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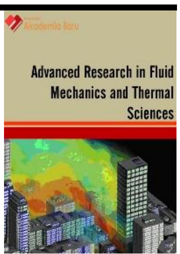

Removal of Methylene Blue and Congo Red Dyes by Pre-treated Fungus Biomass – Equilibrium and Kinetic Studies

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ABSTRACT

Adsorption potential of macrofungi spent mushroom waste (SMW) (Agaricus bisporus) to remove methylene blue (MB) and congo red (CR) dyes from aqueous solution was investigated using native and Pre-treated biomass using autoclave at optimum conditions. Batch experiments for the spent mushroom were carried out. Spent mushroom waste was observed to have uptake capacity of 239.818 mg/g and 76.412 mg/g for MB and CR, respectively. Optimum pH for biosorption uptake onto the fungal biomass was observed to be pH 8 for MB and pH 5 for CR. The optimum contact time was found to be 4 h for MB and 3:30 h for CR. Optimum average particle size was obtained to be 0.089 mm. Three equilibrium isotherm models have been used for representing the experimental statistics. The Langmuir model gave the best results for each dye. Three kinetic models were used for the MB and CR using the spent mushroom biomass, good matching was found between pseudo second order kinetic model and experimental data (R2 > 0.999). Fourier-Transform Infrared (FTIR) test showed that the functional groups (carboxyl, alcohols, and alkanes) at the surface of fungi biomass play the principal role in biosorption of dyes. Scanning Electron Microscopy (SEM) and Scanning Electron Microscopy with energy Dispersive of X-ray (SEM-EDX) revealed surface texture and porosity indicating better surface area for the dye reaction. The usage of autoclaved biomass is a whole lot safer as it does now not pose any danger to the environment.

Keywords:
Spent mushroom waste (SMW); MB; CR; biosorption; isotherm; kinetic

1. Introduction

The treatment of textile effluents to remove dyes in a monetary and value efficient way remains as a primary problem for textile industries. Many conventional methods have been drastically implemented for the removal of dyes from wastewater. Over time, treatments like photocatalytic degradation [1], coagulation [2], membrane filtration [3], microbiological decomposition [4] and many others had been used for the removal of pollutants from aqueous solution but those strategies were proved to be practically not feasible for the effective application in removal of the pollutants [5]. Those treatments additionally pose techno-cost effective shackles for subject-scale applications

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[6]. The low biodegradability of synthetic dyes has made it extra hard for the conventional biological wastewater treatment method to be powerful. Additionally, a few dyes are extraordinarily toxic and/or carcinogenic, and their biodegradation can produce even more poisonous fragrant amines [7]. These challenges have motivated researchers to search for newer and safe alternative material that is low-cost and available for the efficient removal of dyes and pollutants from wastewater. The dye molecules show the affinity to stick at the diverse surfaces, and this feature provided a concept about the exploitation of adsorption system for dyes removal from wastewater [8]. Adsorption is the mass transfer of a substance (adsorbate) from liquid or gas phase onto the solid interface (adsorbent) and becomes attached by physical and/or chemical interactions. It has been concluded that the adsorption process has advantages over other processors due to the lack of sludge and the ease of operation. From the few alternatives available methods of such treatments, biosorption is regarded as the most efficient method. Among various biomasses, spent mushrooms (macrofungi type) are yet to be fully investigated. Mushrooms are found in many regions of the world and grow prolifically. Similarly, the performance of fungal biomass depends on its surface residences as governed through the chemical structure, hydrophobic and hydrophilic characters of the cellular wall [9]. Pre-treatment is used to enhance the surface traits of the fungal biomass with regards to their dye adsorbing mechanism. This could be in terms of increasing the charge at the biomass surface or the binding sites for adsorption and enhancing ion-alternate [10]. Methylene blue (MB) is a tricyclic phenothiazine cationic dye used in different fields: textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical, and food industries [11]. High dosages of MB can cause toxicity, and it is also harmful if swallowed; it irritates the eyes, respiratory system and skin [5]. Congo red (CR) is a benzidine-based anionic diazo dye that can cause allergic reactions and can be metabolized to benzidine – a carcinogenic product [12]. In this study the best biomass was selected from among its four cases (the native, biomass exposed to autoclave, and chemically treated biomass (acid- and base-dealt with) to be used for removal of the dyes MB and CR in a batch system at optimum operating conditions.

The spent mushroom substrate has components of 14% protein and many vitamins and magnesium, calcium, zinc and iron, and higher amount of humic, fatty and amino acids. The lignocellulosic component present in spent mushroom substrate possesses negatively charged groups like phenolic, carboxylic and hydroxyl groups. The presence of these groups gives them ability to bind with dyes and metals. Generally, the adsorption process of spent mushroom substrate typically relies on the fact that surface of spent mushroom substrate possesses negative charge due to the presence of anions such carboxyl, hydroxyl, amide groups; and adsorbates such as dyes, pollutants, and heavy metals possess positive charge ions. The active functional groups and charge on the spent mushroom substrate are analysed by FT-IR spectroscopy. This spectroscopic analysis revealed that hydroxyl, phosphate, amide and carboxyl group of lignocelluloses and glucans, mannans, and chitin of mushroom are involved in the adsorption process. The ability of spent mushroom substrate to bind with the dyes, metal ions, and pollutants depends upon the structural component of fungi and lignocellulosic agricultural residues. Chitin is an important component of spent mushroom substrate for the adsorption of heavy metals and radionuclides, while chitosan is a more effective alternative compared to chitin, to bind and form strong complexes with dyes, metals and other pollutants. During the cultivation of mushroom, lignocellulosic, hemicellulose, and cellulosic fibres are utilized by the mushroom for the growth in the period of cultivation. This leads to the gradual degradation of the substrate and pore formation. The pore size is increased with increase in time due to the continued substrate degradation process, which further increase adsorption properties of spent mushroom substrate [13].

2. Methodology

2.1 Materials and Methods

2.1.1 Materials

Adsorbent: Spent mushroom wastes were obtained from the mushroom farm in Baghdad (Al - wadaq for agricultural investment company). The Spent mushroom was dried at atmospheric temperature (37- 45°C) for five days and washed with deionized water to remove the impurities, and dried in an oven for 8 h at 60 °C. The dried sample was reduced to fine particles using mortar and pestle and sieved in order to select a determined particle size for the experiments. Materials with a particle size of not more than 0.089 mm size were obtained by sieving through mesh size 89 microns (DIN-4188). Table 1 shows the physical characteristics of the fungal biomass. These properties were measured at Oil Research and Development Centre, Ministry of Petroleum, Baghdad, Iraq.

Table 1
Physical characteristic of SMW

Spent Mushroom waste (SMW)	
Mean particle diameter (mm)	0.089
Surface area (m^2/g)	4.63
Actual density (kg/m^3)	1480
Bulk density (kg/m^3)	637
Particle porosity	0.6876

Adsorbate: Methylene Blue (MB, colour index number: 52015, chemical formula – C16H18ClN3S.2H2O, molecular weight: 373.90 g / mol, 98 % dye content) and Congo Red (CR, colour index number: 22120, chemical formula – C32H22N6Na2O6S2, molecular weight: 696.67 g/mol, 98 % dye content) [14] were purchased from Scientific Offices in Baghdad. A methylene blue dye and Congo red dye (1.0 g) was dissolved in 1L of distilled water to prepare (1000 g/l) of (MB and CR) stock solution, and the concentration of (MB and CR) used (50 mg/l) were attained by dilution of the stock solution. 50 ml of concentrated stock solution of MB and CR (1000 mg/l) were added to 1 L of distilled water to obtain a concentration of 50 mg/l. The dye concentrations were determined spectrophotometrically using UV visible spectrophotometer (Model: UV-1 100, Chrom Tech, USA). The absorbances were measured at 665 nm and 497 nm for MB and CR, respectively.

2.1.2 Methods

2.1.2.1 Modification of fungi biomass

The spent mushroom waste can also be used in modified form in order to increase the adsorption capacity. Non-modified SMW has the ability to remove dyes in general, but their ability to remove acidic dyes is limited at the low pH environment [15, 16]. However, the absorption capacity of the SMW in acidic media can be improved by pre-treating the SMW, and this helps to change the surface of biomass from hydrophilic to hydrophobic [17].

