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Biosorption Of Congo Red And Basic Fuchsin Using Micro Fungi *Fusarium Oxysporum* F. Sp. *Pisi* As A Biosorbent: Modeling Optimization And Kinetics Study

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Abstract

This study investigated the potential of *Fusarium oxysporum* f. sp. *pisi* (FOP) on the removal of both important dyes, Congo red (CR) and Basic fuchsin (BF), by batch adsorption experiments. The effects of pH, contact time, and initial dye concentration were investigated. Fourier transform infrared spectroscopy (FT-IR) analysis revealed the involvement of different functional groups, mainly carboxyl, phosphate, amino and amide groups during the biosorption process. Scanning Electron Microscopy (SEM) analysis shows that the fungal mycelia have rough and porous surface. The initial pH of the dye solution strongly affected the chemistry of both the dye molecules and fungal biomass in an aqueous solution. The maximum biosorption capacities of Congo red and Basic fuchsin were found at pH 6 and 303 K, and the values were 08.72 mg/g and 32.08 mg/g, respectively. The results indicated that the bioremoval efficiency of 30 mg/L CR reached approximately 34.70% after 60 min of the exposure time; however, the maximum biosorption of 40 mg/L BF was determined to be about 79%, respectively. The contact time necessary to reach equilibrium was 60 min. Freundlich and Dubinin-Radushkevich isotherm equations well described biosorption data, and the pseudo-second order model provided the best fit to the kinetics rate. This study showed that FOP is an efficacious, eco-friendly, bio renewable and affordable biomaterial for dye removal from industrial effluents.

Keywords: *Fusarium oxysporum* f. sp. *pisi*; Congo red; Basic fuchsin; Biosorption; Kinetics.

1. Introduction

Pigments and dyes, which have complex aromatic structures, are extensively used in leather, textile, paper, printing, cosmetic, plastic, food, and pharmaceutical industries [1, 2]. The effluents generated by these industries are highly visible even at very low concentrations. Discharging of effluents, containing unexhausted dyes into water bodies affect the aquatic and human life [3]. Hence, effluents containing dye molecules must be treated to minimize the threat to the environment. Many physicochemical processes, such as photocatalysis [4], membrane separations [5], adsorption [6] and electrochemical oxidation [7]. However, these methods are found to be ineffectual due to their cost, regeneration or reusability. Biosorption is a cost-efficient and eco-friendly mechanism of removing the contaminants from wastewater, particularly those that cannot easily biodegradable like dyes [8]. There are many publications confirming the high potential of bacterial, fungal and algae species in dye removal [9-11]. Fungal biomass holds distinct advantages over other microorganisms with respect to industrial exploitation due to the large scale availability, ability to grow in cheap medium and ease of harvesting [12,

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13]. Dead fungal biomass is preferred for wastewater treatment because it is not afected by toxic wastes and chemicals and does not pollute the environment by releasing toxins and propagules [14, 15]. Some low cost fungal biomass has been used as biosorbent for the removal of dye and metal ions from or wastewater, which included *Trametes versicolor* [16], *Aspergillus parasiticus* [17], *Aspergillus foetidus* [18], *Aspergillus terreus* [19], *Diaporthe schini* [20], *Trichoderma* sp. [21], *Rhizopus* sp. [22], *Penicillium geastrivous* [23]. It's biomass contain a variety of functional groups such as carboxyl, hydroxyl, sulfate, phosphate and other charged groups which can be suitable adsorption sites [24]. Although many work has been published on sorption studies of dyes using low-cost biosorbents still there is a little literature available on the full study different sorbents used for the removal of cationic and anionic dyes. Consequently, we studied with improvement perspective, the capacities of new biosorbent *Fusarium oxysporum* f. sp. *pisi*, for the biosorption of Congo red (CR) and Basic fuchsin (BF) choosed as a representative of all anionic and cationic dyes, respectively. Batch pH, biosorption kinetic and isotherm studies were conducted to evaluate the adsorption capacity of the biomass of *F. oxysporum* f. sp. *pisi*. The characteristics of the biosorbent were evaluated by scanning electron microscope (SEM) and Fourier transform infrared spectroscopy analysis (FTIR).

