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Utilization of mustard and linseed oil cakes: novel biosorbents for removal of acid dyes

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ABSTRACT

In this research study, the biosorption of Synolon red 3HF and Synolon black HWF-FS dyes onto novel biomasses mustard oil cake and linseed oil cake, respectively, was investigated in the batch mode using different process parameters like pH, particle size, biosorbent dose, initial dye concentration, contact time, and temperature. Maximum biosorption capacity was observed at pH 1 for Synolon red 3HF onto mustard oil cake and pH 2 for Synolon black HWF-FS onto linseed oil cake. The biosorption capacity was efficient at the smallest particle size of biosorbent. The amount of dye sorbed (mg/g) decreased with the decrease in biosorbent dose and increased with increase in initial dye concentration and temperature. The Freundlich isotherm model was best fitted to experimental data. The biosorption followed the pseudo-second-order kinetic model suggesting a chemisorption mechanism. An increase of biosorption capacity with temperature shows an endothermic nature of the process. In this research, the influence of electrolytes, heavy metals, and surfactants on the removal of dyes was also examined.

Keywords: Biosorption; Mustard oil cake; Linseed oil cake; Acid dyes; Modeling

1. Introduction

The rapid urbanization has its great effects on the pollution of water stream and formation of solid waste [1]. There is large number of pollutants of ecosystem. Dyes are one of them having many uses; they have long being used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics, and food industries [2].

Discharge of these dyes into water, may have an effect on the people using these water bodies for living purposes like drinking [3]. These dyes can also influence the aquatic system because they reduce the sunlight transmission through water. They may cause severe damage to human beings, such as defunctioning of kidneys, reproductive system, liver, brain, and central nervous system [4].

In this research work, Synolon red 3HF and Synolon black HWF-FS dyes are used, which are acidic in nature. Acidic dyes are anionic dyes. They are water soluble, can be used with silk, wool, and polyamide, modified acrylic and polypropylene fibers. They have harmful effects on human beings because they are organic sulfonic acids [5].

Dyes have very complex structures and synthetic origin so they are difficult to decolorize. Most dyes are designed in such a way to become resistant to environmental conditions like light, affect of pH, and microbial attack. The removal of color from waste effluents becomes environmentally important because even a small quantity of dye in water can be visible and toxic [6].

The most widely used methods of dye removal from industrial effluents are; (i) chemical, (ii) physical, and (iii) biological methods [7]. Different physiochemical methods employed are coagulation, ultra filtration, flocculation, ozonation, reverse osmosis, photo-oxidation, electro kinetics, precipitation, ion exchange and adsorption on activated carbon, silica and manganese oxide [8]. Many disadvantages are coupled with most of these methods such as high energy cost, formation of by-products in oxidation method, absorbent regeneration, disposal requirement in ion-exchange method, the high sludge production and formation of large particles in coagulation/flocculation method [9].

Adsorption has gained good turn position among all these methods. Adsorption is a method used for the separation of mixtures on laboratory and industrial level where it is a surface phenomenon.

There are two types of adsorptions according to the attractive forces between adsorbent and adsorbate.

(1) Physical adsorption.
(2) Chemical adsorption.

Activated carbon (AC) has been extensively used for the removal of dyes from wastewater. AC is present in granulated or powdered form. But after adsorption, AC will be present in more toxic form, as a result increasing disposal price. Moreover, AC is high [10].

Attempts have been made to find inexpensive and easily available adsorbents of pollutants. Agriculture wastes are most common raw materials used for this purpose, because they are renewable, available in large amount, and are less expensive than other materials. Seed press cakes are used for this purpose for example adsorption of copper by mustard oil cake [11] sugar cane bagasse [12] rice husk [13], and calcinated mussel shells [14] biosorption of safranin by calcinated bones [15].

In this study, adsorbent mustard oil cake and linseed oil cake are used for the adsorption of dye. They contain significant amount of proteins. The chemical composition of oil cakes shows nitrogen (4.5%) and phosphorous penta oxide (1.5%).

Effects of different factors like pH, concentration of dye, time of contact, pore size of adsorbent, temperature, dose of biosorbent, effect of electrolytes, heavy metals, and surfactants were studied.

Table 1
General characteristics of dyes

Dye	λ-max (nm)	Type
Synolon red 3HF	400	Anionic
Synolon black HWF-FS	402	Anionic

2. Materials and methods

2.1. Chemicals

All the analytical grade chemicals were taken from Sigma–Aldrich Chemical Co., (USA) and Merck (Germany).

2.2. Preparation of biosorbent

Mustard and linseed oil cakes were obtained from a local shop. The adsorbents were repeatedly washed with hot water to remove any remaining impurities or oil. Then in order to dry it, adsorbents were kept in sunlight for 3 d and after that dried in oven at 60°C for 24 h. Then, grinded in a grinder and sieved by standard US sieves in order to obtain adsorbent with different particle sizes (60, 80, 100, 120, and 140 mesh sizes). Adsorbent of different particle sizes was then stored in bottles for further use.