Some biomass pre-treatments were performed to reinforce the efficacy of dyes adsorption. The methods that have been used for pre-treatments are [18]

i. Auto calving: The SMW was autoclaved for half an hour at a temperature of 121 ºC and pressure of 18 psii.
ii. Acidic pre-treatment: 10 g of biomass was boiled with 100 ml of phosphoric acid solution (10% (v/v) H_3PO_4) for a quarter of an hour using a hot plate.

iii. Alkali pre-treatment: 10 g of biomass was boiled with 100 ml of (0.5 N NaOH) sodium hydroxide solution for a quarter of an hour using a hot plate.

The biomass was washed after each treatment in abundance of distilled water until the leaky water from the washing process was neutral pH (7.0 ± 0.2).

2.1.2.2 Biomass analysis using fourier transform infrared

Dry biomass samples were examined before and after pre-treatment, before and after loaded it for dyes using the spectrophotometer (FT-IR 8000, Shimadzu Japan). About 0.55 g of spent mushroom biomass was added to 100 ml of dye solution (50 mg/l), and the pH of the dye solution in the volumetric flask was calibrated to 8 and 5. The samples were shaken for4 h and 3:30 h each for MB and CR, respectively, with an agitation speed of 250 rpm. The biomass on the surface of the filter paper was collected, washed repeatedly with double distilled water, dried at 30 °C for 24 h, and analysed by FT-IR test.

2.1.2.3 Scanning electron microscopy (SEM) and energy dispersive of x-ray (EDX)

Scanning electron microscopy (SEM) is a method to signify the surface structure and morphology of the biosorbent substance. It is used to find out the shape of biomass particles and their porous structure [19]. As the number of pores on the surface of the biomass increases, their adsorption increases [20]. The surface morphology of the biomass can be known through the (SEM) technology, and the elemental composition can be obtained from (EDX) analyses, EDX analysis is a useful tool for identification of the kinds of elements contained in the biomass. The elemental composition can be obtained from (EDX) analyses. EDX analysis is a useful tool for identification of the kinds of elements contained in the biomass.

2.2 The Experimental Work

In a batch mode, a set of experiments was carried out using (100 ml) from the solution of each dye (50 mg/l) in (250 ml) volumetric flasks to reach the best conditions and applied in isotherm experiments and kinetic experiments. The dyes adsorption process onto adsorbent was applied by changing the pH (2 - 10), contact time (0 - 240 min), biosorbent dose (0.05 - 0.6 g/100 ml), agitation speed (100 - 300) rpm and the best pre-treatment of biomass. Using an incubator shaker, the volumetric flasks were shaken until they reached equilibrium according to the best time obtained from the contact time experience. A sample volume of 10 ml was taken from each flask and filtered using Whatman filter paper (No.542 England), and the amount of dye removed was measured using a spectrophotometer.

The external mass transfer coefficient was measured by mixing 1 L of each dye solution (50 mg/l) and placing it in a 2 L pyrex beaker and mixing the solution using a mixer with the specified amount of biomass, which was calculated from the constants of the best isothermal model with mass balance equation (Eq. (1)). Mixing was done at four different speeds (200, 400, 600, and 1000 rpm), and the samples were taken at time intervals, to reach equilibrium related (Ce/Co=0.05).

$$q_e = \frac{V(C_o - C_e)}{M} \tag{1}$$

where C_o and C_e are the elementary and equilibrium dye concentrations (mg/l), respectively, the volume of dye solution (l) is denoted by V, and M is the quantity of the used biomass (g), qe is the adsorption capacity (mg / g) of the adsorbent for specific dye at equilibrium .

2.3 Mathematical Models

2.3.1 Adsorption isotherm models

The equilibrium isotherm data were designed using the Langmuir, Freundlich, and Temkin isotherm models given by Eq. (2)-(4), respectively [21, 22].

$$q_e = \frac{q_m b C_e}{1+bC_e} \tag{2}$$

where qe is the equilibrium biosorption capacity (mg/g), Co and Ce are the elementary and equilibrium adsorbate concentrations in water (mg/l), respectively, qm is the maximum sorption capacity for monolayer coverage, (mg/g), b is the constant related to the affinity of the binding site, (l/mg).

$$q_e = K C_e^{1/n} \tag{3}$$

where K is constant indicative of the relative adsorption capacity of the adsorbent (mg/g) (l/mg)1/n, 1/n is constant indicative of the intensity of the adsorption.

$$q_e = B_1 \ln K_T + B_1 \ln C \tag{4}$$

where B1 = RT/b; (R) is the universal constant (8.314 J/mol.K), b is the Temkin constant, and T the absolute temperature (K°). (K_T) (l/mg) is the equilibrium binding constant corresponding to the maximum binding energy, and the constant B1 (KJ/mole) is related to the heat of adsorption.

2.3.2 Kinetics models

Kinetic studies are necessary to optimize different operating conditions for the biosorption. The rate of the biosorption process depends on the physical and chemical properties of the biosorbent material and the mass transfer mechanism. Various kinetic models have been suggested for explaining the order of reaction. The kinetics of dyes onto fungus biomass was analyzed using pseudo-first-order, pseudo-second-order, and Intraparticle diffusion kinetic models. The applicability of these kinetic models was determined by measuring the correlation coefficients (R2). High the value of R2, the model is best applicable to data.

Eq. (5)-(7) represent the pseudo-first-order, pseudo-second-order and the intraparticle diffusion kinetic models, respectively [23, 24].

$$\ln(q_{eq} - q_t) = \ln q_{eq} - (K_L t) \tag{5}$$

where qeq is the adsorbed quantum per SMW at equilibrium (kg / kg); qt is adsorbed quantum per SMW at time t (kg / kg); and KL is the pseudo-firstorder coefficient (sec-1).

$$\frac{1}{q_t} = \frac{1}{k_s q^2 eq}\frac{1}{t} + \frac{1}{eq^t} \tag{6}$$

where Ks pseudo-second order coefficient.

$$q_t = k_{id} t^{1/2} + l \tag{7}$$

where l is the value of intercept (kg / kg), and Kid is the intraparticle diffusion coefficient (kg / kg. sec).

2.4.3 The external mass transfer coefficient (kf)

The external mass transfer coefficient for the solute adsorbed at a certain particle size and optimum speed, can be obtained by the analytical solution using Eq. (8) [25 - 27]

$$k_f = -\frac{R_p \rho_p V_L}{3 W_A t} ln\left(\frac{C_t}{C_o}\right) \; 0 < C_t / C_0 < 1 \tag{8}$$

where Coo (kg/m3) and Ctt (kg/m3) are the solute concentration at time 0 and time t (in sec), respectively; RP is the radius of particle (m); ρp is the particle density (kg/m3); VL is the volume of solution (m3); and WA is the mass of fungus biomass (kg). The samples were taken after (2, 4 and 6min) annualized, for accurate estimation of kf.

3. Result and Discussion

3.1 Effect of pH

The pH is one of the most important factors affecting the process of adsorption because of its impact on the charge of the biological surface and the ionization of its molecules.

The best pH was found to remove each dye by a set of volumetric flasks containing the solution of dye at a concentration of (50 mg/l), and the pH ranges between 2-10. The results showed that the percentage of removal of MB dye gradually increased until it reached the maximum removal at pH 8, and the increase of the removal of the CR dye gradually until it reached the maximum removal at pH 5 as shown in Figure 1. Where, in the low pH solution, electrostatic repulsion occurs between the positive charge on the surface of the biomass and the positive charge on the MB dye molecules, and there is competition between the excess H^+ ions and the MB dye molecules on the biomass contact sites of the fungus, this is consistent with [28, 29]. It is also noted that the CR dye removal ratio has decreased in pH solutions less than five due to competition for biomass surface sites between hydrogen ions and dye molecules [30]. In addition, the low CR dye removal rate in solutions with a pH above five can be caused by electrostatic repulsion between the dye molecules and the surface of the adsorbent [31, 32].

In general, it has been reported that in low pH solution, the removal rate of anionic dyes is increased while the removal rate of cationic dyes is lower. Conversely, a high pH solution increases the removal of the cationic dyes and causes a low removal percentage for anionic dyes. These results are analogous to those reported by [33 - 36].

