Efficient Removal of Methylene Blue Dye from Aqueous Solution Using a New Biosorbent Derived from Enset (Ensete Ventricosum)

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Abstract

In this study, kocho powder, a possible low-cost biosorbent for the efficient removal of MB dye from wastewater is prepared from pseudostem and corm of Enset (Ensete ventricosum). Characteristics of kocho powder were examined by using SEM, TGA, XRD and FTIR to study the surface morphology, functional group and other physico-chemical properties of this newly developed biosorbent. Biosorption experiments were carried out in batch mode to investigate the effects of dosage (0.025–0.2g), pH (2–10), initial concentration of MB (10 to 100 mg/L) and contact time (10 to 120 min).The highest removal efficiency of methylene blue dye (94.2%) was recorded at optimum experimental conditions of biosorbent dosage 0.1g, MB concentration 50 mgL^{-1}, pH 8, contact time 50min and agitation rate of 200rpm at room. Following the removal study, it was determined that the pseudo-second order kinetics (R^2 = 0.997) and Langmuir isothermal (R^2 = 0.996) models may well describe the MB dye biosorption process. Furthermore, this newly developed biosorbent was fairly recyclable up to five cycles without significant loss of re-adsorption efficiency (around 9.6% loss) between 1st and 5th cycle. Thus, the findings of this study revealed that a new kocho biomass derived from Ensete Ventricosum can be used as a promising low-cost, environmentally friendly, and efficient biosorbent for the rapid removal of MB from aqueous solutions.

1. Introduction

Clean and safe water is vital to human health and happiness, ecosystems, and a thriving economy. However, the presence of pollutants[1–3] such as pesticides, heavy metals, fertilizers, dyes, etc. in water systems can lead to degraded water quality, resulting in detrimental effects on organisms and human health[4]. Among these pollutants, dyestuffs emitted by the dyestuff industry are a major environmental challenge facing the world[5].

Dyes are largely used in the manufacturing of various industrial products such as rubber, plastics, cosmetics, textiles, food, leather, pulp, and paper[6, 7]. Recently, the release of toxic dyes into water streams by these industries has received increasing attention due to the adverse effects of these wastes[7–10]. By their nature, exposure time and concentration dyes may cause serious health effects such as skin irritation, respiratory disorders, mental disturbances, vomiting, and in many cases they may be carcinogenic and mutagenic[8, 11]. For example, methylene blue ($C_{16}H_{18}N_3SCl$), a cationic dye used in a variety of industries[12] to dye cotton, wool and silk has several harmful effects on the human body, including increased heart rate, nausea, shock, respiration distress, quadriplegia and necrosis[10]. Therefore, there is a need for efficient and economical methods to remove dyes from wastewater to protect local populations and maintain environmental health.

Several conventional treatment methods [7, 13–16] are used to remove dye contaminants from wastewater, including flocculation/coagulation, adsorption, precipitation, membrane separation electrochemical processes and solvent extraction. However, most of these techniques lack the advantages of being fast, selective, efficient, economical and/or environmentally friendly. Among these

techniques, adsorption is considered to be efficient and cost effective method for the treatment of dye loaded wastewater. The removal of dyes from wastewater is thus made possible by the adsorption of different contaminants on efficient, economical and environment-friendly bio-wastes [7, 17, 18]. Many researchers opt to use biosorbents for the removal of dyes instead of chemical adsorbents/ chemically modified adsorbents as they provide promising results with a minimum disposal problem since the biosorbents could be degraded easily by microorganism.

In order to remediate dye-contaminated water, low cost biosorbents[7, 13, 16, 18, 19] derived from agricultural, residential, and industrial wastes (such as tea waste, rice husk, oil palm biomass, bagasse, maize cob, Azadirachta indica, Alchemilla vulgaris leaves and forest by-products) have been used as effective substitutes[6, 20–22]. Biosorbents[23] have been shown to have significant dye-binding capabilities due to the presence of proteins, polysaccharides, or lipids with functional groups[24] like carboxyl, hydroxyl, amino, and sulfate on the surfaces of their cell walls.

Enset /Ensete ventricosum [Welw.] Cheesman/ is a monocarpic tall perennial herbaceous plant which belongs in the order Scitamineae, family Musaceae and genus Enset[25]. The Enset is frequently referred to as "False Banana" since it looks similar to a banana tree but doesn't yield bananas. It has amazing weather resistance, making it one of the significant native crops that may be used for many different purposes by Ethiopians; including human nourishment, industrial fiber, animal feed, rob material, for building fences and homes, making chairs and beds, local packaging, and as a substitute for tableware or umbrellas[26, 27]. Enset (Ensete ventricosum) plants typically have leaf lamina, leaf midribs, pseudostem and corm and root as basic parts.

The pseudostem and corm are the most important plant components in terms of biomass. Kocho[28] traditional culinary item in the central and southern regions of Ethiopia[28], is created when these two ingredients are combined and fermented. However in most parts of Ethiopia and the rest of the world, pseudostem and corm of Enset plants are considered as waste products which can be gainfully used to synthesize a cheap biosorbent for the elimination of dyes from the aqueous solution.

Therefore, the primary goal of the current experiment is to determine the suitability of a fermented composite product made from the pseudo stem and corm of Enset (Ensete ventricosum) as low cost biosorbent for the removal of methylene blue (MB) from wastewater. To the best of our knowledge, no reports of the removal of MB cationic dye by a sort of eco-friendly biosorbent derived from the pseudo stem and corm of Enset have been made to date. The effects of several factors influencing the adsorption of dyes, such as contact time, pH, adsorbent dosage, and initial dye concentration, are investigated. Moreover, many characteristics related to adsorption kinetics and isotherms are determined. Adsorption-desorption tests are also used to look at the biosorbent's regeneration.

2. Materials And Methods

2.1 Materials and reagents

Methylene Blue (MB, chemical formula – $C_{16}H_{18}ClN_3S$, molecular weight: 319.85 g mol^{-1}, 98% dye content) was obtained Aladdin Co., Ltd., China. The stock solutions (100 mg L^{-1}) of MB were prepared by dissolving accurately weighed amount of the dye in distilled water **(ESI.1)**. All the chemicals used throughout this study were of analytical-grade. All working solutions of required concentrations were obtained by diluting the stock solution with distilled water. The pH value of water was adjusted by 0.1M HCl and/or 0.1M NaOH. Method used for the preparation Kocho is given in **ESI.2**

2.2 Characterization and instruments

The biosorbent (kocho) morphologies of the samples were examined using FE-SEM (JEOL, Tokyo, Japan). Gravimetric thermal analysis (TGA) was carried out using a thermo gravimetric analyzer (TA instruments, UDA). The powder XRD patterns of the samples were obtained using Cu Kα radiation with a diffractometer (Rigaku, RINT 2000). FTIR spectroscopy (Bruker, Germany) was used to identify the functional groups present in the adsorbent before and after adsorption of MB. The pH value was determined by Orion 4-Star Plus pH/ISE Benchtop Multiparameter Meter. A UV – Vis spectrophotometer (V-650, JASCO,Japan) was used to determine the concentration of MB solutions with a measurement range of 800 to 200 nm and a data interval of 0.1 nm. (**See ESIS.3)**.

2.3 Batch Biosorption experiments

Batch experiments were done to get equilibrium data and validate the best parameters for the biosorption treatment process. These variables included the Kocho dosage (0.01-0.2g), initial concentrations MB (10–100 mg/L), the pH solution (2–10) and contact time (10–120 min) at a constant agitation speed of 200 rpm and a temperature of 278K in a batch mode. To carry out the dosage-dependent removal efficiency experiments, different kocho dosages (0.01, 0.025, 0.05, 0.1, 0.15and 0.2g) and 20 mL of MB solution (50 mg/ L) were mixed with the Kocho biosorbent under optimized pH (8) and incubated for 50 minutes. For studying the effect of pH on removal efficiency, 20 mL MB dye solutions (50 mg/ L) were incubated for 50 minutes with 0.1 g Kocho powder under various pH values (2,3,4,5,6,7,8,9 and 10) of 20 mL of MB solution (50 mg/L). To investigate the effect of MB dye concentration on removal efficiency, 20 mL dye solutions with various concentrations (10, 25, 50.75 and 100mg/L) were incubated for 50 minutes with 100 mg kcoho. For studying the effect of contact on removal efficiency, 20mL MB dye solutions (50mg/L) were incubated with different contact time (10,20,30,40,50,60,90 and 120 min) under optimized pH(8),dose(0.1g) and MB(50mg/L) of 20 mL solution. For each experiment, after filtering the agitated adsorbate solution over a 0.22μm microfiltration membrane, the remaining MB dye concentration in the filtrate was measured using a UV-VIS spectrophotometer. The following equations were applied to compute the amount of dye biosorption at preset time t (qt, mg/g), equilibrium adsorption amount (qe, mg/g) and removal efficiency (R, %) biosorbent Kocho.

$$q_{e=(Co-Ce)x\frac{V}{m}}(1)$$

$$q_{t=(Ce-Ct)x\frac{V}{m}}(2)$$

$$\%Removal=\frac{(Co-Ct)}{Co}x100(3)$$

Where Co (mg/L) is the initial concentration of the MB dye, Ct (mg/L) is the concentration of MB dye at any time, Ce (mg/L) is the liquid-phase dye concentration at equilibrium, V (L) is the volume solution, and m (g) is the mass of the biosorbent.