2.3. Preparation of dyes solution

In this study, Synolon red 3HF and Synolon black HWF-FS dyes (obtained from local market) were used without further purification. Stock solution of dyes, concentration of 1,000 ppm, was made by dissolving 1 g of dye in 1,000 ml of distilled water. The experimental solutions of different concentration ranging from 50 to 250 ppm were made by further dilution of this stock solution.

General characteristics of dyes are given in Table 1.

2.4. Batch biosorption experimental studies

Biosorption experiments were conducted in batch mode to investigate the effects of different process parameters such as pH, biosorbent dose, particle size, initial dye concentration, contact time, and temperature on the biosorption of dyes. Effect of salts, surfactants, and heavy metals on the biosorption capacity was also studied.

The amount of biosorbed dye was calculated using the following equation:

$$q = (C_o - C_e)\ V/W \quad (1)$$

where q is the amount of dye biosorbed on the biosorbent (mg/g), C_o and C_e are the initial and equilibrium

concentration of dye solution, respectively. V is the volume of the dye solution (ml) and M is the amount of biomass (g). The % sorption was measured using the following equation:

$$\% \text{ sorption} = C_o - C_e/C_o \times 100 \quad (2)$$

All the experiments were conducted in triplicate.

2.5. Adsorption isotherm studies

The equilibrium data commonly known as adsorption isotherms are basic requirements for the design of adsorption systems. Two most commonly employed adsorption isotherm models were applied in this present investigation, viz. the Langmuir [16] and Freundlich [17] isotherm models.

2.6. Adsorption kinetics studies

The transient behavior of dyes onto the mustard and linseed oil cake biomass was analyzed using the pseudo-first-order [18] and pseudo-second-order [19] kinetic models.

3. Results and discussion

3.1. Influence of pH

Adsorption of a dye, greatly depend upon the pH of the solution. The pH of the solution influences the properties of the biomass materials, effects the adsorption mechanism and dissociation of the dye molecule. Previous studies on the dye removal indicated that solution pH has significant effect on the surface charge of the biosorbent and ionization degree of the dye molecule.

The pH of a medium will control the magnitude of electrostatic charges which are imparted by the ionized dye molecules. As a result, the rate of adsorption will vary with the pH of an aqueous medium [20]. In order to find out the optimum pH of the Synolon red 3HF and Synolon black HWF-FS dyes, experiments were performed ranging the pH from 1 to 6. The results are shown in Fig. 1.

The graph indicates that an increase in the initial pH of the dyes solution had reverse effect on the adsorption of the dye, that is, with an increase in pH, there is a significant decrease in the biosorption of dye. The maximum adsorption (1.542 mg/g) is observed at pH 1.0 for Synolon red 3HF dye and at pH 2 for Synolon black HWF-FS dye.

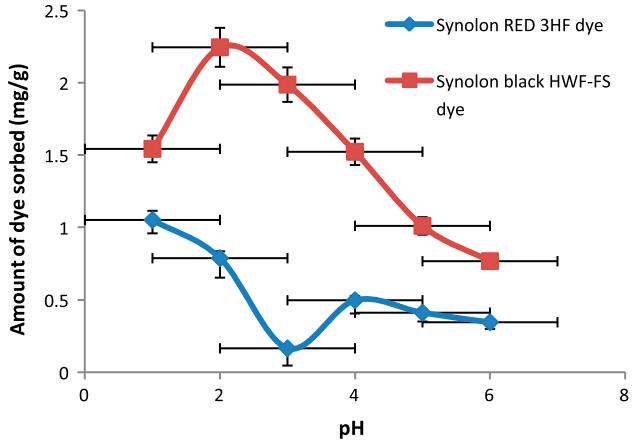

Fig. 1. Effect of pH on the biosorption of Synolon red 3HF and Synolon black HWF-FS dyes.

The decrease in the removal of dye with an increase in pH can be elucidated by considering the surface charge of the adsorbent materials. The higher adsorption of the dye on each adsorbent at low pH may result due to the neutralization of negative charge at the surface of the adsorbents, thereby increasing the protonation. This facilitates diffusion and provides more of the active surface of the adsorbents resulting thereby enhanced adsorption at their surface. A constant fall in the amount adsorbed with increasing pH may be due to deprotonation, which hinders the diffusion [21].

Akar et al. [22] observe similar behavior for the biosorption of RR198 by untreated olive pomace. It was observed that the overall surface charge of the biomass was positive up to pH 3. Maximum adsorption was observed at pH 2. As the pH increased, the surface charge on the biomass surface becomes negative, and thus, the biosorption capacity of olive pomace sharply decreases.

Similarly, Sathishkumar et al. [23] also observed a decrease in the adsorption of Remazol Brilliant Blue R (RBBR) dye, by *Jatropha curcas*, with an increase in the pH of the solution.

Generally, at low pH solution, the percentage of dye removal will decrease for cationic dye adsorption, while for anionic dyes, the percentage of dye removal will increase. In contrast, at a high pH solution, the percentage of dye removal will increase for cationic dye adsorption and decrease for anionic dye adsorption.

