacity, and environment-friendly nature, *C. polygonoides* could be used as a promising adsorbent in future for effective large-scale removal of MB from aqueous solution.

## Acknowledgment

The authors acknowledge the Department of Chemistry, University of Science and Technology, Bannu 28100, Khyber Pakhtunkhwa, Pakistan for supporting this research work.

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