2. Materials and methods

Biosorbent preparation

The biomass *Fusarium oxysporum* f. sp. *pisi* was obtained from the fungal collection of Laboratory of mycology, agronomy department of Blida. For this work, *Fusarium oxysporum* f. sp. *pisi* spores were inoculated to petri dishes which contain 20 mL of PDA. These petri dishes were incubated in darkness at 30 °C for 7 days. At the end of the incubation, fungal spores were transferred to 250 mL Erlenmeyer flasks containing 100 mL of liquid Sabouraud medium (10 g sucrose, 7 g peptone in 1 L of distilled water, final pH 6.9 at 30 °C). After 15 days of incubation, the collected mycelia were washed with distilled water to remove dirt particles and dried for 24 h at 80 °C in an oven until the weight was constant. The obtained biomass, called *Fusarium oxysporum* f. sp. *pisi* biomass (FOP), was stocked in desiccators, without any pre-treatment, for further utilization.

Preparation of dye solution

Stock solutions (0.1 g/L) were prepared in distilled water and diluted to get the desired concentration of dyes. Calibration curves for dyes were prepared by measuring the absorbance of different concentrations of the dyes. The two dyes used in this experimental work Congo red (CR) and Basic fuchsin (BF) were purchased from Sigma Aldrich. The initial pH value of the solutions was adjusted with 1 mol/L HCl or NaOH solutions. The chemical structure and other physicochemical data of the two dyes are reported in **Table 1**.

Characterization of adsorbent

Surface morphology of FOP was studied by Scanning Electron Microscopy (SEM) at 15.0 kV and 1000X magnification. To detect the various functional groups present, Fourier Transform Infra-Red (FTIR) spectra of the above sample was recorded in the spectral range of 4000 cm^{-1} to 400 cm^{-1}.

Batch biosorption experiments

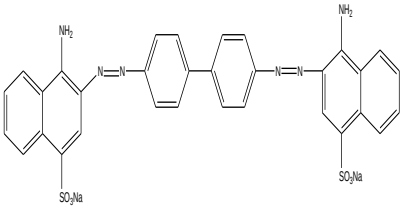
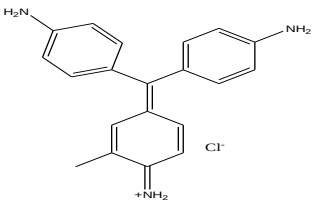
The biosorption experiments were carried out in batch mode to check the removal efficiency of FOP for dyes. The experiments were performed by interacting various concentrations of dye (5–50 mg/L) solutions with FOP (1 g/L) and agitated continuously in a thermostatic water bath shaker at 303 K until the establishment of equilibrium. After shaking, the mixtures were filtered and the supernatants were measured for the remaining dyes. The concentration of dyes remaining in the solution were evaluated by measuring the absorbance using a UV–Vis spectrophotometer (JENWAYUV–Vis 6705) at the maximal wavelength of each dye (**Table 1**). The biosorption capacity q_e (mg/g) at equilibrium conditions and the percentage of removal (%) were calculated by using Eqs. (1) and (2), respectively.

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

$$Removal\% = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (2)$$

Where C_o and C_e are the initial and equilibrium concentrations of dye mg/L, respectively; V is the volume of the dye solution (L) and m is the amount of biosorbent used (g). The effects of initial dye concentration, contact time, and pH on the adsorption of CR and BF onto FOP were studied and optimized.

Table 1. Physico-chemical characterization of the selected dyes.

Name	Congo red	Basic Fuchsin
Empirical formulae	$C_{32}H_{22}N_6Na_2O_6S_2$	$C_{20}H_{20}N_3Cl$
Chemical structure		
Molecular weight (g/mol)	696.66	337.86
C.I. number	22120	42510
Chemical/Dye Class :	Azo	Triaminotriphenylmethane
λ_{max} (nm)	500	543

Biosorption kinetics

Adsorption kinetics describes the relationship of solute uptake rate of the adsorption and the adsorption time. The study was carried out on three mathematical equations: the pseudo-first-order (Equation (3)), pseudo-second-order (Equation (4)) and intraparticle diffusion (Equation (5)) kinitic models [25].