2.5 Determination of point of zero charge (PZC) of the Kocho

The pH of the point of zero charge (pHPZC) of Kocho was determined by salt addition method[29] using 0.1M KNO_3. The pH was adjusted with 0.1 M HNO_3 and 0.1 M NaOH using a digital pH meter as needed, to obtain the appropriate pH range of 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11. After mixing with 0.1g of the Kocho sample, the solutions were shaken for 24 h using an agitator at 200 rpm. After settling, the pH values of the supernatant in each tube were measured and denoted as pHf. The PZC is obtained from the plot of ΔpH (ΔpH = pHf − pHi, pHi, is the initial pH and pHf is the final pH) versus pHi, where the point of intersection of the graph is equal to zero. Each set of experiments was performed in triplicate and the mean value was recorded.

2.6 Desorption studies

Solvents such as alcohols, alkalis, and acids are used as desorbents for removing the sorbates from the biosorbents[30, 31]. Therefore, to perform regeneration study of our used biosorbent, the adsorbed MB dye on the surface of kocho is initially treated with HCl (0.1M) followed by drying the free biosorbent in an oven at 70 ^{O}C for further use to remove MB dye from the aqueous solution. After each regeneration, a batch biosorption experiment was conducted to estimate the Kocho regeneration ability using methylene blue dye solution (Co = 50 mg /L), contact time(50 min) and pH(8) and agitation speed of 200 rpm at 25°C for a total of five cycles of adsorption-desorption processes.

The desorption and reusability behavior of Kocho powder is studied in successive five cycles of adsorption-desorption processes. Initially 0.1g of Kocho powder is added into the 20 mL dye mixture and stirred at 200 rpm for 50 min. The dye load Kocho powder is taken out from the dye solution and washes with distilled water for several times, and then dried. The dye loaded Kocho powder is added into 20 mL 0.1 M HCl and stirred for 6 h. The process is repeated for five successive cycles. The percentage of desorption[32] is calculated using Eq. (4).

$$\%\mathrm{Desorption} = \frac{\mathrm{ConcentrationofDesorbedDye(mg/L)}}{\mathrm{ConcentrationofAdsorbedDye}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right)}\mathrm{x100}\ (4)$$

3. Result And Discussion

The biosorbent Kocho powder was used to remove methylene blue from an aqueous solution. Below is a discussion of the outcomes from characterization, optimization, biosorption kinetics and isotherms studies.

.3.1 Characterization

In this section, we will first characterize the porosity and surface area of kocho biosorbemt. Figure 1 shows scanning electron microscopy (SEM) images of the kocho powder sample at different magnifications. It is obvious from SEM analysis (Fig. 1a **and b**) that the surface of Kocho is mostly dispersed by highly heterogeneous porous structures and cave type apertures of various sizes, which offer a significant specific surface area for efficient biosorption of dyes. The Kocho powder may therefore be a suitable biosorbent and have sufficient shape for MB dye biosorption in wastewater treatment. Large pores and a higher surface area are important factors in increasing dyes biosorption[33].

Thermogravimetric analysis (TGA)

The thermogravimetric profile of the Kocho powder as a function of temperature is shown in Fig. 2a. The decomposition of the Kocho occurs in multistep processes. The first step weight loss (7%), which occurred around 120°C due to the elimination of water molecules from the surface of the kocho biomass. The second step registered consistency, the thermal stability of Kocho and then decrease of weight started at 270 ^{O}C and persisted until 340°C, which may be due to the decomposition of carbon-based functional groups (cellulose*)*.[34] The deterioration temperature was then started at 370°C and showed quick weight loss (80%) up to 540°C. After that, the final decomposition may be seen, where a maximum component in the Kocho substance was decomposed. The overall weight loss (98%) corresponds to the loss of carbon and oxygen due to the decomposition of Kocho's lignocellulosic components. This could be explained by the presence of lignin, which protects the cellulose chains in the cell wall.

X-ray powder diffraction spectrometry (XRD)

X-ray diffraction (XRD) instrument was used to characterize the crystallite nature[34] of Kocho powder. Figure 2b shows the typical XRD spectrum of the degree of crystallinity and amorphosity of Kocho powder. The x-ray diffractogram of the Kocho powder shows four distinct Bragg peaks near 2θ = 14.86, 17.03, 22.11, and 23.99°, as shown in Fig. 2b. The crystalline phase of Kocho powder cellulose correlates to the highest diffraction intensity, which was discovered at 2θ = 17.039. The amorphous phase of Kocho lignocellulose is represented by the diffraction intensity obtained at 2θ = 23.99°, which is the least intensity. In addition, few diffused peaks at higher 2θ values indicating the decrease in crystallinity of the cellulose and corresponds to amorphous phase of lignin and hemicellulose. In agreement of this research other researchers have also noted the broad peaks at about 16° and 22° in a variety of woods, including rubber wood sawdust, pinewood, and pinus elliotii plantation wood[17].

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of Kocho powder were analyzed before and after MB biosorption (Fig. 3) to detect any differences due to the interaction between the functional groups on the Kocho biomass and MB dye during biosorption process.[35] As can be seen in Fig. 3, the pristine Kocho main peaks in the functional group region have appeared at 3676, 3272, 2901, 2888, 1635, 1452, 1394, 1250 1150,

1075,1066,1048,1015,892 and 571 cm^{-1}. Peaks at 3674 cm^{-1} is ascribed to the free –OH stretching vibrations. The broad peak at 3269 cm^{-1} is attributed to -OH stretching vibrations due to inter and intramolecular hydrogen bonding of macromolecular associations, such as alcohols, phenols and carboxylic acids, cellulose and lignin, thus showing the presence of hydroxyl groups “free” on the surface of the adsorbent.[36] The peaks at 2901 and 2888 cm^{-1} can also assigned to the C–H stretching of lignocellulosic components. The characteristics peak at 1635 cm^{-1} shows the presence of the ester (C = O) linkage of the carboxylic group of lignin and hemicelluloses.[37] Other prominent peaks are C-O-C stretching vibrations (1075 cm^{-1}), C-O stretching (at 1252 cm^{-1}), C = O (1066 cm^{-1}), C-O-C deformation (at 1048 cm^{-1}), and glycosidic linkage at 892 cm^{-1}. Therefore,the peaks in pristine kocho shows the presence of cellulose, hemicellulose, and lignin in the selected biosorbent.[38].[39]

As shown in Fig. 3, some distinct changes are observed between the spectra before and after methylene blue biosorption on biomass. The increase in intensity and shift in peak positions in Kocho following MB biosorption demonstrate the involvement of different functional groups during the adsorption. Figure 3 clearly illustrates the shift in peak locations from 3676 to 3675, 3272 to 3269, 1635 to 1638 and 1450 to 1452 cm^{-1} following the biosorption process. The peaks assigned to 2901, 2888, 1394, 1250, 1075 and 1066 cm^{-1} in sample were same before and after MB biosorption but also there is a remarkable change of the intensities of infrared bands with no change positions. From the changes in the FTIR spectra, the results confirmed that the process involved is type inclusion of methylene blue with functional groups present in the biomass. Moreover, the FTIR results therefore revealed that Kocho's hydroxyl and carboxylic groups actively participate in the bisosorption of MB cationic dye. These may result from an interaction between the positive centers of the MB dye and the negative centers of the kocho bisorbent, which involves significant attractive forces. Based on previous studies, the various functional groups from cellulose, hemi-cellulose and lignin contained in biomass have a beneficial effect by generating active binding sites for dye adsorption through different mechanisms[40, 41].