Aksu and Isoglu [24] studied the effect of solution pH on the adsorption of Gemazol turquoise blue-G as a reactive dye using sugar beet pulp and they noticed that the adsorption was at maximum at pH 2 where

the adsorption capacity was 83.7 mg/g and then decreased with a further increase in pH and reached zero at pH 6.

3.2. Influence of particle size of adsorbents

Particle size of adsorbent has great effect on the adsorption of dye because adsorption depends on the surface area.

Three particle sizes (60, 80, 100, 120, and 140 mesh sizes) of adsorbents (mustard and linseed oil cakes) were taken to study this effect. The results are shown in Fig. 2.

The results indicate that there is an increase in the rate of adsorption of dye with a decrease in particle size. The maximum biosorption capacity 1.012 mg/g for Synolon red 3HF and 1.754 mg/g for Synolon black HWF-FS dye was noted at the smallest particle size of 60 mesh. This smallest size is used for all other studies.

The increase in biosorption capacity may be attributed to the large surface area of the smallest particle size biosorbent and a large number of the exchange site. The higher surface area not only allowed an initial period of highly effective dye removal, but continued to effective binding with dye molecules at a much more efficient rate [25].

In a study performed by Gupta et al. [21], three different particle sizes, 170 BSS mesh, 100 BSS mesh, and 36 BSS mesh, were selected for each adsorbent, that is, de-oiled soya and bottom ash. The sorption of the dye increases with decreasing mesh size.

Mittal et al. [26] studied the process for the removal and recovery of hazardous dye erythrosine using different sieve sizes (0.425–0.15 mm (36 mesh), 0.15–0.08 mm (100 mesh), and ≤0.08 mm (170 mesh)) in the case of bottom ash as an adsorbent and (0.30–0.15 mm (50 mesh), 0.15–0.08 mm (100 mesh) and ≤0.08 mm (170 mesh)) in the case of de-oiled soya. It was observed that in each case, the uptake of the dye capacity increased with increasing mesh size.

Punjongharn et al. [27] studied the influence of particle size on adsorption of basic dyes by agricultural waste (dried Seagrape (*Caulerpa lentillifera*)). The dried algal sorbent was ground and sieved into three sizes: *S* (0.1–0.84 mm), *M* (0.84–2.0 mm), and *L* sizes (larger than 2.0 mm). Among three sorbent sizes, *S* size gave the highest adsorption capacity followed by *M* and *L* sizes. A reduction of sorbent size increased the specific surface area for mass transfer, and also increased the total pore volume, thus providing more active sites for adsorption.

3.3. Influence of the adsorbent dose

The effect of the biosorbent dose on the biosorption of Synolon red 3HF and Synolon black HWF-FS dyes on the mustard and linseed oil cakes was evaluated by varying the biosorbent dose and results are reported in Fig. 3.

The graph indicates that there is a decrease in the biosorption of dyes with an increase in the adsorbent dose. The quantity of dye adsorbed decrease from 1.548 to 0.1125 mg/g for Synolon red 3HF dye onto mustard oil cake biosorbent and from 3.125 to 0.8141 mg/g for Synolon black HWF-FS dye onto linseed oil cake.

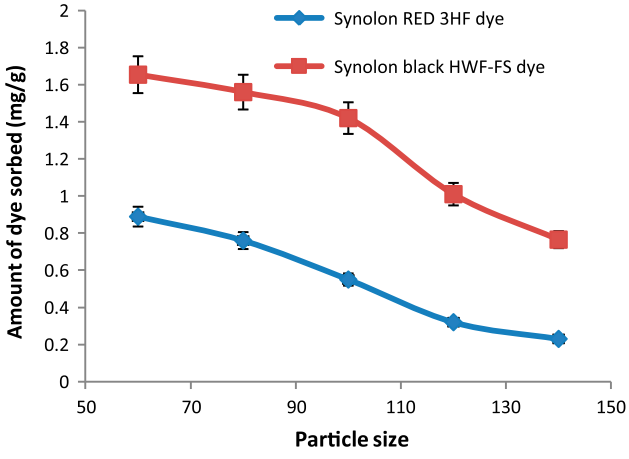

Fig. 2. Effect of particle size on the biosorption of Synolon red 3HF and Synolon black HWF-FS dyes.

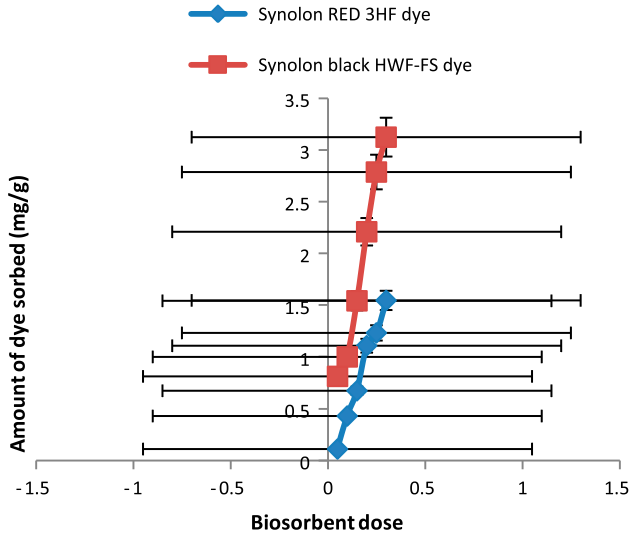

Fig. 3. Effect of biosorbent dose on the biosorption of Synolon red 3HF and Synolon black HWF-FS dyes.