Pseudo-first-order model:

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

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Intraparticle diffusion model:

$$q_t = k_{id} t^{\frac{1}{2}} + C \quad (5)$$

where, q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and any time t, respectively; k_1 is the pseudo-order rate constant (min^{-1}), k_2 is the pseudo-second order rate constant (g/mg.min), k_{id} is the intraparticle diffusion rate constant ($mg/g.min^{1/2}$), C is the thickness of the boundary layer, α is the initial rate of adsorption (mg/g.min) and β is related to surface coverage (g/mg).

Biosorption isotherm

Equilibrium biosorption isotherm is the most important design parameter that describes how the adsorbate interacts with the biosorbent [26]. Therefore in the present study, the Langmuir, Freundlich, Temkin, and Dubinnin–Radushkevich isotherm models were used to describe the equilibrium biosorption data [27].

Langmuir adsorption isotherm model assumes monolayer adsorption with adsorption occurring at fixed number of definite localized active sites on the surface of the adsorbent [28]. The linear form of the Langmuir isotherm equation is given as:

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L} \frac{1}{C_e} + \frac{1}{q_{max}} \quad (6)$$

Where q_e is the equilibrium dye concentration on the adsorbent (mg/g); C_e, the equilibrium dye concentration in solution (mg/L); q_{max}, the monolayer capacity of the adsorbent (mg/g); K_L is the Langmuir constant.

The Freundlich isotherm, on the other hand, assumes heterogeneous surface energies [29]. The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

$$Ln\ q_e = Ln\ K_F + \left(\frac{1}{n}\right) Ln\ C_e \quad (7)$$

Where q_e is the equilibrium dye concentration on the adsorbent (mg/g); C_e, the equilibrium dye concentration in solution (mg/L); K_F (mg/g (L/mg) $^{1/n}$) and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The Temkin isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [30], which is expressed in the following equation:

$$q_e = \frac{RT}{b_T} Ln\ K_T + \frac{RT}{b_T} Ln\ C_e \quad (8)$$

Where K_T (L/g) and b_T (kJ/mol) are the Temkin constants.

The D–R (Dubinnin–Radushkevich) isotherm equation used to distinguish between physical and

chemical adsorption is described by Equation. (9) [31]:

$$Ln\ q_e = K\varepsilon^2 + Ln\ q_{DR} \qquad (9)$$

Polanyi potential (ε) is given as Equation (10):

$$\varepsilon = RT\ Ln\ (1 + \frac{1}{C_e}) \qquad (10)$$

Where q_{DR} is the Dubinin–Radushkevich maximum adsorption capacity of dye (mg/g), K is the Dubinin–Radushkevich constant (mol^2/kJ^2), R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

The Dubinin–Radushkevich constant can give valuable information regarding the mean energy of adsorption by the following equation:

$$E = (-2K)^{-1/2} \qquad (11)$$

3. Results and discussion

Characterization of the F. oxysporum f. sp. pisi

The surface morphology of the fungus FOP mycelia is exemplified by the scanning electron micrograph in **Fig. 1.** As shown in the SEM micrograph, the fungal mycelia have rough and porous surface. According to the surface to volume ratio, large areas for dye biosorption could be created by this rough surface. Further, a large volume of pores is developed by the aggregation of these small-scale particles which increase biosorption capacity [32].

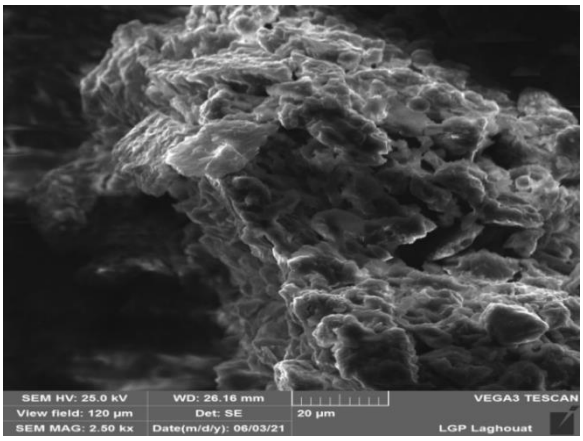


Fig. 1. SEM image of dead fungal biomass *Fusarium oxysporum* f. sp. *pisi*.