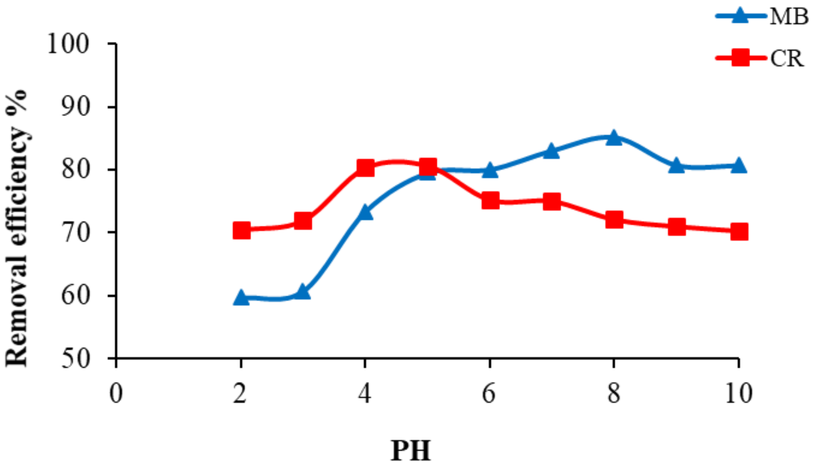


Fig. 1. Effect of pH on removal efficiency of MB and CR dyes onto SMW; dose of biomass 0.1 g/100 ml, C_0= 50 mg/L, contact time = 240 min, and agitation speed = 200 rpm

3.2 Effect of Contact Time

The uptake of the dyes was rapid in the first 30 min. This rapid phase was followed by a secondary slower phase until equilibrium was reached at 240 min for MB and 210 min for CR, respectively. shown in Figure 2. The rapid phase could be explained with the availability of enough free active binding sites on the biosorbent surface, but during the second phase, the number of binding sites is limited and the effectiveness decreased [12, 37].

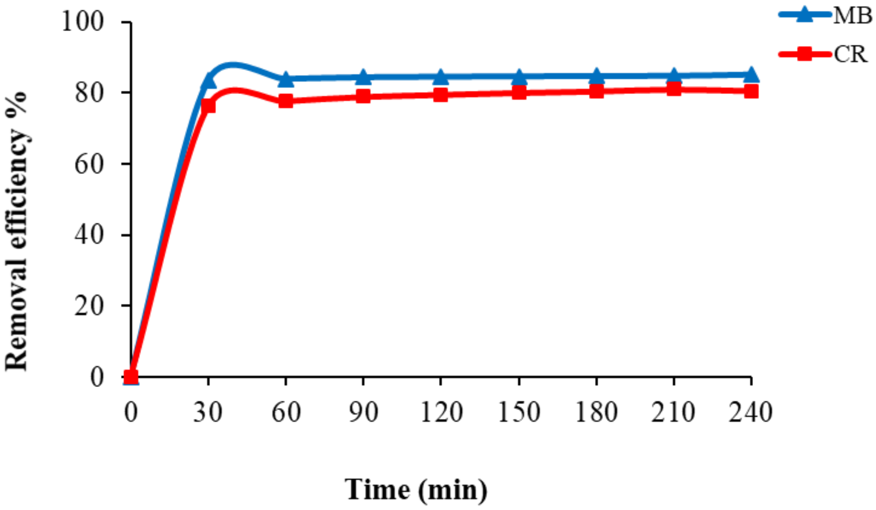


Fig. 2. Effect of contact time on removal efficiency of MB and CR dyes onto SMW; dose of biomass 0.1 g/100 ml, C_0= 50 mg/L, pH=8, 5 (MB, CR), and agitation speed = 200 rpm

3.3 Effect of Biosorbent Dose

The best dose of biomass needed to remove each dye was found through the use of amounts of adsorbent ranging from (0.05 to 0.6 g / 100 ml of dye solution), as shown in Figure 3. It is noted that the removal rate of both dyes increased with the increase of the dose of the adsorbent until it reached the maximum removal when the dose was 0.55 grams. This is due to the increased binding sites on the surface of the biomass by increasing the dose [38]. While the reason for the stability of the removal rate and reduced after 0.55 g is due to agglomeration of the adsorbent when increased the dose [39].

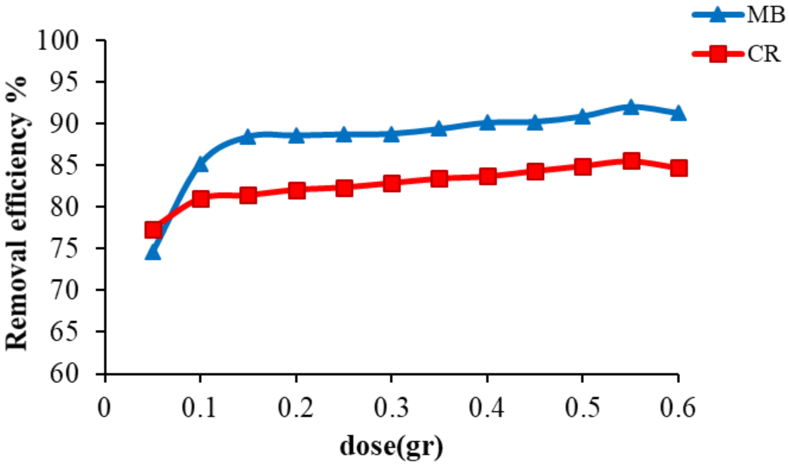


Fig. 3. Effect of dose of SMW on removal efficiency of MB and CR dyes onto SMW; contact time = (240 ,210) min, C_0= 50 mg/L, pH=8, 5 (MB, CR), and agitation speed = 200 rpm

3.4 Effect of Agitation Speed

Figure 4 shows the relationship between the removal efficiencies of MB and CR onto fungus particles at different agitation speeds. It was observed that the removal efficiency of the dyes increases when the agitation speed increases until it reaches its maximum removal efficiency at 250 rpm. The reason for this is that the high agitation speed reduces the thickness and resistance of the film. Lower the removal efficiencies after 250 rpm are may be due to sticking a part of the biosorbent on the internal surface of the volumetric flask neck during the process of the shaker, which lowers biosorptions of MB and CR. Therefore, 250 rpm was taken as the optimum agitation speed as the maximum removal efficiencies can be obtained for MB and CR (93.53% and 88.21%), respectively. These results are analogous to those reported by [40, 41].

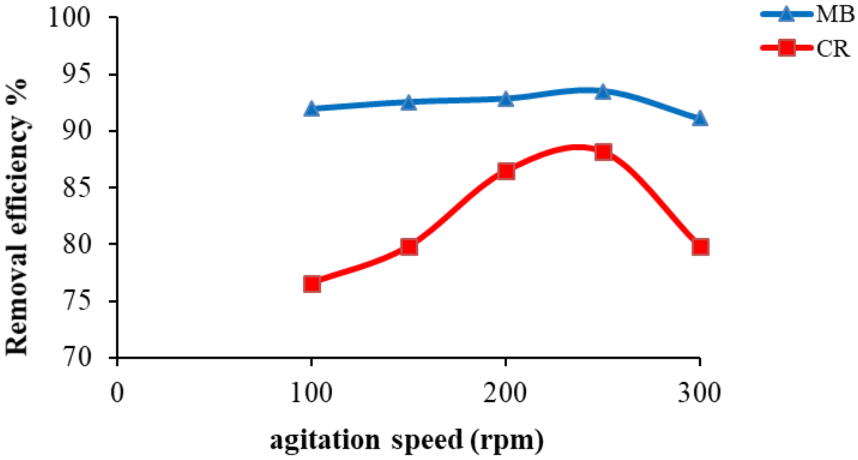


Fig. 4. Effect of agitation speed on removal efficiency of MB and CR dyes onto SMW; dose of biomass 0.55 g/100 ml, C_0= 50 mg/L, pH=8, 5 (MB, CR), and contact time= (240,210) min (MB, CR)

3.5 Effect of Modification Fungus

The effect of modification fungus biomass on the rate of adsorption by autoclaved, acid-pre-treated and alkali-pre-treated was studied. The experiments were conducted at optimum conditions for each dye. It was noted that the removal efficiency of the biomass exposed to autoclave is higher than the removal efficiency of the original biomass or treated biomass either with acid or alkali shown in Figure 5. The autoclaved biomass was found to be more efficient because cell surfaces are mainly anionic due to the presence of ionized groups such as carboxylate, hydroxyl, and phosphate in various cell wall polymers. Cells, when subjected to autoclaving, can suffer rupture and denaturation of the cell wall that can allow free access of adsorbates to cell wall binding sites [42 - 44].