Usually, the percentage of dye removal increases with increasing adsorbent dosage, where the number of sorption sites at the adsorbent surface will increase by increasing the dose of the adsorbent [28] and as a result increase the percentage of dye removal from the solution. Study of the effect of adsorbent dosage gives an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed with a minimum dosage, so as to identify the ability of a dye from an economical point of view. Sonawane and Shrivastava [29] studied the effect of adsorbent dose on the removal of Malachite green by maize cob and they concluded that at 20 mg/L of dye, pH of 8 and a contact time of 25 min, the increase of percentage of dye removal from 90.0 to 98.5% when the adsorbent dose increased from 0.5 to 12 g/L.

The dye removal capacity decrease due to the unsaturation of the binding sites, at large amount of biosorbent dose.

In another study, Bhattacharyya and Sharma [30] reported the effect of biosorbent dose on the removal of Congo red dye. With low dose of Neem leaf powder, the dye removal was the maximum because the minute amount of Neem leaf powder showed good interaction with Congo red dye.

Akhtar et al. [31] investigated the effect of adsorbent dose on the uptake of 2,4-dichlorophenol. By increasing the biosorbent dose from 0.025 to 0.1 g, the percentage adsorption increased fast up to 66% and then remained constant.

3.4. Influence of the initial concentration of dye

The percentage removal of dye is highly dependent on the initial amount of dye concentration. The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface.

The effect of initial concentration of Synolon red 3HF and Synolon black HWF-FS on the adsorption capacity of mustard oil cake and linseed oil cake was investigated by varying the concentration from 50 to 250 ppm.

The results are shown in Fig. 4. From the graph, it can be seen that there is an increase in the amount of dye adsorbed with an increase in the initial concentration of the dye. The quantity of Synolon red 3HF dye adsorbed increases from 1.549 to 3.834 mg/g onto the mustard oil cake and from 2.1076 to 6.5422 mg/g for Synolon black HWF-FS dye onto the linseed oil cake.

Generally, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites

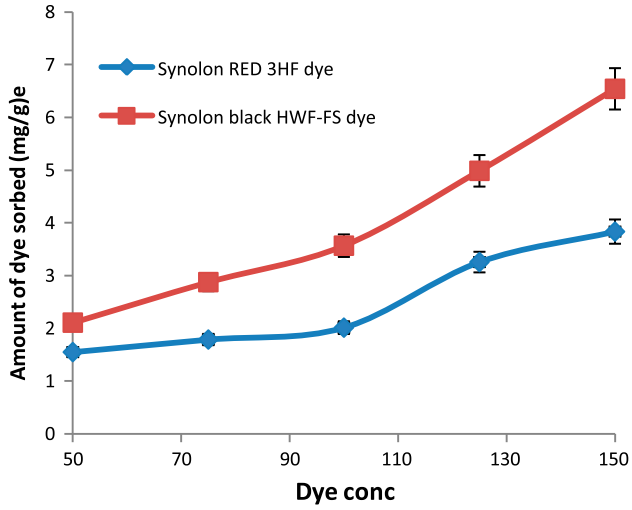

Fig. 4. Effect of dye concentration on the biosorption of Synolon red 3HF and Synolon black HWF-FS dyes.

on the adsorbent surface [32]. On the other hand, the increase in initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration [33].

The initial concentration of dyes provides an important driving force to overcome the mass transfer resistance of all molecules between the aqueous and solid phase.

In 2009, Ergene et al. [34] studied the removal of RBBR dye from aqueous solutions by adsorption onto immobilized *Scenedesmus quadricauda*. According to the results biosorption capacity, q_e (mg/g), of Sq increased with increasing concentration of RBBR at equilibrium (C_e, mg/L). Aksu and Tezer reported that the uptake of Remazol Black B and Remazol Red R was also increased with increasing the initial dye concentration ending to the saturation at higher dye concentrations.

Mahmoud et al. [35] also observed that the amount of methylene blue (MB) adsorbed increased with the increasing initial MB concentration. The amount of MB adsorbed increased from 10.616 to 17.788 mg/g with the increase in dye concentration from 50 to 200 mg/L.

3.5. Influence of contact time

The effect of contact time can be seen from Fig. 5. It can be seen that the amount biosorbed (mg/g) by the adsorbents increased rapidly with the increase in contact time. But when the contact time was further increased there was no visible change in the biosorption of dyes.

It can be seen from Fig. 5 that rapid adsorption for Synolon red 3HF dye takes place in the first 60 min and for Synolon black HWF-FS dye takes place in the first 180 min after that there is no significant increase in adsorption.

This may be due to strong attractive forces between the dye molecules and the adsorbent. Fast diffusion on the external surface was followed by fast pore diffusion into the intra particle matrix to attain rapid equilibrium [36].