FTIR analysis is an important tool for the identification of functional groups, which in this study are capable of interacting with dyes. The FTIR spectra of FOP, before and after treatment with CR and BF, are shown in **Fig. 2.** FTIR spectral results of FOP biomass before and after treatment of dye showed the distinctive band at 3414 cm^{-1}, which is attributed to -OH Stretching vibration and –NH stretching of protein or acetamide groups of chitin fraction [33]. The peaks at 2,935 and 2877 cm^{-1} can be attributed C-H stretching vibrations [34]. Band at 1618 cm^{-1} is assigned for -NH bending vibration and the peak around 1384 cm^{-1} is due (-COO-) stretching vibration. Polysaccharides of the biomass were identified by the C-O-C group found between 1150 and 1160 cm^{-1}. It is noted that the intensities of the bands at 2935 and 1032 cm^{-1} in the spectrum of FOP decreased after the loading of biomass by dye molecules. At band 1032 cm^{-1} phosphate ($-PO_4^{3-}$) is identified in the spectrum of absorption. The biosorbent spectrum after the CR and BF adsorption process showed no significant changes in peaks, but only a slight change in intensity caused by the dye adsorption on the cell surface [30, 35]. The variety of involved functional groups in dye adsorption have been confirmed in several works and can be revealed to the dyes chemical structure and adsorbent type [36]. From these results, the functional groups potentially involved in the biosorption of CR and BF dyes included phosphate, carboxyl, amine and amide groups. Similar functional groups were found in other studies using fungal biomasses [37-39].

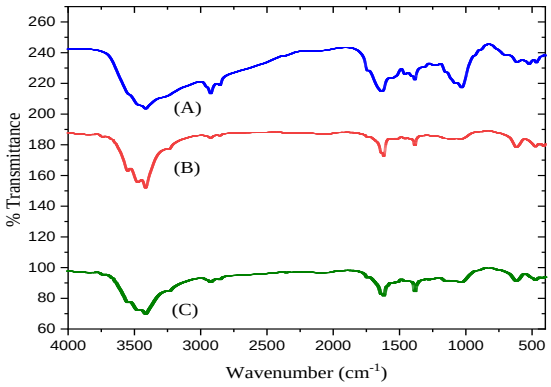


Fig.2. FTIR spectra *of Fusarium oxysporum* f. sp. *pisi* (A) before dye treatment, (B) after CR treatment and (C) after BF treatment.

Effect of pH on biosorption

pH is one of the most influencing factors for dye biosorption as it directly affects the dissociative and adsorptive ability of the dye on the biosorbent surface. The range of pH studies used for CR and BF is 2.0–7.0 and 2.0–10.0, respectively. The biosorption of CR and BF on FOP were presented in **Fig. 3**.

The biosorption of CR onto FOP is affected by change of pH, highest adsorption was observed at pH 2.0, and the biosorption decreases with increasing pH. When the pH of solution changed from 2 to 7, the biosorption capacities of FOP for CR decreased

from 20.20 to 0.34 mg/g. In basic conditions, presence of excess OH^- competed with the anionic dye for adsorption sites. For this reason, the biosorption amount of CR decreased in basic conditions [40]. While, acidic conditions could be favorable for the biosorption between the CR dye and the fungal biomass, because a significantly strong electrostatic attraction could exist between the positively charged surface of the biosorbent and the anionic dye molecule [41].

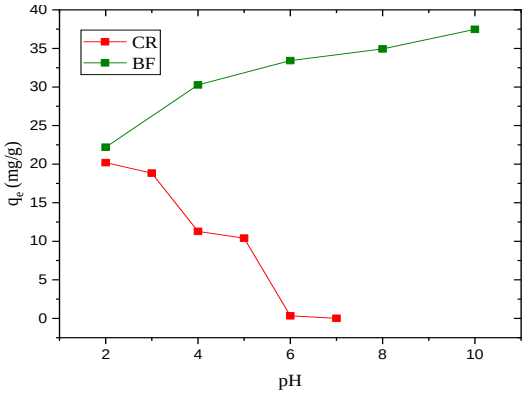


Fig. 3. Effect of pH on the removal of CR and BF dye by *Fusarium oxysporum* f. sp. *pisi* from aqueous solution.