3.2 Effect of Various Parameters on Dye Biosorption

The dosage, initial concentration of the MB dye solution, pH and contact time are some of the crucial variables that affect how well dyes adhere to biosorbent surfaces. In this study, the effect of one parameter on the MB dye biosorption process could be monitored when the other parameters are kept constant. Following the description of the pristine and loaded Kocho, a thorough investigation of how these variables impact the biosorption of cationic contaminant (MB) dye is briefly presented as follow as: below (the plot of biosorption for every parameter is given in **ESI (Fig. S4, 5, 6, 7**).

The Effect of Dosage

The biosorbent should be able to adsorb a sizable amount of adsorbate at low doses in an effective removal process with minimal operating costs. In this study, the effect of amount of biosorbent on the removal capacity of MB dye was investigated by varying the amounts of kocho powder (0.01, 0.025, 0.05, 0.1, 0.15 and 0.2 g). For this purpose, specific amounts of adsorbents were added in 20 mL dye solutions

at room temperature with optimized pH (8), initial MB concentration (50 mg/L), contact time (50 min) and 200 rpm agitation. As shown in Fig. 4a, when the amount of biosorbent dosage was elevated from 0.01g to 0.1g, the removal of efficiency of MB increased dramatically from 57.18–94.2%, and after that the increase was only marginal. It was also found that the increase in biosorbent dosage from 0.01 to 0.2 g resulted in decrease of amount of adsorbed dye from 57 mg/g to 4.9 mg/g (**Fig. S4**). Although a slight increase in the percentage biosorption was observed at adsorbent amounts higher than 0.1g, the subsequent biosorption studies were carried out using 0.1g of biosorbent for the sake of simplicity and process efficiency.

Biosorption typically increases as adsorbent amounts rise, which is caused by an increase in surface area [7, 16, 18]. However, there comes a point where adding more biosorbent does not further increase biosorption; instead, it stays virtually constant. The increase in the total surface area of the adsorbent, which results in a greater number of active sites available for binding MB dye, is what causes the percentage of removal to rise with dosage.

Effect of Initial MB Dye Concentration

Studying the variation in biosorption capacity with a change in starting dye concentrations allows researchers to better understand the concentration gradient between the dye and adsorbent surface, one of the forces that drives the adsorption process. In this work, the removal of methylene blue dye from aqueous solution was evaluated by varying the initial dye concentration in the range of 25–100 mg/L at pre-optimized dose (0.1g), pH (8) and contact time (50 min) at agitation of speed 200 rpm. As shown in Fig. 4b, the percentage of removal for Kocho biosorbent reduced from 98–64% when the initial MB concentration increased from 10 mg/L to 100 mg/L, respectively. About 97%, 94%, and 80% percent elimination was accomplished with dye doses of 25, 50 and 75mg/ L (Fig. 4b). As clearly seen in **Fig. S5**, when the initial MB concentration increased from 10 to 100 mg/L, the biosorption capability correspondingly increased from increased 1.96 mg/g to 12.8 mg/g. This trend can be attributed to the saturation of the active sites for biosorption on the biosorbent surface at higher concentrations of dyes.

Therefore, at greater dye concentrations, we discovered that the adsorption capability was less effective. A lower percentage of dye removal was observed at greater concentrations because there were more dye molecules in the solution and all of the open sites were filled. This is explained by the fact that fewer dye molecules were accessible and occupied the open adsorbent sites at lower starting MB concentrations[16, 42]. This is a common phenomenon in the biosorption process and revealed in results of previous studies on removal of MB by pine cone[43], oak sawdust[44] and activated carbon from rice husk[45].

Effect of Initial pH

Depending on the chemical structure of the dye and biosorbent, pH has a noticeable effect in affecting the biosorption capacity of the adsorbent. It influences the adsorbent's surface charge as well as the functional groups' degree of protonation[16, 46]. Here in, using an initial MB dye concentration of 50

mg/L and 0.1 g biosorbent, the influence of pH on MB adsorption of the kocho at 50 min biosorption time was examined in the pH range of 2–10. The pH of dye solutions was adjusted by using 0.1 M aqueous sodium hydroxide and 0.1 M aqueous hydrochloric acid solutions.

In the pH range of 2 to 8, as depicted in Fig. 5a, the clearance rate increased quickly from 29.2–94.2%. However, the highest biosorption was at pH 10(95.4%, 9,54mg/g), whereas the lowest removal was at pH 2 (29.2%, 2.9 mg/g), Fig. 5a and **Fig. S6**. And also for pH 3 (34.3%, 3.4 mg/g) to pH 8 (94.2%, 9.4 mg/g), the removal percentage and biosorption capacity of MB dye on Kocho powder increased with increased in solution pH. A slightly lower percentage removal observed at pH 2 compared to pH 3 can be attributed to a higher extent of protonation of carboxylic functional group resulting in the reduction in net negative change on the dye molecules that led to a reduced electrostatic interaction between Kocho MB dye. Increase in the removal efficiency at pH 6(74.3%, 7.4 mg/g) and above can be related to the decrease in the extent of protonation of functional groups of the biosorbent.

The surface of the Kocho powder gained a negative charge when the pH of the dye solution rose, which led to an increase in the MB's adsorption as a result of an increase in the electrostatic attraction between the negatively charged adsorbent and the positively charged dye. Due to competition between the increased H^+ and the cationic dye for the Kocho group adsorption sites, the adsorption was unfavorable in an acidic environment. It is evident that the amount of MB adsorbed was significantly influenced by the pH of the solution. As a result, this findings revealed that alkaline conditions were preferred over acidic ones for removal efficiency. This implies that alkalinity improves the electropositive biosorption of materials where acidity decreases the biosorption of positively charged dye due to electrostatic repulsion[7, 47]. On the other hand, the lower uptake rate of cationic dyes at acidic pH may be attributed to the excess presence of (H^+) ions competing with the dye cation groups for biosorption sites. Similar findings on MB adsorption onto banana peel powder, papaya seeds, bamboo and banana stem debris, garlic peel, grass waste, yellow passion fruit peel and citrus limetta peel were also reported [7, 18, 48] biomass.

The point of zero charge, an attribute of adsorbents, can better explain the significant impact of pH on adsorption (pHpzc). The adsorbent surface is neutral at pH = pHzpc (zero-point charge), negatively charged at pH > pHzpc, and positively charged at pH < pHzpc. In this study, the PZC was obtained from the plot of ΔpH (= pHf – pHi) against pHi, where the point of intersection of the graph is equal to zero. As shown in Fig. 5b, the pHpzc of the Kocho biosorbent was determined to be 5.69. This demonstrates that the surface has a positive charge due to protonation at pH < 5.69 whereas the adsorbent surface gets a negative charge due to deprotonating in the excess of hydroxyl ions at pH > 5.69. As a result, the Kocho's removal of MB cationic dye was most effective at pH > pHpzc where the functional groups get protonated and less MB dye are adsorbed by the biosorbent. The approximately close values were reported for other biosorbents:5.6 for Raspberry (Rubus idaeus) leaves powder[49] 5.77 for Syringa vulgaris leaves powder[50], 6.3 for papaya leaf powder and Typha angustifolia leaves powder[51].

Effect of Contact Time

The effect of contact time on the biosorption of MB was examined to determine the optimum time required for the maximum uptake of dye for various time intervals ranging from 10 to 120 min (Fig. 6a). According to Fig. 6a, the MB dye quickly adsorbs to the surface of kocho in the first 40 minutes, and then the rate of adsorption declines until equilibrium is reached in around 50 minutes. A further increase in the contact time did not result in any appreciable increase in the removal percentage, and for the sake of process simplicity and efficiency, all the subsequent adsorption studies were performed using contact times of 50 min.

Additionally, the discolorations of the MB solution under different adsorption times are shown in Fig. 6b. When the Kocho was used as the biosorbent, the color of the MB solution varied from dark blue to light blue. It finally became nearly transparent with the increasing biosorption time, which suggests that most of the MB molecules in the solution were adsorbed by the Kocho. The presence of a large number of vacancies on the adsorbent surface that reached saturation at equilibrium is believed to be responsible for the sharp increase in adsorption capacity at the initial contact time. Due to a paucity of active sites for dye biosorption once equilibrium was established, it remains nearly constant[52].