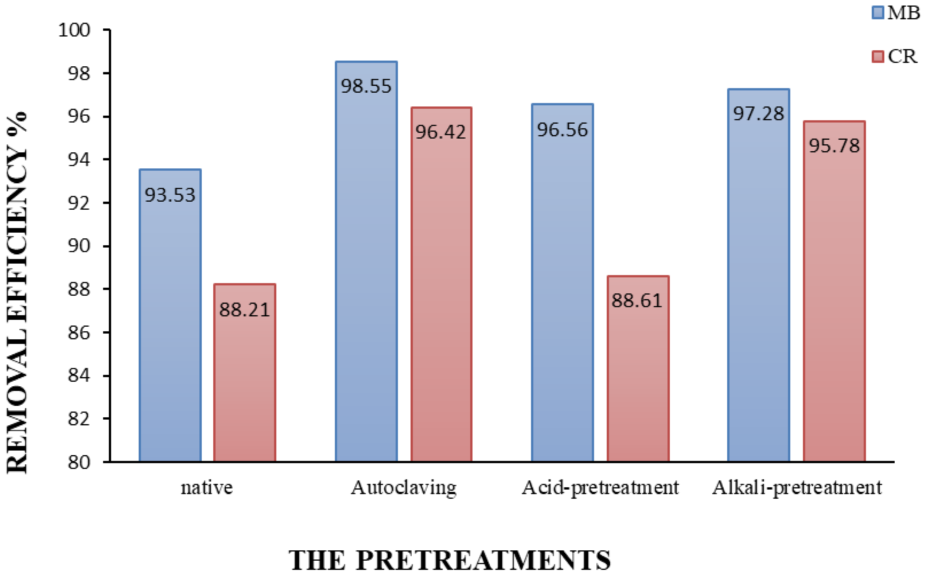


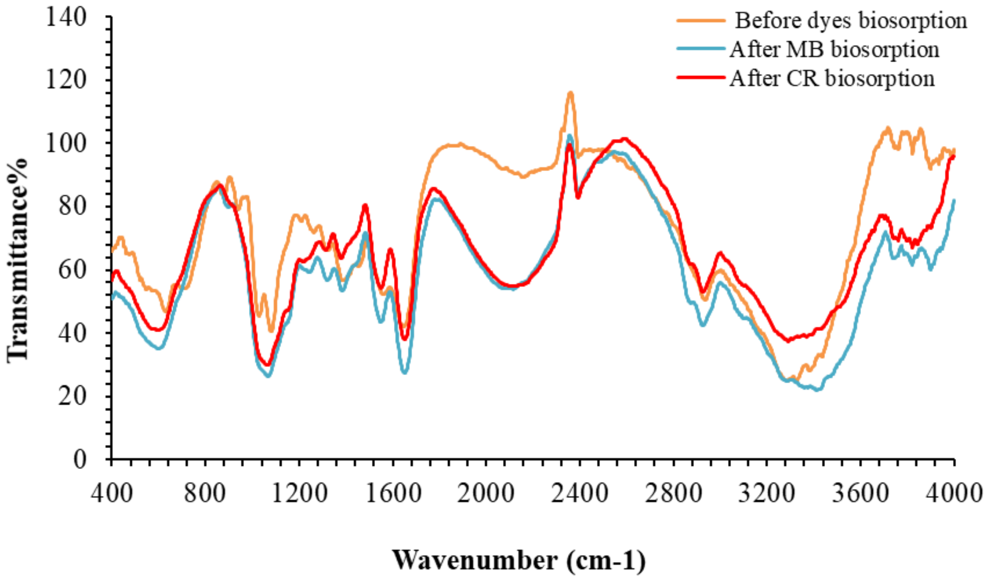
Fig. 5. Effect of the pre-treatments of SMW on removal efficiency of MB and CR dyes; dose of biomass 0.55 g/100 ml, C_0= 50 mg/L, pH=8, 5 (MB, CR), and agitation speed = 250 rpm; contact time= (240,210) min (MB, CR)

3.6 Characterization of Biosorbent

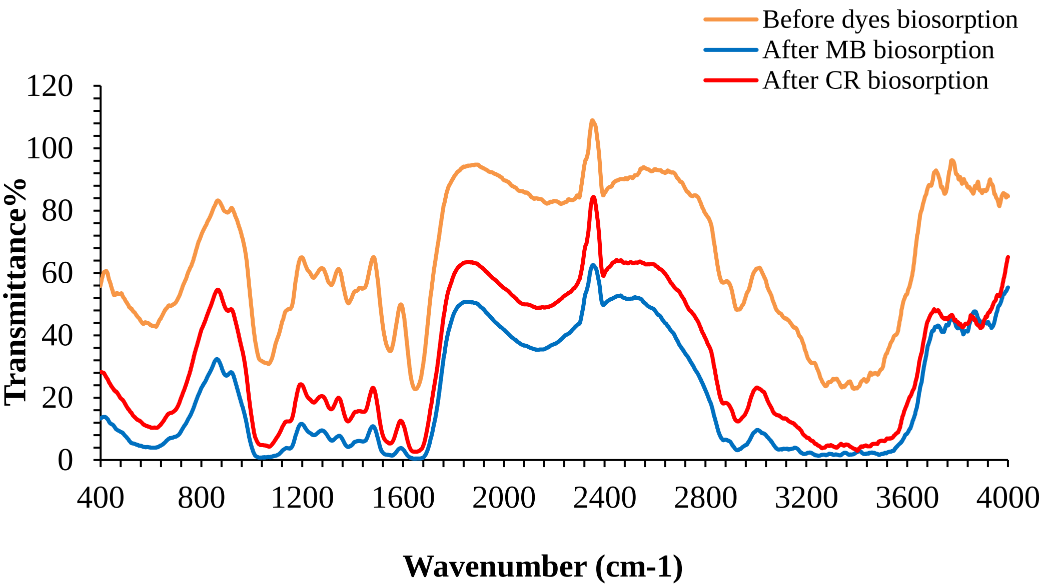
Nitrogen adsorption isotherm method was used to measure the BET analysis,which is revealed that the surface area of the used biosorbent was found to be 4.63 m2/g. FTIR test were conducted to indicate the nature of the cell wall active groups onto spent mushrooms biomass that explains the adsorption of the MB and CR dyes. The adsorption capacity of solid adsorbents not only depends on surface area but also on chemical surface functional groups.

The peaks shown in the FTIR spectrum were allocated to several active sites according to their own wave numbers. Figure 6 shows the FTIR spectrum of fungus biomass before and after sorption of MB dye and CR dye, and modified fungus after and before sorption of MB dye and CR dye. Within the range of 400 - 4000 cm-1, the wave number was measured.

Where, the FTIR spectroscopic analysis evidenced strong bands at 3750 -2900 cm-1, which indicated of (–OH) as the carboxylic group. The peaks about 2370 - 2925 cm-1 show the (-C-H+) stretching vibration of the alkanes groups and the peaks ranging 530, 900, 1072 and 3440 cm-1are described generally to the (-C-Br, C-O, -P-H+ and C-N-) stretching vibration in alkyl halides, phosphines, alcohols, and amine, respectively. These results agreed with the results obtained by [45]. The modified fungus (at autoclaving) has lower transmittance intensity than the one without treatment, and this indicated the higher removal efficiency of the treated fungus [46, 47].