This was under the results reported in the literature, that acid dyes largely adsorbed at highly acidic pH values [42]. However for biosorption of BF onto FOP, the **Fig.3.** shows that the optimum pH value for removal of the BF was found as pH 10, and the removal % of the BF dye was calculated about 94%, which indicates that the negative form of POF is responsible for biosorption in this range [43]. At lower pH values, the FOP surface and BF dye molecules were identically charged, which could inhibit BF dye removal due to the mutual electrostatic repulsions [44]. This phenomenon was clearly observed by other studies, such as the adsorption of basic fuchsin dye onto Yttrium oxide-doped ZnO [45].

Biosorption kinetics

The study of equilibrium time is significant to understand the optimum time involved in the distribution of the dye between the fungal biomass and the solution in wastewater treatment process. Effect of time for CR (30 mg/L) and BF (40 mg/L) biosorption onto FOP was investigated as shown in **Fig. 4.**

The experiments are preceded by varying shaking time from 5 to 120 min. From **Fig. 4.**, it can be observed that the rate of BF dye removal is high during the initial stage of contact time (5 min) followed by a slow rise until reaching equilibrium. It was observed that the percent removal (adsorption capacity, q_e) increased from 08.21 (02.46) to 36.32 (10.90 mg/g) and from 73.35 (29.34) to 79.0 (36.32 mg/g) for CR and BF, respectively attaining equilibrium at 60 min.

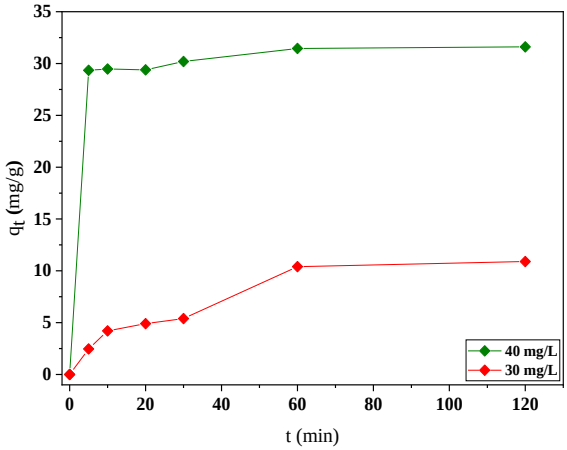


Fig. 4. Effect of contact time on biosorption of dyes onto *Fusarium oxysporum* f. sp. *pisi*.

The initial high rate might relate to the great numbers of available sites on the surface of the biosorbent [46] and the subsequently decreased sorption rate was due to gradual occupancy of those free binding sites [47]. Similar observations were also reported for other dyes and several adsorbates by other adsorbents [48, 49]. To fit the data obtained from the experimental adsorption assays the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were used. The parameters obtained from the above-mentioned kinetic models and the regression coefficients (R^2) are presented in **Table 2**.

According to the correlation coefficient R^2, the adsorption of CR and BF onto FOP both fit the pseudo-second-order model, with the determined values of 0.918 and 0.999, respectively. Additionally the equilibrium concentration q_e obtained from this model is closely in line with the experimental q_e value (see **Fig. 5 (b)** and **Table 2**). The intraparticle diffusion model was plotted to confirm the mass transfer influence on CR and BF biosorption by FOP. The intercept value of q_t vs $t^{0.5}$ plot (**Fig. 5(c)**) for each dye concentration shows that the line was not passing through the origin; it suggests that the intra particle diffusion was not the only factor on the rate limiting step deeming the entire dye removal process [50]. It may be due to the variation of mass transfer

rate in initial and final stage of biosorption. Similar trend was observed with biosorption of Congo red and Acid blue 25 onto jute stick powder and biomass of *Penicillium* YW01, respectively [51].