4.3 Adsorption kinetics and Isotherm model

Dye Adsorption Kinetics

In the adsorption mechanism, kinetic prediction of the adsorption capacity and adsorption time is crucial. The kinetic adsorption studies were conducted with an initial MB dye concentration of 50 mg/L, biosorbent dose of 0.1g, pH(8) and contact time of 120 min at the agitation speed of 200 rpm. To assess the adsorption kinetics process, the pseudo-first-order[53] and pseudo-second-order[54] kinetic models were taken into consideration. These kinetic models are given by Eqs. (5) and (6):

Pseudo-first-order:

$$\ln^{(qe-qt)} = \ln^{qe} - k1t$$

5

Pseudo-second-order:

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{t}{qe} \quad (6)$$

Where, qe and qt (mg/g) are the sorption capacities at equilibrium and at time t, respectively.

The adsorption kinetic models can be used to predict the equilibrium adsorption capacity and clarify the adsorption mechanism of MB onto the surface of the Kocho. The kinetic models of pseudo-first-order and pseudo-second-order were built in accordance with the results of adsorption experiments, as shown in Fig. 7a and Table 1. The values of qe, R^2, k_1, and k_2 in Table 2 were obtained from the linear plots of Fig. 7a.

The experimental value of qe, 9.6 mg/g, did not agree well with the calculated one qe, cal (7.21 mg/g) as obtained from the linear plots (Fig. 7a), and the value of the correlation coefficient (R^2) was relatively low (0.9454 in Table 1). This indicates that the biosorption process does not comply with the pseudo-first order rate model. The pseudo-second-order model showed a better fit to describe the biosorption of MB onto Kocho with the calculated value qe, cal (11.72 mg/g) closer to the experimental value qe,exp value (9.6 mg/g) and a higher correlation coefficient (R^2 = 0.9743 in Table 2) than the first-order kinetics model. So it can be said that the pseudo-second-order kinetic model was followed during the biosorption of MB dye on the imaginary kocho powder, confirming that the biosorption should involve a chemical interaction between active sites of kocho and ionic groups present in the dye molecules. Similar type of conclusion was documented from biosorption study of methylene blue dye e using rice (Oryza sativa L.) straw[55].

Table 1
Kinetic parameters for the adsorption of MB on Kocho powder.

Kinetic mode	Kinetic parameter	Values
Pseudo first order	$k_1 x10^{-2}$ (min^{-1})	10.7
	Qe, cal(mg/g)	7.26
	Qe, exp(mg/g)	9.63
	R^2	0.9454
Pseudo second order	K_2 $x10^{-2}$ (g/mg min)	6.36
	Qe, cal(mg/g)	11.72
	Qe, exp(mg/g)	9.63
	R^2	0.9743

Adsorption Isotherm

To shed light on how the adsorption achieved equilibrium and to pinpoint the interaction between the adsorbent and the adsorbate, Freundlich and Langmuir isotherms were used. The two models are evaluated to fit the isotherm data, and their linear plots are displayed in Fig. 9 (a) and the related parameters were calculated from the two isotherms (Table 2).

The Langmuir isotherm model, which may be written as (Eq. 7), relies on the assumption that the monolayer formation of the adsorbate molecules/ions over the surface of the adsorbent molecule through mainly chemical interactions between the adsorbate and adsorbent.

$$\frac{1}{\mathrm{qe}} = \frac{1}{\mathrm{qmkLCe}} + \frac{1}{\mathrm{qm}}$$

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Where qe represents adsorption capacity at equilibrium, Ce represents equilibrium concentration, qm denotes maximum adsorption capacity, and KL denotes the Langmuir constant (L mg^{-1}), which is a measure of the free energy of adsorption and is associated to the affinity of the binding site.

The plot of 1/qe versus 1/Ce is shown in Fig. 7b, and the slope and intercept obtained from the plot are used to determine KL (1.09 L mg^{-1}) and qm (11.54 mg g^{-1}), respectively, (listed in Table 2). Additionally, the Langmuir adsorption constant, KL, is related to the separation factor, RL, as shown in Eq. (8):

$$\mathrm{RL} = \frac{1}{1 + \mathrm{KLCo}} (8)$$

The RL number indicates whether the adsorption affinity is irreversible (RL = 0), favorable (0 < RL < 1), linear (RL = 1), or unfavorable (RL > 1). In this study, the RL value ranges[56] from 0.01 to 0.08 (0 < RL < 1)) and it corresponds to favorable adsorption of MB on Kocho. The regression coefficient (R^2) of the plot for Langmuir Eq. (7), which confirms that the adsorption process follows the Langmuir isotherm model, and the adsorption process mainly takes place via chemical interactions between the adsorbate and adsorbent.

The Freundlich isotherm model is used to depict the adsorption on a heterogeneous surface. The adsorption on a surface with a heterogeneous energy distribution is represented using the Freundlich isotherm model[57]. The linear form of this model is written as (Eq. 9):

$$\mathrm{lnqe} = \frac{\mathrm{l}}{\mathrm{n}} \mathrm{lnCe} + \mathrm{lnkF}$$

9

Where qe and Ce are the adsorbed MB amount (mgg^{-1}) at equilibrium and equilibrium concentration (mgL^{-1}), respectively. KF (mg/g/(L/mg) $^{1/n}$) is the Freundlich coefficient, which reflects the adsorption capacity, and n is the Freundlich coefficient, which reflects the degree of heterogeneity. For the favorable adsorption process, the value of n should be 1 < n < 10. The plot of $\ln^{qe}$ versus $\ln^{Ce}$ (Fig. 8a) yields the slope (1/n) and intercepts (ln ^{KF}). From the slope and intercept values, n (2.87) and KF (4.57 (mg/g (L/mg) $^{1/n}$) values are determined, respectively (Table 2). 1 < n (2.87) confirms the favorable nature of the adsorption process. The regression coefficient R^2 of the plot for Eq. 9 is (0.855).

The data demonstrate the highest adsorption capacity using the Langmuir model, with mean R^2 values of 0.99845, which is very much close to 1. The outcomes suggested that the Langmuir model was the most appropriate one to explain the experimental data, which conveys the chemical interactions between the adsorbate and adsorbent[55]. The n value of kocho in the Freundlich model is 2.85. Since all of the n

values are bigger than 1, this further supports the idea that the biosorption process will be effective at high MB concentrations.

Table 2
Parameters for the Langmuir and Freundlich Isotherm Equations.

Isotherm Model	Isotherm constants	Values
Freundlich	N	2.85
	K_F (mg/g)(L/mg)$^{1/n}$	4.57
	R^2	0.94426
Langmuir	Qm (mg/g)	11.54
	K_L (L/mg)	1.0914
	R^2	0.99845

3.4. Regeneration Study

A desorption study helps in understanding the reusability of the biosorbents, also reducing the cost of the biosorption process due to the reuse of the sorbents. Therefore, to perform regeneration study of our used biosorbent, the adsorbed MB dye on the surface of kocho poweder was initially treated with HCl (0.1M) followed by drying the free adsorbent in an oven for further use as an biosorbent for the removal of MB dye from the aqueous solution. In this study, 0.1M HCl acid solutions at pH (2) are used as desorbents for Kocho removal from MB-loaded biosorbents for five cycles (Fig. 9). After each regeneration, a batch biosorption experiment was conducted to estimate the Kocho powder regeneration ability using methylene blue dye solution (Co = 50 mg /L), contact time (50 min) and pH (8) at 25°C. The highest biosorption rate occurred during the first 50 min of 200 rpm agitation rate; hence, the biosorption experiment after the regeneration was tested for 50 min. As seen in Fig. 9, at the initial biosorption process after 50 min, the removal efficiency was about 94.2%. The biosorption after the regeneration studies was very close to the initial 94.2% for all the four cycles, reducing only 3.8% from the initial dye removal after the fourth cycle. Figure 9 demonstrates that the biosorbent still showed 84.6% dye removal efficiency even at the fifth cycle. As a result, the Kocho biosorption ability is hardly affected after five uses, that is, only 9.6% decrease (Fig. 9). Thus, it can be concluded that Kocho is very applicable for removal of MB with excellent recycling ability.