Tan et al. [37] studied the effect of contact time on the adsorption of direct red-23 dye on pretreated mangrove bark. The results indicate that there is an increase in the removal of dye with increase in contact time. For the first 30 min, the removal was fast and became slower thereafter. The higher concentration solution of dyes employed, the longer equilibrium time was needed. The rate of removal of the adsorbate is higher in the beginning due to the large surface area of the adsorbent available for the adsorption of dye ions. After a certain period, only a very low increase in the dye uptake was observed because there were few active sites on the surface of the sorbent.

The amount of dye (Congo red) adsorbed (mg/g) by AC prepared from coir pith increased with increase in agitation time and reached equilibrium after 10 min [38].

3.6. Influence of temperature

Mostly the effluent discharged from the industries is at higher temperature than the normal. So study of temperature effect on the adsorption of dye becomes very important. Fig. 6 shows the temperature dependency of Synolon red 3HF and Synolon black HWF-FS dyes onto oil cakes. The results show that the adsorption capacity of both oil cakes increases with the increase in temperature from 30 to 70°C.

Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process. If the adsorption capacity increases with increasing temperature, then the adsorption is an endothermic process. This may be due to increasing the mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature [39].

As high temperature favors the biosorption of acidic dye using oil cakes, this suggests that the biosorption process is kinetically controlled by an endothermic process.

This increase may be due to the increase of the number of active sites for the adsorption corresponding to the increase in temperature. Furthermore, the increase in the amount of dye adsorption with the increasing temperature may be due to the increase in the mobility of the large dye molecules, also due to the higher affinity of sites for dye and an increase of binding sites in the biomass [40].

Increasing temperature can also produce a swelling effect within the internal structure of the adsorbent enabling large dyes to penetrate further.

The biosorption mechanism was affected by the elevated temperature which modified the biosorption capacity of biosorbent for the dye molecules [41].

Mahmoud et al. [35] reported the effect of temperature increase on the removal of basic dye using acid-treated kenaf fiber char. They studied biosorption process by changing the temperature between 30 and

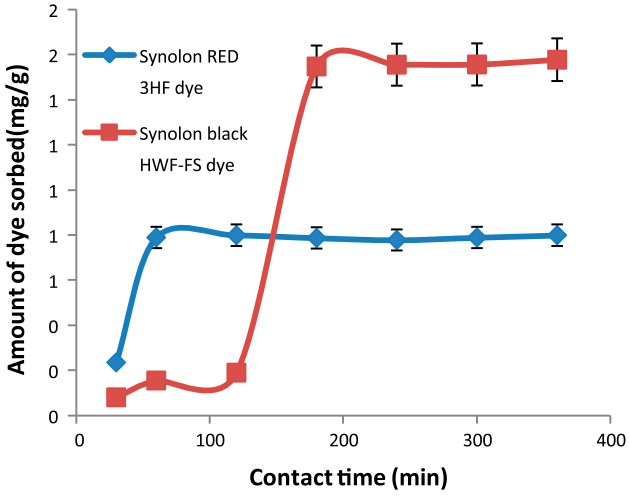

Fig. 5. Effect of contact time on the biosorption of Synolon red 3HF and Synolon black HWF-FS dyes.

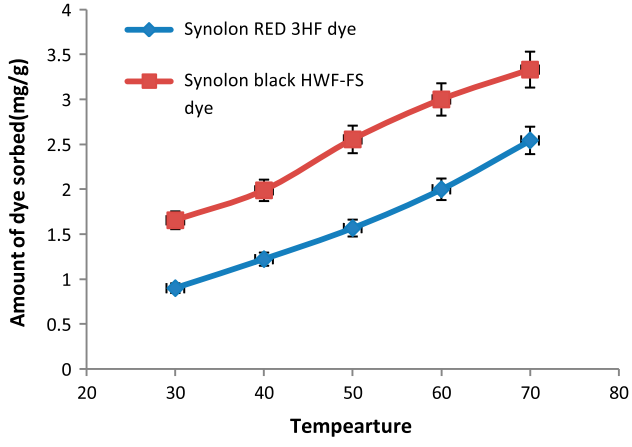

Fig. 6. Effect of temperature on the biosorption of Synolon red 3HF and Synolon black HWF-FS dyes.

50°C. The results indicate that the biosorption of dye increases with the increase in temperature.

3.7. Biosorption kinetic models

The dynamics of the adsorption can be studied by the kinetics of adsorption in terms of the order of the rate constant. The adsorption rate is an important factor for a better choice of material to be used as an adsorbent, where the adsorbent should have a large adsorption capacity and a fast adsorption rate. In this study, pseudo-first-order and pseudo-second-order models to study the adsorption kinetics are used. The applicability of these kinetic models was determined by correlation coefficients (R^2). When the value of R^2 is high, the model is best applicable to data.

3.7.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model is based on the fact that the change in dye concentration with respect to time is proportional to the power one. The differential equation is described as follows:

$$\mathrm{d}q_t/\mathrm{d}_t = k_1(q_e - q_t) \tag{3}$$

where q_e and q_t are biosorption capacities (mg/g) at equilibrium and time t, respectively, k_1 is the rate constant (1/min) of pseudo-first-order kinetic model.