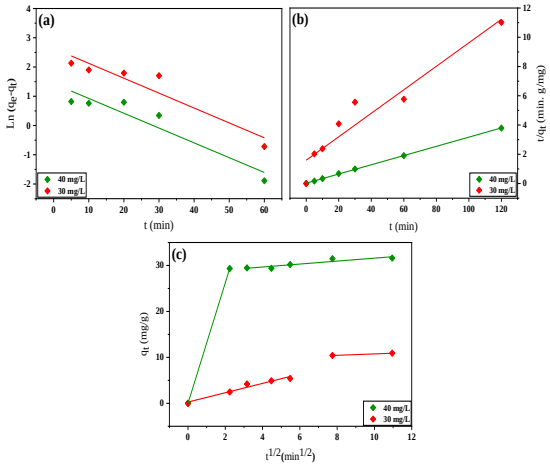


Fig 5. (a) Pseudo-first-order kinetics model (b) Pseudo-second-order kinetics model, (c) Intra-particle diffusion Kinetic model for sorption of CR and BF on FOP at 30 °C; speed of agitation 250 rpm and pH 6.0; FOP dose 1 g/L.

Table 2. Kinetic biosorption parameters at (T = 30 °C, pH = 6; absorbent dosage 1 g/l; stirring speed=250 rpm and 5-120 min) based on respective pseudo-first-order, pseudo-second-order and intra-particle diffusion models.

Sample	FOP	
Model	CR	BF
Initial concentration, C_0 (mg/L)	30	40
Kinetic		
$q_{e,\,exp}$ (mg/g)	10.90	31.60
Pseudo-first-order		
k_1 (1/min)	0.0488	0.0688
$q_{e1,cal}$ (mg/g)	12.80	08.46
R^2	0.902	0.780
Pseudo-second-order		
k_2 (g/mg.min)	0.40×10^{-2}	3.99×10^{-2}
$q_{e2,cal}$ (mg/g)	12.46	31.77
R^2	0.918	0.999
Intraparticle diffusion		
K_{id} (mg/g $min^{1/2}$)	1.017	13.121
C_1	0.271	2.51
R^2	0.958	1
K_{id} (mg/g $min^{1/2}$)	0.152	0.320
C_1	9.23	28.38
R^2	1	0.862

Biosorption isotherms

Adsorption isotherm is an invaluable curve, which describes the phenomenon governing the mobility of a substance from aqueous solution to a solid-phase at a constant pH and temperature. Biosorption isotherm studies were carried out on four selected isotherm models: Langmuir, Freundlich, Temkin and Dubini Radushkevich (D-R). The parameters obtained from the experimental data using the isotherm and the regression correlation coefficients were presented in **Table 3**.

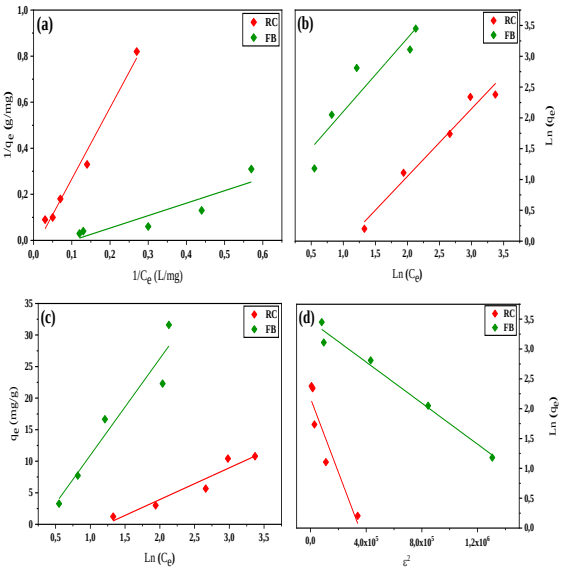


Fig. 6. Linear adsorption Isotherm; (a) Langmuir Isotherm; (b) Freundlich isotherm (c); Temkin Isotherm; (d) Dubinin–Radushkevich (D–R) Isotherms for sorption of CR and BF on FOP at 30 °C; speed of agitation 250 rpm and pH 6.0; FOP dose 1 g/L.