3.5 Comparison of biosorption capacity of Kocho with other biosorbents

A comparison of the candidate kocho's biosorption abilities with those of different other adsorbents from literature was conducted.Table 3 displays the performance of the proposed kocho powder as biosorbent efficiency comparing with different biomass in terms of removal efficiency of MB dye from aqueous

solution. From these data in Table 3, it can be suggested that the maximum MB removal efficiency obtained in the present study is higher than most of other biomaterials Thus, it can be concluded that the biosorbent Kocho powder derived from pseudostem and corm of Enset is highly efficient for removal of MB dye from aqueous solution.

Table 3
Reported removal efficiencies (%) of various biomass-derived adsorbents for the removal of MB dye.

Material	Efficiency (%)	Reference
Rice husk	95.81	[58]
Sawdust	89.0	[59]
Banana fiber	85.0	[59]
Coconut fiber	96.0	[59]
Eucalyptus bark	86.33	[60]
Pine Cone (Pinus radiate)	90.14	[45]
Kocho powder	94.2	Present study

4. Conclusions

This study assessed Kocho powder derived from psedustem and corm of Enset(Ensete ventricosum)as a viable option for removing cationic MB dye from wastewater. Characterizations with SEM, XRD, and TGA and FTIR reflected that biosorbent (Kocho) made from pseudostem and corm of Enset has the appropriate physical-chemical characteristics for the biosorption procedure. It is most likely that the complex nature of surface functionalities, heterogeneity, and porosity of the biosorbent Kocho surface play significant role to remove MB from aqueous solution. Batch studies were performed to analyze the effects of dosage, initial MB concentration, pH and contact time. The results showed that the optimum parameters for biosorption process were 0.1g of biosorbent dose, 50 mg/L MB concentration, pH 8 and contact time of 50 minutes. The highest removal efficiency was 94.2% under the optimum experimental parameters. Depending on biosorbent dosage at room temperature and pH (8), contact time 50 min with an initial MB concentration of 50 mgL^{-1}, the Kocho biosorption capacity at equilibrium ranged between 4.9 and 57.8 mgg^{-1} and the equilibrium biosorption percentage between 57.8% and 97.2%. The removal of MB dye increased from 64–98% with decreasing initial concentration of MB from 100 mgL^{-1} to 10 mgL^{-1} at optimum parameters. Furthermore, the higher MB removal was obtained at higher pH and the removal efficiency increased from 29–94.2% with increasing the pH from 2 to 8. A pseudo-second-order model provided the best fit between the experimental data. The biosorption for the Kocho is also better adjusted to the Langmuir model. The desorption study presented 94.2% desorption of Kocho with a 1M HCl desorbent accompanied by an 84.6% regeneration efficiency at the fifth cycle. On the basis of experimental results and their analyses, it can be concluded that the newly developed biosorbent kocho

powder from pseudostem and corm of Enset (Ensete ventricosum) is one of the most effective biosorbents among those obtained from the domestic, agricultural and industrial wastes. Thus, encouraging results of biosorption presented by the Kocho powder with respect to biosorption of MB reveal its future scope of utilization in the removal of other dyes on a large scale from aqueous media.

Declarations

Conflicts of interest

The authors are no conflicts to declare.

Author Contributions

Belete Tewabe Gebeyehu designed the research, wrote the paper, edited the paper and performed batch biosorption experiments. Temesgene Alehegne Tasew helped in preparation of Kocho powder sample and characterizes the FTIR and TGA data. Daniel Manaye Kabtamu helped with the in SEM and XRD experiments. All authors have given approval to the final version of the manuscript.

Data Availability

All relevant data are included within the article and supplementary information.

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Figures

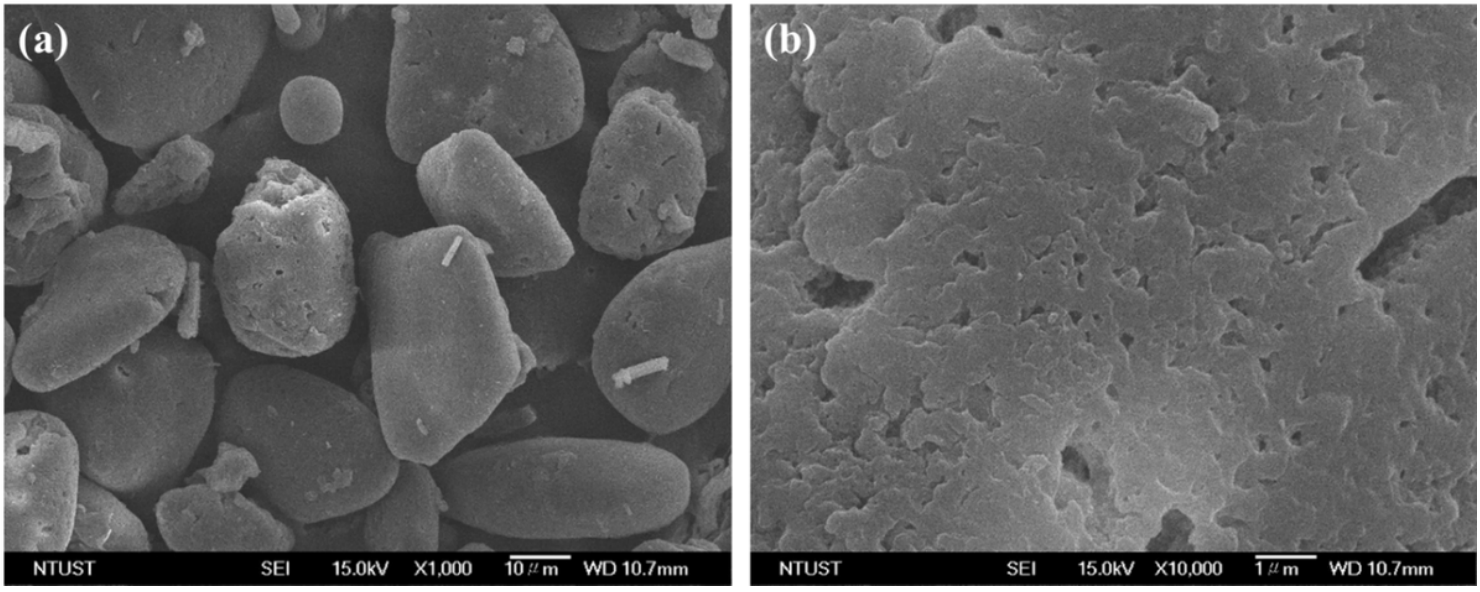

Figure 1

SEM images of the biosorbent surface at different magnifications of: (a) x1, 000 and (b) x10, 000.