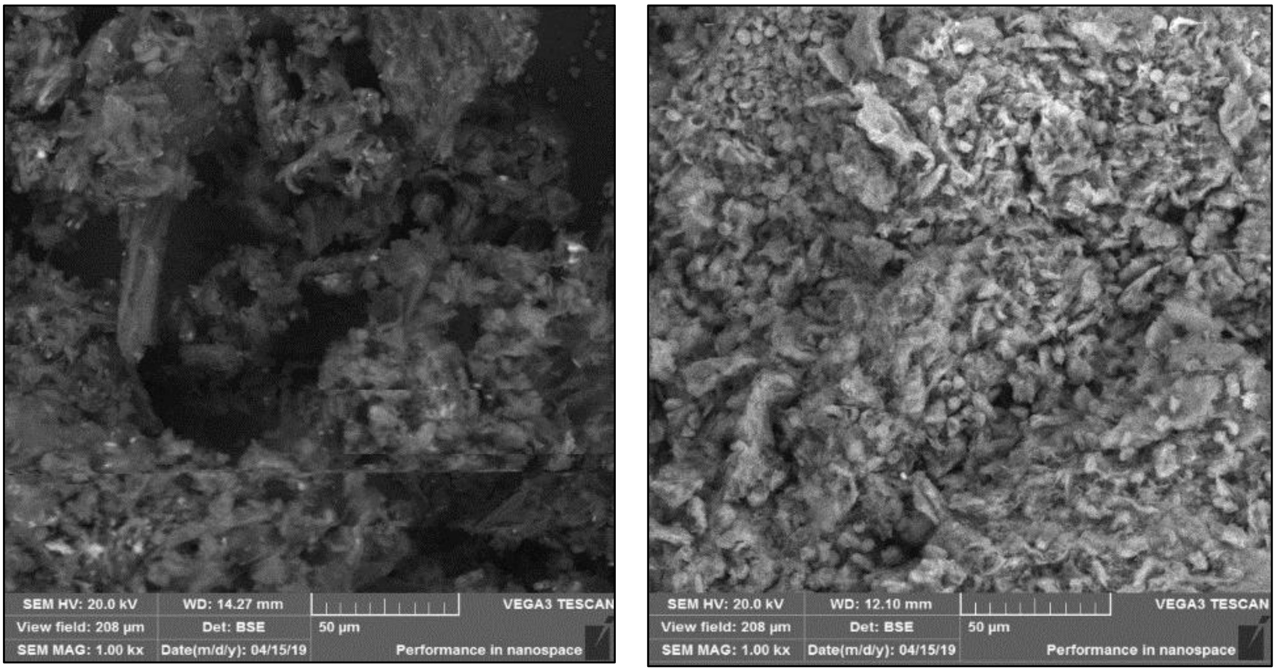
(a)



(b)

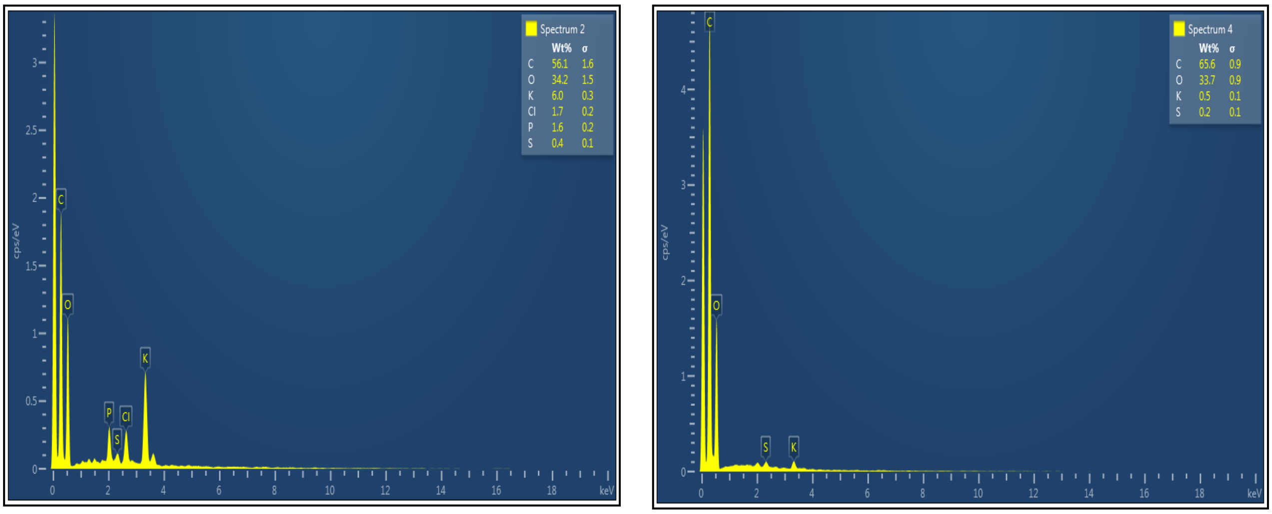
Fig. 6. FTIR spectra. (a) FT-IR spectra for SMW biomass before and after dyes loaded (50 mg/l) (b) FT-IR spectra for modified SMW biomass before and after dyes loaded (50 mg/l)

Figure 7 and Figure 8 are the SEM and EDX spectra images of the spent mushrooms biomass before and after modification, respectively. From the micrograph of fungus show surface texture and porosity. Fibrous nature of wall components was found and the surface of fungus biomass, which in turn made feasible to visualize small pores. These significant features impart a positive property onto the outer and inner surface of fungus biomass since these characteristics increase the surface area of the dyes reaction [48]. Additionally, the SEM and EDX showed that the fibrous nature of the biomass was caked when autoclaved, implying that physical strength of hyphae of the fungus was weak [36]. The amorphous homogeneous hetero-polysaccharides, often in association with proteins, play the role of cementing materials [49, 24].



(a) (b)

Fig. 7. SEM micrograph of SMW (a) Before modified (b) After modified



(a) (b)

Fig. 8. EDX spectra of SMW (a) Before modified (b) After modified

3.7 Adsorption Isotherm

Figure 9 shows the plots of equilibrium isotherms of MB and CR onto modified fungus particles at an initial concentration of 50 mg/l, pH= 8.0 and 5.0 shaking time 240 min,210 min agitation speed was 250 rpm for MB and CR respectively, and mass of adsorbent ranges from 0.05 to 0.6 g/ 100ml.

The Figure 9 and Table 2 indicate the following: The equilibrium isotherm for the removal. Of MB and CR were of a favourable type. The maximum removal efficiencies of MB and CR were achieved at high mass of adsorbent, while the maximum uptake was achieved at low mass of adsorbent. The best fit model to describe the biosorptions of MB and CR onto modified fungus particles in single system is Langmuir isotherm model with higher correlation coefficient of 0.994, and 0.984 respectively. These results are analogous to those reported by [10, 50].