Fig.6 gave results on Langmuir, Freundlich, Temkin and Dubini Radushkevich (D-R) fittings for the biosorption of CR and BF on FOP. The Langmuir adsorption isotherm model was found to be inadequate to be used in this case as q_m was found to be negative. A similar result was also observed in the case of uranium (VI) - *Aspergillus fumigatus* and adsorption of MB onto *Cucumis sativus* peel, respectively [52, 53]. The correlation coefficient for the Freundlich model was found to be better in predicting the CR biosorption, whereas the Dubini-Radushkevich (D-R) model better adapts to the adsorption of BF onto FOP biomass. The values of Freundlich model parameter (n = 0.91) indicates that the cooperative isotherm model has a high correlation with the experimental data. The calculated q_e (qDR) value for FB is 32.08 mg/g which is closed to experimental q_e value (31.60 mg/g). The R^2 values were 0.981 it is indicated that the adsorption of FB onto FOP follow the Dubini–Radushkevich isotherm. For FOP, the mean free energy of adsorption was found to be 0.285 and 0.539 kJ/mole for CR and BF, respectively. Hence, the present biosorption of CR and BF seems to involve a physical mechanism [54].

A comparison of the maximum adsorption capacity with those of some other adsorbents reported in literature is given in **Table 4**. It is clearly evident from the comparison that maximum adsorption capacity of FOP was fairly high compared with the other reported adsorbents [55-67], indicating that FOP can be classified as a good adsorbent for botmh dyes CR and BF.

Table 4. Comparison of biosorption capacities of various biosorbents for removal of Congo Red and Basic Fuchsin

Biosorbent	Dye	pH	q_m (mg/g)	References
Zeolite	CR	3.0	4.30	[55]
Aspergillus niger	CR	6.0	14.72	[56]
Rice husk ash	CR	6.0	7.05	[57]
Cabbage waste powder	CR	8.0	2.31	[58]
Olive leaves	CR	7.0	24.51	[59]
Cashew nut shell 5	CR	2.5	5.18	[60]
Pine cone	CR	3.5	32.65	[61]
Waste red mud	CR	2.0	4.05	[62]
kaolin	CR	3.0	5.60	[55]
Fusarium oxysporum	CR	6.0	8.76	This study
Mussel powdered eggshell membrane	BF	6.0	48	[63]
Bottom ash	BF	9.0	9.15	[64]
Euryale ferox salisbury seed shell	BF	6.0	19.48	[65]
Reduced graphene oxide	BF	9.0	34.1	[66]
Oxide coated kaolinite (IMK)	BF	9.0	9.5	[67]
Deoiled soya	BF	9.0	13	[64]
Fusarium oxysporum	BF	6.0	32.08	This study

Table 3. Freundlich, Temkin and Dubinin-Radushkevich isotherm parameters for removal of CR and BF by the biomass *Fusarium oxysporum* f. sp. *pisi* at (T = 30 °C, pH = 6; time =1 h; absorbent dosage = 1 g/l; stirring speed=250 rpm).

Sample	POF	
Dye	CR	BF
Initial concentration, C0 (mg/L)	30	40
Freundlich		
KF (mg/g) (mg/L)1/n	0.315	2.488
n	0.91	0.84
R2	0.967	0.868
Temkin		
KT (L/g)	3.38	1.33
bT (kJ/mole)	0.501	0.164
R2	0.921	0.923
Dubinin-Radushkevich		
qDR (mg/g)	8.76	32.08
KDR (mole2/kJ2)	6.17E-06	1.72E-06
E (kJ/mole)	0.285	0.539
R2	0.890	0.981

4. Conclusions

The removal of both dyes Congo red and Basic fuchsin from an aqueous solution using *Fusarium oxysporum* f. sp. *pisi* was studied. The maximum biosorption capacities were 08.72 mg/g for the CR and 32.08 mg/g for the BF, at pH 6 and 303 K. The equilibrium isotherms were carried out at pH of 6 and temperature of 303 K. The pseudo-second-order best represented the kinetics experimental data. The adsorption of CR and BF molecules using FOP biosorbent obeyed Freundlich and Dubinin–Radushkevich adsorption isotherm, respectively. The results of the present investigation suggested that biomaterial *F. oxysporum* f. sp. *pisi* can be used as an environmentally and economically feasible low cost biosorbent for the removal of CR and BF from aqueous solutions

5. Conflicts of interest

We wish to confirm that there are no known conflicts of interest associated with this publication.

6. References

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