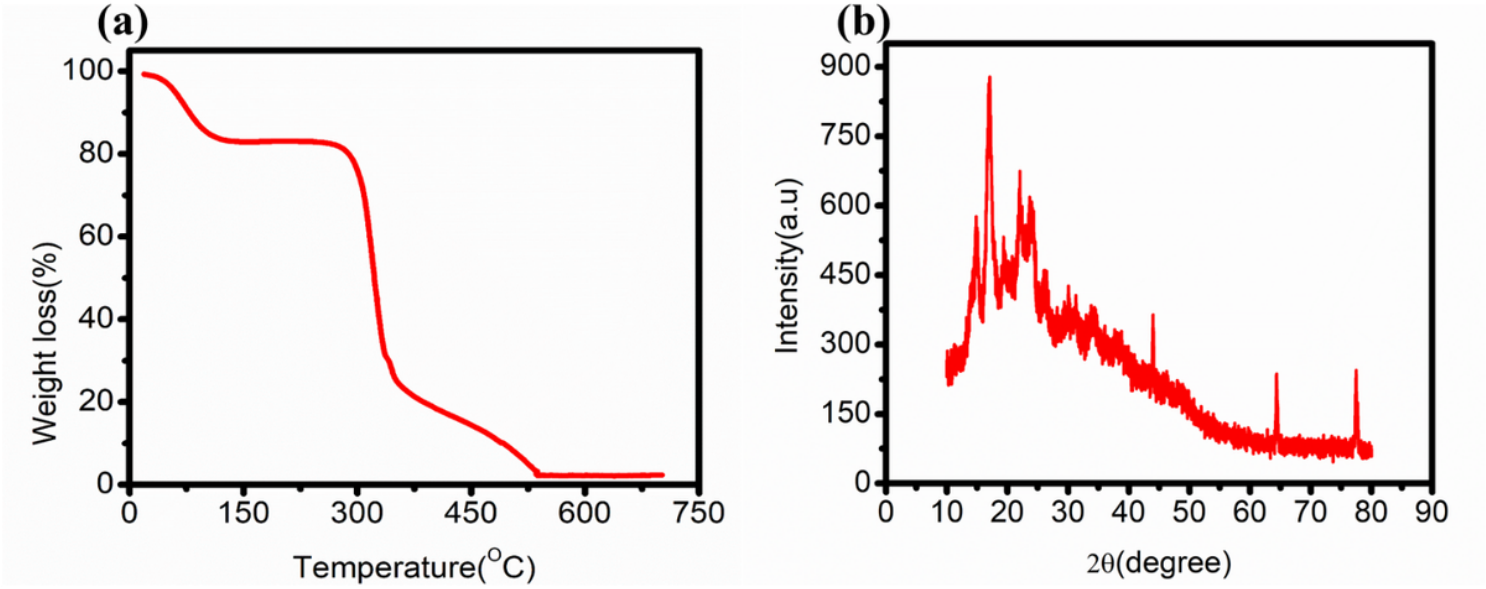

Figure 2

(a) TGA of Kocho powder and (b) XRD patterns of Kocho powder.

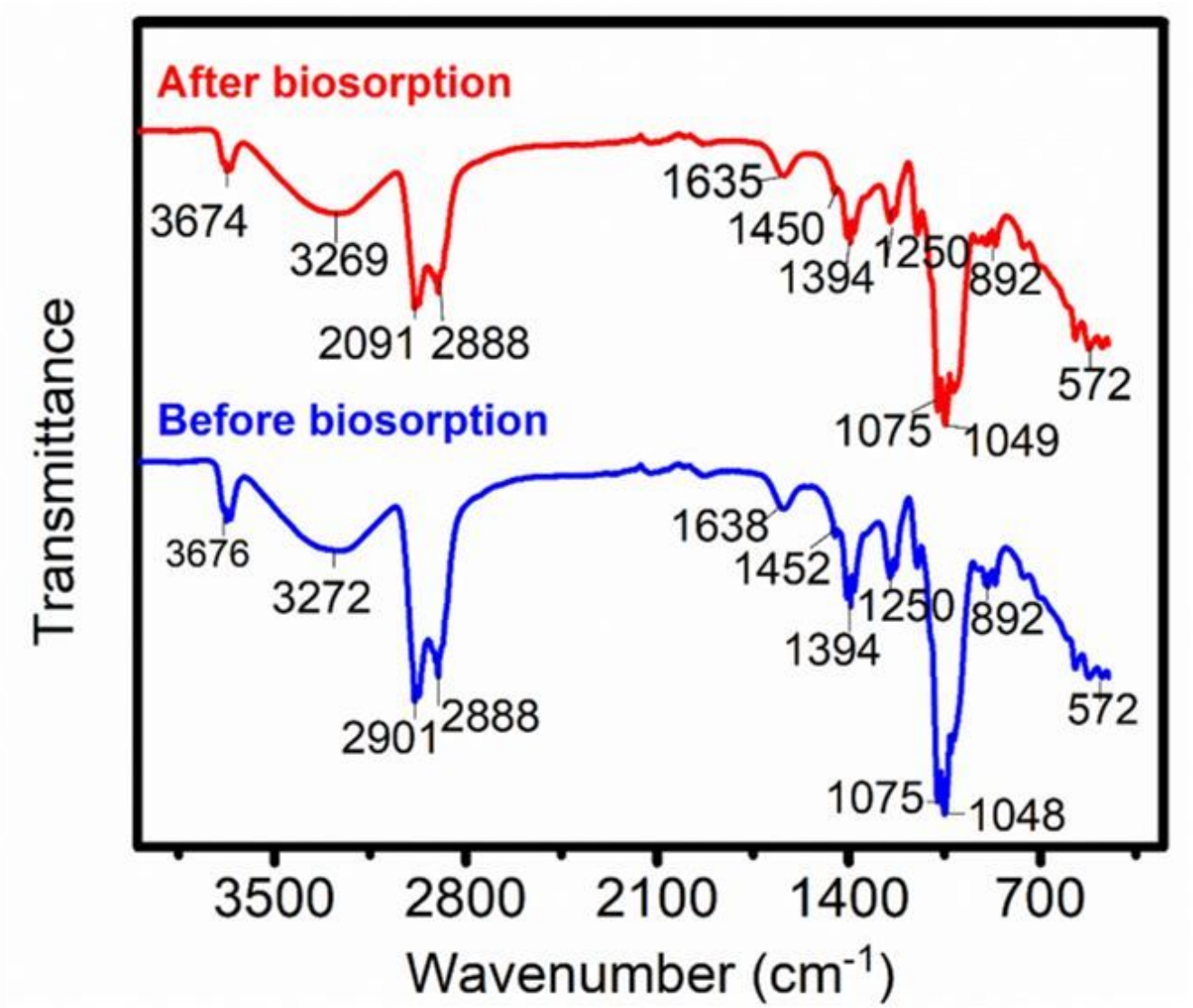

Figure 3

FTIR spectra of Kocho before and after biosorption of MB dye.

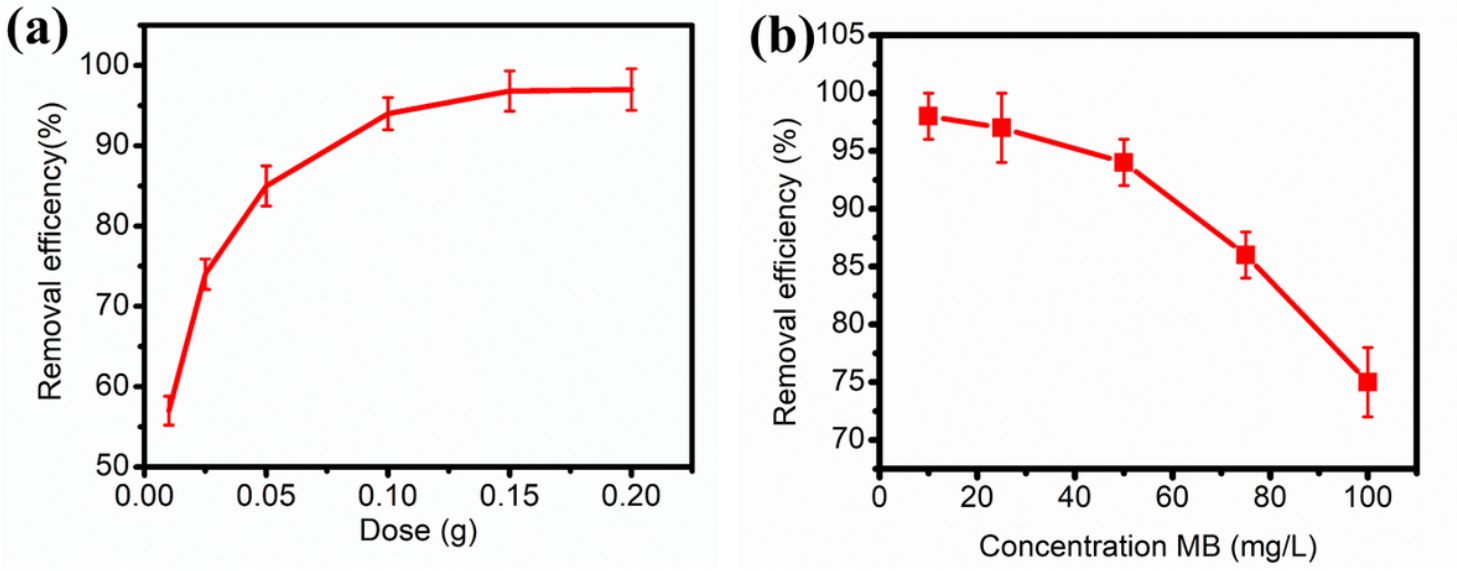

Figure 4

(a) Effect of biosorbent dosage on removal efficiency and (Co=50mg/L, contact time =50min and pH= 8) and (b) Effect of initial MB concentration on removal efficiency (dose= 0.1g, contact time = 50min and pH=8).