After interacting the above equation and applying boundary conditions $t = 0 - t = t$ and $q_t = 0 - q_t = q_t$, the equation becomes:

$$\log\,(q_e/q_e - q_t) = (k_1/2.303)t \tag{4}$$

By rearranging the above equation, following linear form is obtained:

$$\log\,(q_e - q_t) = \log\,q_e - (k_1/2.303)t \tag{5}$$

The values of q_e experimental, q_e calculated, R^2 and k_1 of both dyes are given in Table 2.

This table shows that in pseudo-first-order kinetics, the calculated and experimental value of q_e does not match and the value of R^2 is not satisfactory in both dyes. Mostly the first-order kinetic model does not fit well for the whole range of contact time when it failed theoretically to predict the amount of dye adsorbed and thus deviated from the theory. In that case, the pseudo-second-order model is not best fitted.

3.7.2. Pseudo-second-order kinetic model

Pseudo-second-order kinetic model is also based upon the biosorption capacity of the biosorbent material. The biosorption mechanism over a complete range of contact time is explained by the pseudo-second-order kinetic model.

Pseudo-second-order kinetic equation is shown below:

$$\mathrm{d}q_t/\mathrm{d}_t = k_2(q_e - q_t)^2 \tag{6}$$

where k_2 (g/mg min) is the second-order rate constant for the biosorption process, q_e and q_t are the biosorption capacities at equilibrium and time t, respectively.

By integrating and applying boundary conditions $t = 0 - t = t$ and $q_t = 0 - q_t = q_t$, the above equation can be written in the linear form as follows:

$$t/q_t = 1/K_2q_e^2 + 1/q_e(t) \tag{7}$$

The second-order parameters k_2, q_e calculated, q_e experimental, and R^2 values are shown in Table 3. The values of q_e experimental and calculated are not too much different from each other. The correlation coefficient R^2 values for dyes are also very high. These results indicate that pseudo-second-order kinetic model is well fitted to kinetic data. The results predicted that the effectiveness, suitability, and applicability of pseudo-second-order kinetic model were more than the pseudo-first-order kinetic model.

Bulut and Aydin [33] investigated the adsorption of MB using wheat shells and they found that the values of the constants for the pseudo-first- and pseudo-second-order models were increased with increasing temperature, and the R^2 values for second-order model were greater than 0.999 indicating the second-order nature of the adsorption process.

Senthilkumaar et al. [39] studied the use of guava leaf powder for adsorption of MB. They found that the values of R^2 of the pseudo-first-order model were between 0.70 and 0.85, while the values of R^2 for the second-order model were 0.999, indicating the conformity of second-order model.

3.8. Adsorption isotherms

The adsorption isotherm is important for the description of how the adsorbate will interact with the adsorbent and give an idea of the adsorption capacity of the adsorbent. There are different isotherms which can be used to describe the biosorption equilibrium data. In

Table 2
Comparison of the kinetic parameters for the biosorption of EBT and A-FGGL dyes onto almond and cotton seed oil cake biomasses

Kinetic models	Synolon red 3HF	Synolon black HWF-FS
Pseudo-first-order		
k_1 (1/min)	0.09212	0.00776
q_e (experimental)	1.215	2.544
q_e (calculated)	1.056	0.447
R^2	0.502	0.668
Pseudo-second-order		
k_2 (g/mg min) 10^{-3}	0.1384	0.0634
q_e (experimental)	1.215	2.544
q_e (calculated)	1.254	2.101
R^2	0.997	0.977

Table 3
Comparison of the isotherm parameters for the biosorption of EBT and A-FGGL dyes onto almond and cotton seed oil cake biomasses

Isotherm models	Synolon red 3HF	Synolon black HWF-FS
Langmuir		
R_L	0.11	0.321
R^2	0.707	0.891
q_m	37.037	6.889
Freundlich		
K_F	3.123	1.989
R^2	0.927	0.997
N	0.601	0.233

this study, two very famous isotherms Langmuir isotherm and Freundlich isotherms are used.

3.8.1. Langmuir isotherm

The Langmuir isotherm is frequently applied for the biosorption of organic and inorganic pollutants from aqueous solution. The adsorption isotherm is important for the description of how the adsorbate will interact with the adsorbent and give an idea of the adsorption capacity of the adsorbent. The surface phase may be considered as a monolayer or multilayer. Langmuir isotherm is based on the ideal monolayer adsorbed model [42]. The Langmuir isotherm is the most popular isotherm model and it is used to describe the adsorption process where the occupancy occurs at one adsorption site at an energetically homogeneous range of adsorption sites [43]. Langmuir isotherm is represented by the following equation:

$$C_e/q_e = 1/Kq_m + C_e/q_m \quad (8)$$

where C_e is the concentration of dye solution (mg/L) at equilibrium. The constant q_m signifies the adsorption capacity (mg/g) and K is related to the energy of adsorption (L/mg). Values of q_m and K were calculated from the slope and intercept of the linear plots and are presented in Table 3.