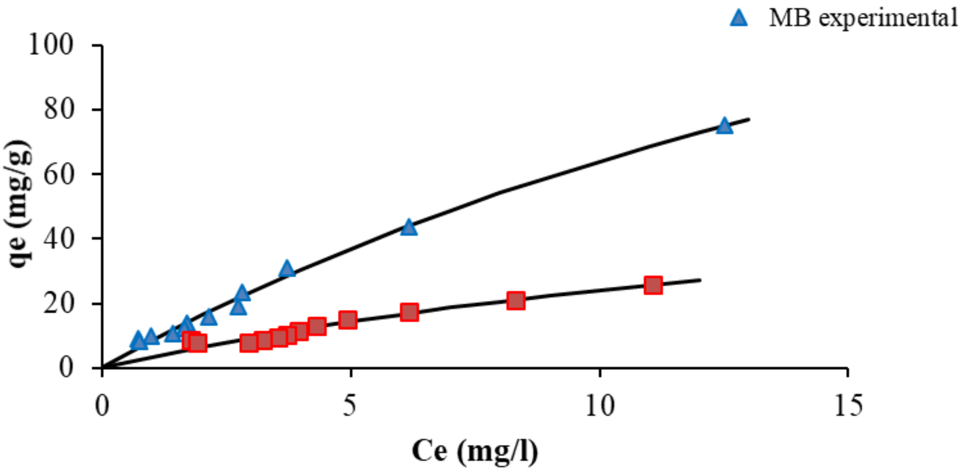


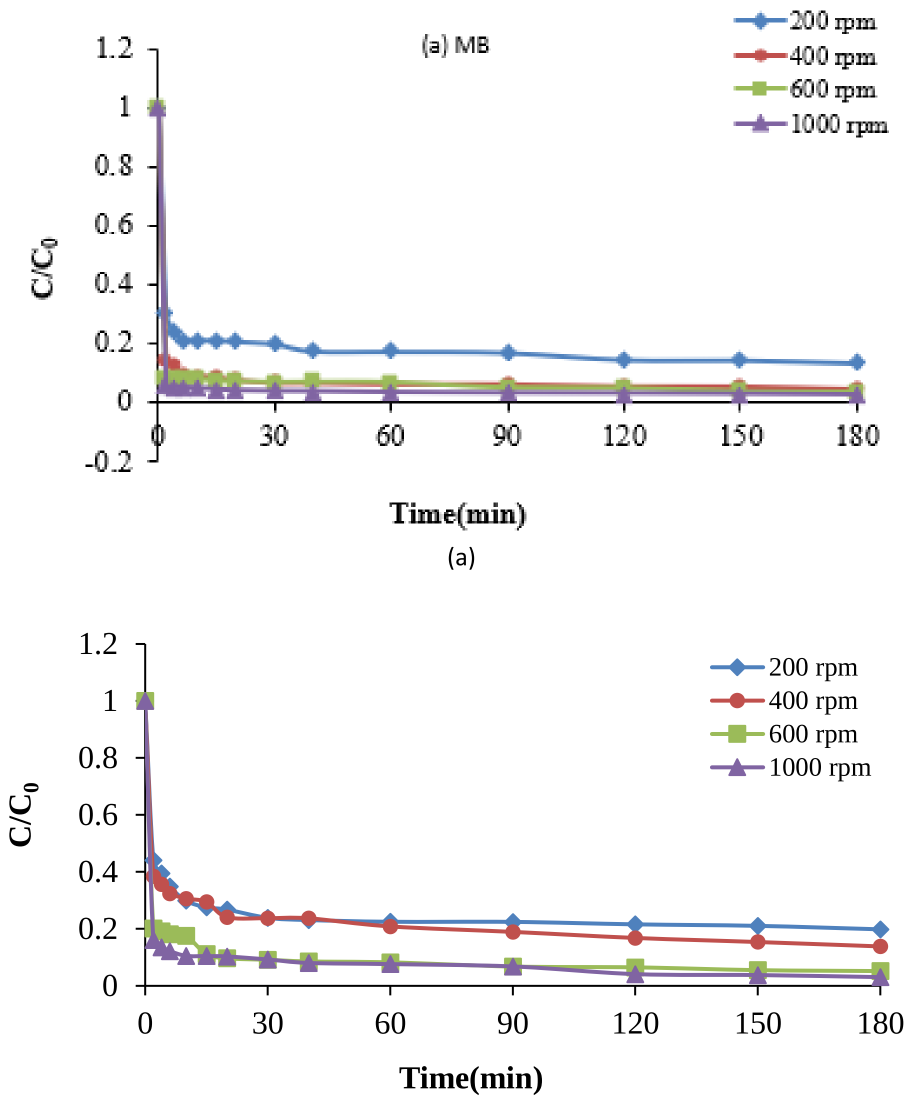
Fig. 9. Biosorption isotherms of MB and CR dyes onto modified SMW

Table 2
Isotherm models parameters for MB and CR dyes onto SMW

Model	Parameters	MB	CR
Langmuir	q_m(mg/g)	239.818	76.412
$q_e = \frac{bq_mC}{1+bC}$	b(l/mg)	0.0364	0.0460
	R^2	0.994	0.984
Freundlich	K, (l/g)	9.3514	4.0599
$q_e = K\,C^{1/n}$	n,-	1.207	1.293
	R^2	0.991	0.977
Temkin	K_T(mg/g)	1.332	0.907
$q_e = \frac{RT}{b}\ln(k_TC)$	B_1=RT/b (l/mg)	21.439	10.001
	R^2	0.918	0.860

3.8 Kinetic of Biosorption

The mass of fungus particles used for adsorption of MB and CR dyes was determined from the equilibrium related concentration of (C/C_o=0.05) using Langmuir model constants with a mass balance in 1 L of solution (50 mg/l). The optimum mass of fungus particles was found to be (2.374×10^{-3}, and 6.027×10^{-3}) kg for MB and CR respectively. The concentration decay curves of solutes were carried out at different speeds of the mixing of (200, 400,600 and 1000) rpm as shown in Figure 10. It found that the optimum agitation speed needed to a chive C/C_o= 0.05 is 400 rpm for MB and 600 rpm for CR. The kinetic constants of each model were obtained using the nonlinear analysis results of these models with the experimental data by Microsoft Excel Software. The results show that pseudo-second-order model gives the best description for the experimental data (it has the highest value of R^2) as shown in Table 3 and Figure 11. On the other hand, the uptake values were obtained from experiments are close to the calculated values. These results suggested the chemisorption nature of adsorption of MB and CR dyes onto the surface-active sites of fungus biomass [23].



(a)

(b)

Fig. 10. Concentration-time decay curves for(a) MB and (b) CR dyes biosorption onto modified fungus at different agitation speed

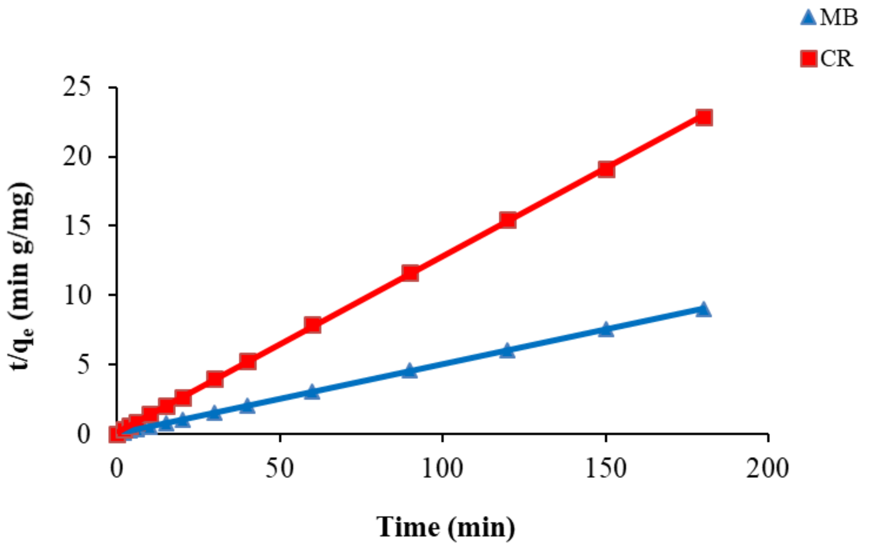


Fig. 11. The pseudo-second-order model for MB and CR dyes; C_0=50 mg/L

Table 3
Kinetic model parameters for MB and CR dyes biosorption onto fungus biomass

Model	Parameters	MB	CR
q_e experiment (mg/g)		20	7.88
Pseudo-first-order	q_e (mg/g)	1.13	0.946
	K_L (min^{-1})	0.0143	0.0223
	R^2	0.808	0.915
Pseudo-second-order	q_e (mg/g)	19.96	7.874
	K_s (g/mg.min)	0.0831	0.122
	R^2	0.999	0.999
Intraparticle diffusion	C (mg/g)	18.456	6.728
	K_{id} (mg/g.min$^{0.5}$)	0.13	0.099
	R^2	0.712	0.783

The external mass transfer coefficient (kf) is the principle parameter required for solving the batch model which was obtained using the concentration decay curve Resulting from experimental data at optimum mixing speed (400 rpm for MB and 600 rpm for CR) and (Eq. (7)). The average calculated values of (kf) for MB and CR dyes were found to be 4.053×10-5 and 1.306×10-5 m/s respectively.

3.9 Effect of Competition between Dyes on Biomass

The industrial wastewater effluents have a high content of organic pollutants such as dyes. In the biosorption systems, these contaminants interact among them with the sorbent used in different ways and different capacities, thus competing for the binding sites of the sorbent [51].

Therefore, the effect of competing resulted from the MB and CR dyes were studied at pH = 7, the dose of biosorbent = 0.55 g/100 ml, agitation speed = 250 rpm, and initial concentration 50mg/l. The experiment was conducted using different times as shown in Figure 12. The results show that the removal of MB was greater than CR; this can be due to the chemical and physical properties of MB which is more favourable to biosorbent than CR. The lowers adsorption capacity of CR may be due to its higher solubility compared to MB. These results agree with [52].