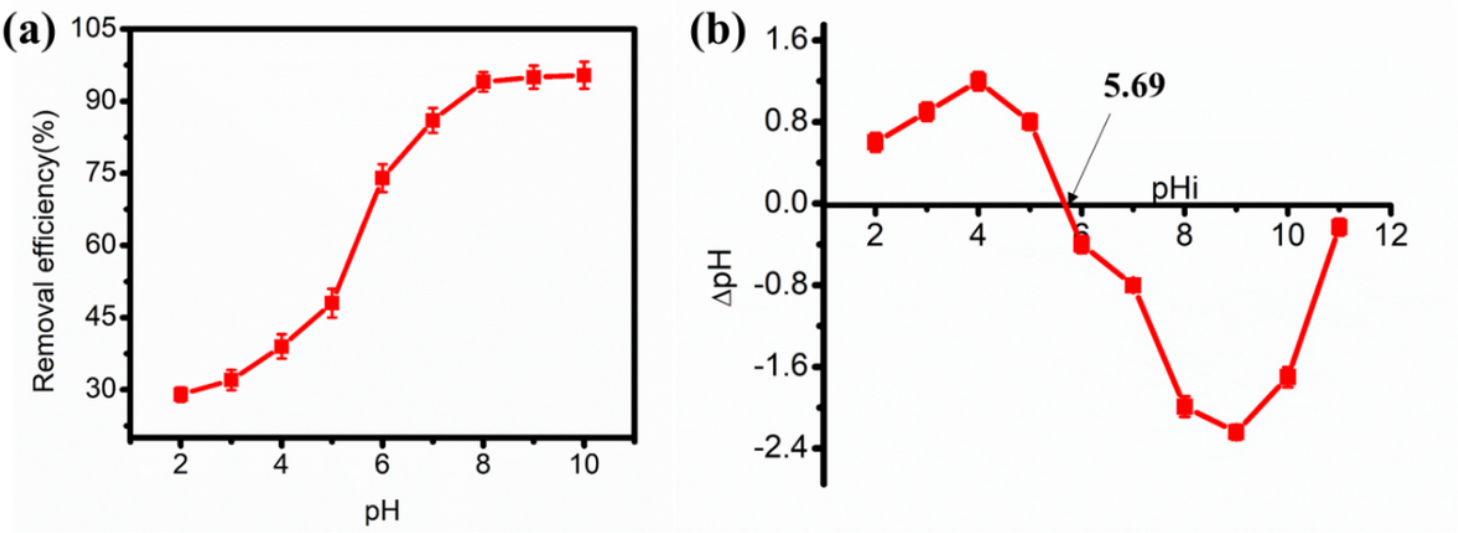

Figure 5

(a) Effect of pH on removal efficiency and (Co=50mg/L, dose= 0.1g and contact time= 50 min) and (b) Determination of zero point of charge of Kocho.

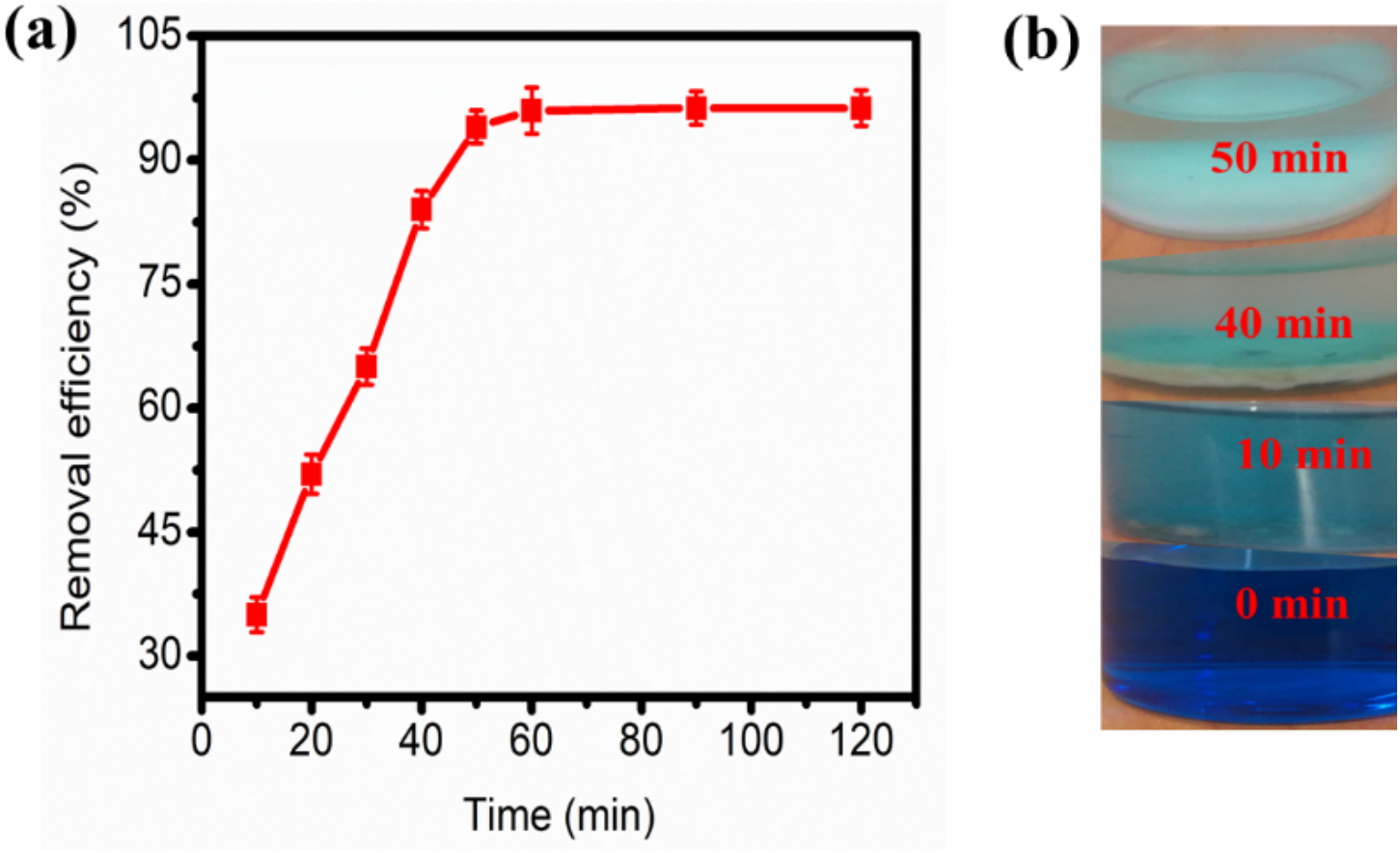

Figure 6

(a) Effect of contact time on removal efficiency and (Co=50mg/L, dose= 0.1g and pH=8) and (b) discoroziation of MB dye at different incubation time with Kocho powder.