3.8.2. Freundlich isotherm

This is the earliest known equation explaining the biosorption mechanism. This model based on the assumption that the biosorption process takes place by the interaction of the dye molecules on the heterogeneous surfaces. There is a logarithmic decline in the energy of biosorption with the increase in occupied binding sites. The Freundlich isotherm form is given by the following equation:

$$q_e = K_f(C_e)^{1/n} \quad (9)$$

where q_e is the amount adsorbed per unit mass of the adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and K_f, n are the Freundlich constants related to adsorption capacity and intensity, respectively. The logarithmic form of Eq. (9) gives the following linearized expression:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (10)$$

The values of Freundlich constant n are given in Table 3. From the values, it can be concluded that the adsorption of Synolon red 3HF and Synolon black HWF-FS dyes best fitted the Freundlich isotherm.

Ozacar and Sengil [44] suggested that the removal of reactive dyes onto calicinated alunite obeyed the second-order kinetic model.

3.9. Effect of electrolytes on the biosorption of acid dyes

Industrial water contains various salts/electrolytes which significantly affect the dye biosorption. The effect of ionic strength of NaCl was investigated in this study. The salt concentrations range from 0.1 to 1.0 was used to investigate the effect on the dye removal. Figs. 7 and 8 show that the amount of dye sorbed of Synolon red 3HF and Synolon black HWF-FS dyes onto mustard and linseed oil cake biomasses decreased with increase in the concentration of electrolyte.

This may be due to masking effect of Na^+ ion on the biomass surface and decreased the biosorption of dyes onto the oil cakes [45].

Janos et al. [46] investigated that the biosorption of acidic dye increased with increase in the concentration of salts using wood shaving biomass. At low concentration of salts, the amount of dye sorbed (mg/g) decreased. This was due to screening effect of salt which decrease the electrostatic interactions between dye molecule and biosorbent surface [47].

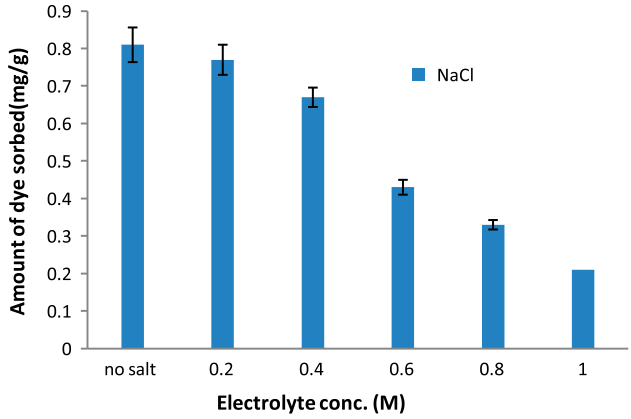

Fig. 7. Effect of electrolytes concentration on the biosorption of Synolon red 3HF dye.

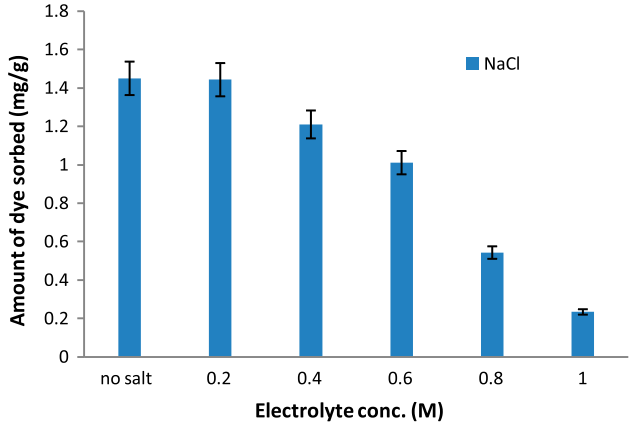

Fig. 8. Effect of electrolytes concentration on the biosorption of Synolon black HWF-FS dye.

3.10. Influence of heavy metals on the biosorption of acid dyes

In this research, influence of heavy metals (Hg^{2+} and Pb^{2+}) on acid dyes biosorption was studied and is depicted in Figs. 9 and 10.

The biosorption capacity of dyes enhanced in the case of Hg^{2+} and Pb^2. The increase in the biosorption capacity of dyes with addition of metals may be due to complex formation between metal ions and dyes and binding to the surface of the biosorbent [48]. The other reason is that the addition of metals produced the aggregation and flocculation of biomass and increased the biosorption capacity. Pb^{2+} caused greater aggregation than any other metal [49].

3.11. Influence of surfactants on the biosorption of acid dyes

Textile industries also discharge surfactants along with dyes into the water stream. The effect of surfactants on the acid dyes uptake was determined in this study. The effect of surfactants is illustrated in Figs. 11 and 12.

Cationic surfactant, CTAB (cetyltrimethyl ammonium bromide), increased the biosorption of two direct dyes. This may be due to impregnation of cationic surface which gives positive charge to the biomass surface and attracts strongly toward the negatively charged direct dyes [50].

The biosorption capacity of dyes decreased by adding anionic surfactant, SDS (sodium dodecylsulfate). The reduction of biosorption capacity may be due to repulsive interactions between anionic surfactant and anionic dye molecules. The solubility of anionic dyes is less in SDS micelles than in the aqueous phase [51].