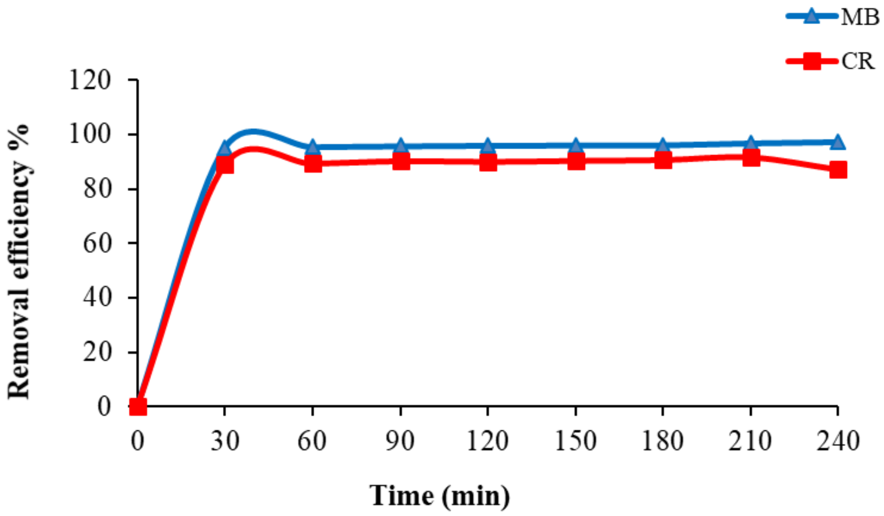


Fig. 12. Effect of Competition between Dyes onto fungus; pH=7, dose of biomass = 0.55 g/100 ml, agitation speed = 250 rpm and C_0= 50 mg/l

4. Conclusion

1. The present study shows that the modified fungus biomass by autoclave at optimum conditions is more efficient for the adsorption of MB and CR from aqueous solutions compared to untreated, acid-pre-treated and alkali-pre-treated biomass.
2. Characterization by the SEM of the biomass showed that the fibrous nature of the biomass was caked when autoclaved, implying that physical strength of hyphae of the fungus was weak.
3. FTIR analysis indicated that functional groups (Carboxyl, alcohols, and alkanes) on the surface of fungus biomass play the major role in biosorption of the dyes by complexation mechanism.
4. The optimum biosorption conditions were found to be: initial pH 8.0 (MB) and pH 5.0 (CR); contact time of 240 min (MB) and 210 min (CR); biosorbent dosage of 0.55 g/100 ml; initial concentration 50 mg/l and agitation speed 250 rpm.
5. The equilibrium data for MB and CR biosorption fitted well into the Langmuir, Freundlich and temkin models. It was found out that biosorption process is favourable, and Langmuir model gives the best fit for the experimental data.
6. The experimental kinetic data used to analyse the effect of external film boundary layer revealed that MB and CR biosorption onto fungus particles followed Pseudo-second order model for the two dyes. These suggest suitability of the adsorbent in dyes removal.

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References

[1] Mahmoodi, Niyaz Mohammad, Mokhtar Arami, Nargess Yousefi Limaee, and Nooshin Salman Tabrizi. "Decolorization and aromatic ring degradation kinetics of Direct Red 80 by UV oxidation in the presence of hydrogen peroxide utilizing TiO2 as a photocatalyst." *Chemical Engineering Journal* 112, no. 1-3 (2005): 191-196.

[2] Bozdogan, A., and H. Goknil. "The removal of the color of textile dyes in wastewater by the use of recycled coagulant, MU Fen." *Billimeri Dergisi Sayi* 4 (1987): 83-90.

[3] Wu, Jiangning, Mark A. Eiteman, and S. Edward Law. "Evaluation of membrane filtration and ozonation processes for treatment of reactive-dye wastewater." *Journal of environmental engineering* 124, no. 3 (1998): 272-277.

[4] Pearce, C. I., J. R. Lloyd, and J. T. Guthrie. "The removal of colour from textile wastewater using whole bacterial cells: a review." *Dyes and pigments* 58, no. 3 (2003): 179-196.

[5] Doğan, Mehmet, Yasemin Özdemir, and Mahir Alkan. "Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite." *Dyes and Pigments* 75, no. 3 (2007): 701-713.

[6] Akbal, Feryal. "Adsorption of basic dyes from aqueous solution onto pumice powder." *Journal of colloid and interface science* 286, no. 2 (2005): 455-458.

[7] DULMAN, Viorica, Simona CUCU-MAN, and Valentin I. POPA. "Sorption of some textile dyes by oak wood sawdust." *Cellulose chemistry and technology* 36, no. 5-6 (2002): 515-525.

[8] Mittal, Atul K., and S. K. Gupta. "Biosorption of cationic dyes by dead macro fungus Fomitopsis carnea: batch studies." *Water science and technology* 34, no. 10 (1996): 81-87.

[9] Tsezos, Marios, and Bohumil Volesky. "Biosorption of uranium and thorium." *Biotechnology and Bioengineering* 23, no. 3 (1981): 583-604.

[10] Jing, Xiaobing, Yanru Cao, Xiyu Zhang, Desheng Wang, Xiaozhe Wu, and Heng Xu. "Biosorption of Cr (VI) from simulated wastewater using a cationic surfactant modified spent mushroom." *Desalination* 269, no. 1-3 (2011): 120-127.

[11] Chen, Yue-Ming, Tsung-Ming Tsao, and Ming-Kuang Wang. "Removal of crystal violet and methylene blue from aqueous solution using soil nano-clays." In *International conference on environment science and engineering, IPCBEE*, vol. 8, pp. 252-254. 2011.

[12] Mittal, Alok, Jyoti Mittal, Arti Malviya, and V. K. Gupta. "Adsorptive removal of hazardous anionic dye “Congo red” from wastewater using waste materials and recovery by desorption." *Journal of Colloid and Interface Science* 340, no. 1 (2009): 16-26.

[13] Kulshreshtha, Shweta. "Mushroom Biomass and Spent Mushroom Substrate As Adsorbent to Remove Pollutants." In *Green Adsorbents for Pollutant Removal*, pp. 281-325. Springer, Cham, 2018.

[14] Sulaymon, Abbas H., and Shahlaa E. Ebrahim. "Saving amberlite XAD4 by using inert material in adsorption process." *Desalination and Water Treatment* 20, no. 1-3 (2010): 234-242.

[15] Ebrahim, Shahlaa E., Abbas H. Sulaymon, and Hasanain Saad Alhares. "Competitive removal of Cu2+, Cd2+, Zn2+, and Ni2+ ions onto iron oxide nanoparticles from wastewater." *Desalination and Water Treatment* 57, no. 44 (2016): 20915-20929.

[16] Farooq, Farah. "Development and Adsorption Study of Macro fungus Biocomposite for Removal of Metal Pollutants." PhD diss., Fatima Jinnah Women University, Rawalpindi, 2014.

[17] Sulaymon, Abbas Hamid, Shahlaa Esmail Ebrahim, and Mohanad Jasim Mohammed-Ridha. "Equilibrium, kinetic, and thermodynamic biosorption of Pb (II), Cr (III), and Cd (II) ions by dead anaerobic biomass from synthetic wastewater." *Environmental Science and Pollution Research* 20, no. 1 (2013): 175-187.

[18] Ebrahime, Shahlaa E., and Saja H. Alsaade. "Competitive Adsorption of Cd (II) and Zn (II) in Single and Binary systems from Aqueous Solutions onto Cork Stopper Particles." *Association of Arab Universities Journal of Engineering Sciences* 26, no. 1 (2019): 17-27.

[19] Ziagova, M., G. Dimitriadis, D. Aslanidou, X. Papaioannou, E. Litopoulou Tzannetaki, and M. Liakopoulou-Kyriakides. "Comparative study of Cd (II) and Cr (VI) biosorption on Staphylococcus xylosus and Pseudomonas sp. in single and binary mixtures." *Bioresource technology* 98, no. 15 (2007): 2859-2865.

[20] Ebrahim, S. E. "Evaluation of a mixture adsorbent and glass bead for the removal of phenol and methylene blue from water." PhD diss., Ph. D. thesis, University of Baghdad, 2008.

[21] Tian, Xiuli, Chuang Li, Huaijin Yang, Zhixiang Ye, and Heng Xu. "Spent mushroom: a new low-cost adsorbent for removal of congo red from aqueous solutions." *Desalination and Water Treatment* 27, no. 1-3 (2011): 319-326.