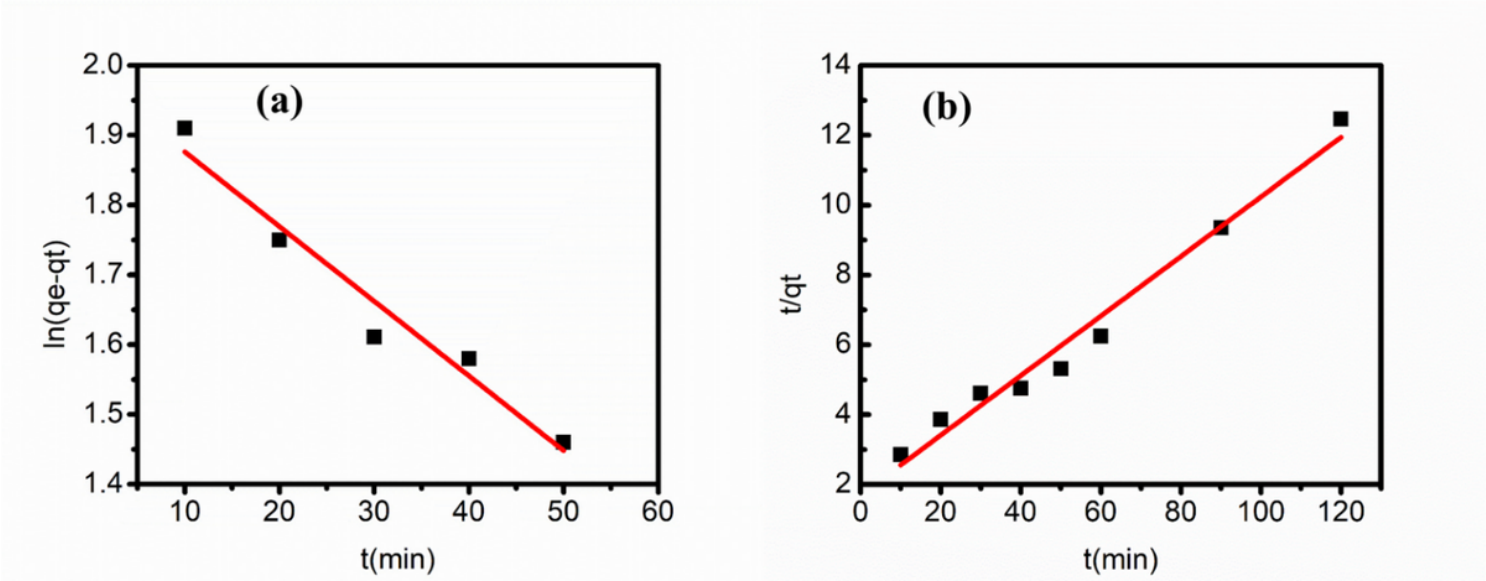

Figure 7

(a) Pseudo-first-order kinetics and (b) Pseudo-second-order kinetics.

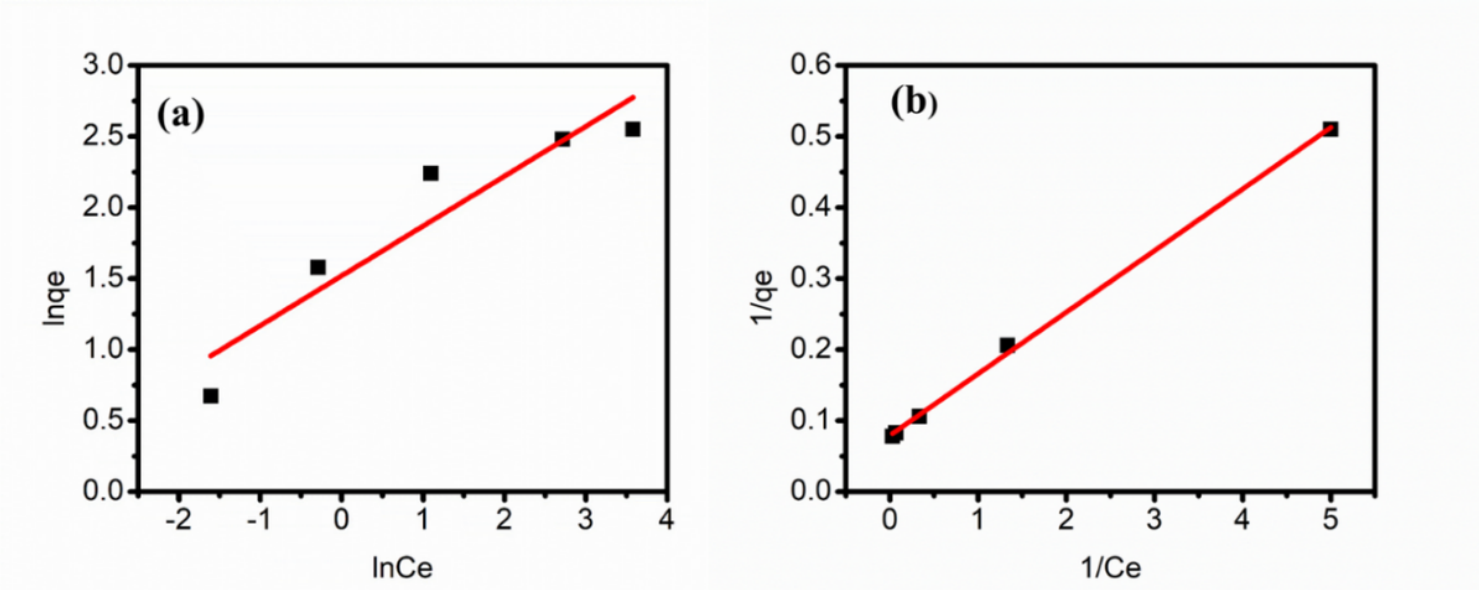

Figure 8

Isotherm study for the adsorption of MB on Kocho (a) Freundlich adsorption isotherm and (b) Langmuir adsorption isotherm.

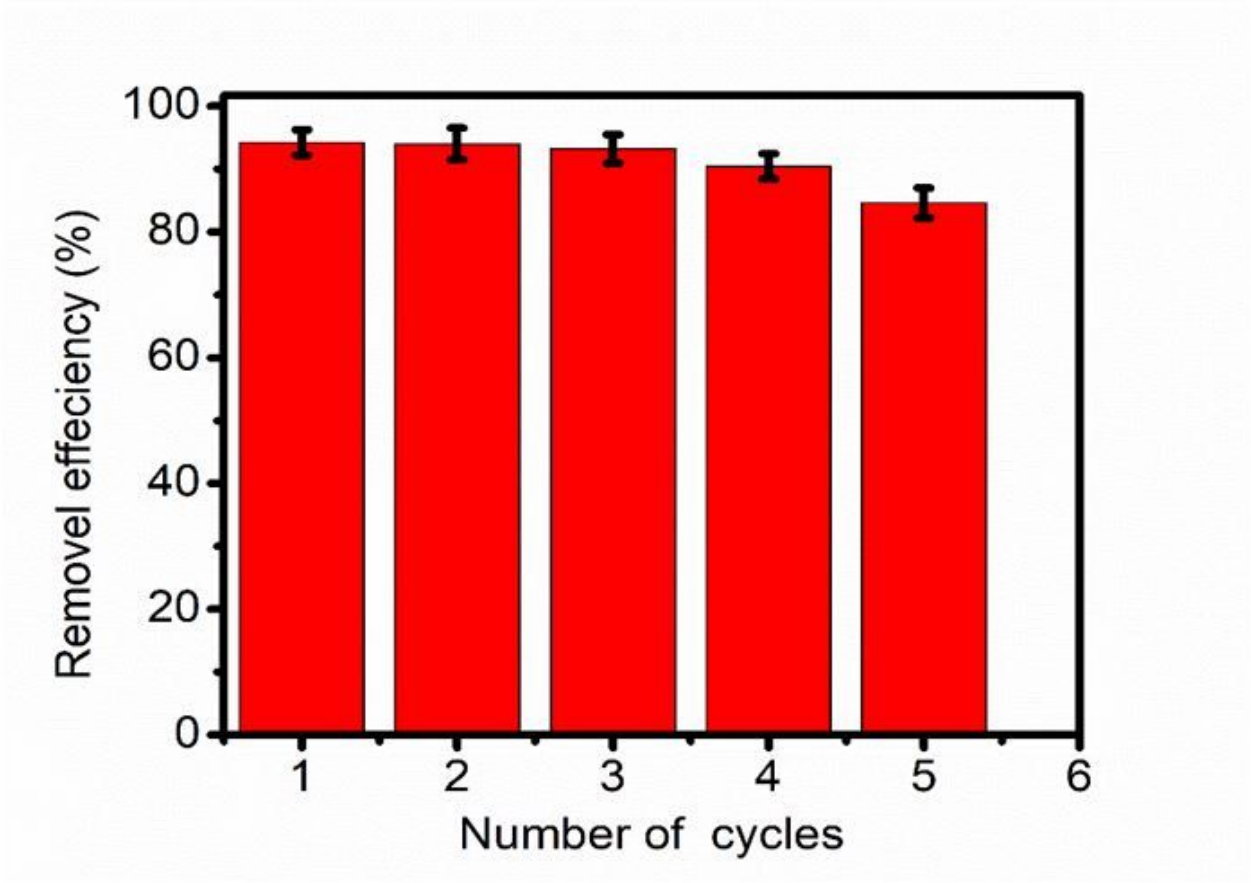

Figure 9

Reusability of adsorbent for five cycle adsorption−desorption process.

Supplementary Files

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- ElectronicsSupplementaryInformationESI1.docx