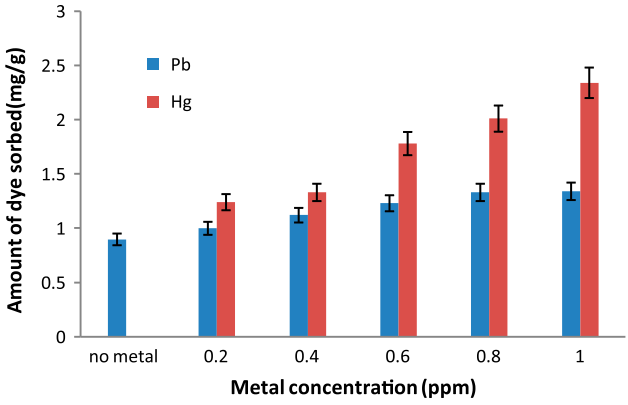

Fig. 9. Effect of metals concentration on the biosorption of Synolon red 3HF dye.

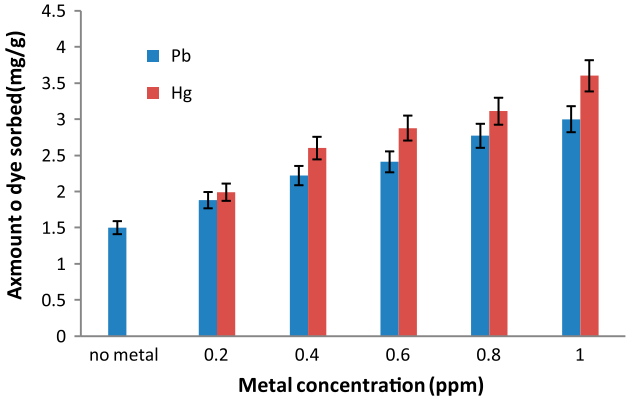

Fig. 10. Effect of metals concentration on the biosorption of Synolon black HWF-FS dye.

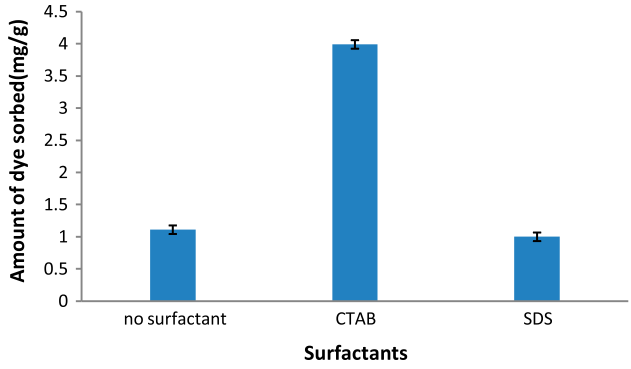

Fig. 11. Effect of surfactants on the biosorption of Synolon red 3HF dye.

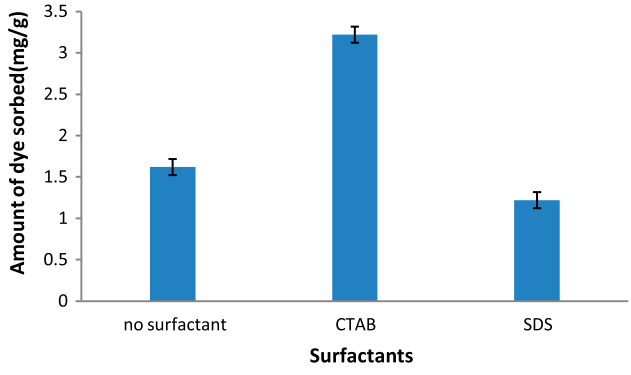

Fig. 12. Effect of surfactants on the biosorption of Synolon black HWF-FS dye.

4. Conclusion

Removal of Synolon red 3HF and Synolon black HWF-FS dyes from aqueous solution by adsorption with mustard and linseed oil cake was experimentally determined and the following observations were made:

(1) The percentage of color removed was influenced by initial dye concentration, contact time, adsorbent dose, particle size, temperature, and varied with dye solution pH.
(2) The adsorption rates increase with increasing temperature of the solution.
(3) Optimum contact time for equilibrium to be achieved was found to be 1 h (60 min) for Synolon red 3HF dye. It is basically due to saturation of the active site which does not allow further adsorption to take place.
(4) Maximum adsorption of Synolon red 3HF and Synolon black HWF-FS dyes was found to be at pH 1 and pH 2, respectively. In fact, adsorption was found to decrease with the increase in pH of the solution. The adsorption of this negatively charged dye on the adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH.
(5) The decrease in the adsorption capacity with the increase in the adsorbent concentration could be ascribed to the fact that some of the adsorption sites remained unsaturated during the process and agglomeration of adsorbent takes place as a result all the surface area is not available for adsorption process.
(6) The adsorption capacity of adsorbents increased with temperature. This may be a result of the increase in the mobility of the large dye ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface.

(7) The adsorption best fitted the pseudo-second-order kinetic model and the Freundlich isotherm.
(8) Effects of electrolytes, metals, and surfactants were also studied.

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