[22] Toptas, Aslı, Salih Demierege, Ebru Mavioglu Ayan, and Jale Yanik. "Spent mushroom compost as biosorbent for dye biosorption." *CLEAN–Soil, Air, Water* 42, no. 12 (2014): 1721-1728.

[23] Alhujaily, Ahmad, Hongbo Yu, Xiaoyu Zhang, and Fuying Ma. "Highly Efficient and Sustainable Spent Mushroom Waste Adsorbent Based on Surfactant Modification for the Removal of Toxic Dyes." *International journal of environmental research and public health* 15, no. 7 (2018): 1421.

[24] Binupriya, A. R., M. Sathishkumar, K. Swaminathan, C. S. Kuz, and S. E. Yun. "Comparative studies on removal of Congo red by native and modified mycelial pellets of Trametes versicolor in various reactor modes." *Bioresource Technology* 99, no. 5 (2008): 1080-1088.

[25] Sivapriya, J. "Studies on removal of textile dyes using dried biomass derived from aquatic plants." (2015).

[26] Bulut, Yasemin, Numan Gözübenli, and Haluk Aydın. "Equilibrium and kinetics studies for adsorption of direct blue 71 from aqueous solution by wheat shells." *Journal of hazardous materials* 144, no. 1-2 (2007): 300-306.

[27] Uzun, Ilhan. "Kinetics of the adsorption of reactive dyes by chitosan." *Dyes and pigments* 70, no. 2 (2006): 76-83.

[28] Özcan, Adnan, Çiğdem Ömeroğlu, Yunus Erdoğan, and A. Safa Özcan. "Modification of bentonite with a cationic surfactant: an adsorption study of textile dye Reactive Blue 19." *Journal of hazardous materials* 140, no. 1-2 (2007): 173-179.

[29] Osma, Johann F., Verónica Saravia, José L. Toca-Herrera, and Susana Rodríguez Couto. "Sunflower seed shells: a novel and effective low-cost adsorbent for the removal of the diazo dye Reactive Black 5 from aqueous solutions." *Journal of Hazardous Materials* 147, no. 3 (2007): 900-905.

[30] Aksu, Zümriye, and I. Alper Isoglu. "Use of agricultural waste sugar beet pulp for the removal of Gemazol turquoise blue-G reactive dye from aqueous solution." *Journal of hazardous materials* 137, no. 1 (2006): 418-430.

[31] Hameed, B. H., D. K. Mahmoud, and A. L. Ahmad. "Sorption equilibrium and kinetics of basic dye from aqueous solution using banana stalk waste." *Journal of Hazardous Materials* 158, no. 2-3 (2008): 499-506.

[32] Salleh, Mohamad Amran Mohd, Dalia Khalid Mahmoud, Wan Azlina Wan Abdul Karim, and Azni Idris. "Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review." *Desalination* 280, no. 1-3 (2011): 1-13.

[33] Tripathi, Namit. "Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review." *Journal of Applied Chemistry* 5 (2013): 91-108.

[34] Rangabhashiyam, S., and P. Balasubramanian. "Performance of novel biosorbents prepared using native and NaOH treated Peltophorum pterocarpum fruit shells for the removal of malachite green." *Bioresource Technology Reports* 3 (2018): 75-81.

[35] Bayramoglu, Gulay, and Mehmet Yakup Arica. "Adsorption of Congo Red dye by native amine and carboxyl modified biomass of Funalia trogii: Isotherms, kinetics and thermodynamics mechanisms." *Korean Journal of Chemical Engineering* 35, no. 6 (2018): 1303-1311.

[36] Kaushik, Prachi, Abhishek Mishra, Anushree Malik, and Kamal Kishore Pant. "Biosorption of textile dye by Aspergillus lentulus pellets: process optimization and cyclic removal in aerated bioreactor." *Water, Air, & Soil Pollution* 225, no. 6 (2014): 1978.

[37] Anirudhan, T. S., and M. Ramachandran. "Adsorptive removal of basic dyes from aqueous solutions by surfactant modified bentonite clay (organoclay): kinetic and competitive adsorption isotherm." *Process Safety and Environmental Protection* 95 (2015): 215-225.

[38] Rajesh, Kannan R., M. Rajasimman, N. Rajamohan, and B. Sivaprakash. "Equilibrium and kinetic studies on sorption of malachite green using Hydrilla verticillata biomass." *International Journal of Environmental Research* 5, no. 4 (2010): 817-824.

[39] Malekbala, Mohamad Rasool, Soraya Hosseini, Sara Kazemi Yazdi, Salman Masoudi Soltani, and Mohammad Rahim Malekbala. "The study of the potential capability of sugar beet pulp on the removal efficiency of two cationic dyes." *Chemical Engineering Research and Design* 90, no. 5 (2012): 704-712.

[40] Maurya, Rahulkumar, Tonmoy Ghosh, Chetan Paliwal, Anupama Shrivastav, Kaumeel Chokshi, Imran Pancha, Arup Ghosh, and Sandhya Mishra. "Biosorption of methylene blue by de-oiled algal biomass: equilibrium, kinetics and artificial neural network modelling." *PloS one* 9, no. 10 (2014): e109545.

[41] Anwar, Jamil, Umer Shafique, Muhammad Salman, Amara Dar, and Shafique Anwar. "Removal of Pb (II) and Cd (II) from water by adsorption on peels of banana." *Bioresource technology* 101, no. 6 (2010): 1752-1755.

[42] Fu, Yuzhu, and T. Viraraghavan. "Removal of Congo Red from an aqueous solution by fungus Aspergillus niger." *Advances in Environmental Research* 7, no. 1 (2002): 239-247.

[43] Sathishkumar, M., G. S. Murugesan, P. M. Ayyasamy, K. Swaminathan, and P. Lakshmanaperumalsamy. "Bioremediation of arsenic contaminated groundwater by modified mycelial pellets of Aspergillus fumigatus." *Bulletin of environmental contamination and toxicology* 72, no. 3 (2004): 617-624.

[44] Deepa, K. K., M. Sathishkumar, A. R. Binupriya, G. S. Murugesan, K. Swaminathan, and S. E. Yun. "Sorption of Cr (VI) from dilute solutions and wastewater by live and pretreated biomass of Aspergillus flavus." *Chemosphere* 62, no. 5 (2006): 833-840.

[45] Peydayesh, Mohammad, and Ahmad Rahbar-Kelishami. "Adsorption of methylene blue onto Platanus orientalis leaf powder: Kinetic, equilibrium and thermodynamic studies." *Journal of Industrial and Engineering Chemistry* 21 (2015): 1014-1019.

[46] TU, Xiang, and Guo-he HUANG. "A novel biosorbent: characterization of the spent mushroom compost and its application for removal of heavy metals." *Journal of Environmental Sciences* 17, no. 5 (2005): 756-760.

[47] Arıca, M. Yakup, and Gülay Bayramoğlu. "Biosorption of Reactive Red-120 dye from aqueous solution by native and modified fungus biomass preparations of Lentinus sajor-caju." *Journal of hazardous materials* 149, no. 2 (2007): 499-507.

[48] Deokar, Rekha Ratnakar. "Biosorption of commercial dyes using green seaweeds." (2015).

[49] Loukidou, Maria X., Kostas A. Matis, Anastasios I. Zouboulis, and Maria Liakopoulou-Kyriakidou. "Removal of As (V) from wastewaters by chemically modified fungal biomass." *Water Research* 37, no. 18 (2003): 4544-4552.

[50] El-Dhuwaib, Ibtisam MB, Fawzi S. Al-Zubaidi, and Alaa MY Al-arraji. "Biosorption of Cadmium From Aqueous Solution by Using Powdered Dead of Aspergillus Niger." *World Journal of Pharmaceutical Research* 4, no. 9 (2015): 2139-2146.

[51] Noreen, Saima. "Removal of synthetic dyes from aqueous media using biocomposites." PhD diss., University Of Agriculture, Faisalabad, Pakistan, 2017.

[52] Abood, W. M. "Removal of three textile reactive dyes (Blue, Red and Yellow) by Activated carbon and Low-Cost Adsorbents." *University of Baghdad, Iraq* (2012).