Biosorption of Eriochrome Black T and Astrazon FGGL blue using Almond and Cotton seed Oil Cake Biomass in a Batch Mode

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(Received on 9th May 2013, accepted in revised form 7th March 2014)

Summary: In the present research study, the biosorption of Eriochrome Black T (EBT) and Astrazon FGGL blue (A-FGGL) onto novel biomasses Almond (*Prunus dulcis*) oil cake and Cotton seed 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 3 for EBT onto almond oil cake and pH2 for Astrazon FGGL blue onto cotton seed 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. Optimum contact time for equilibrium to achieve was found to be 120 and 180 minutes for EBT and A-FGGL blue, respectively. The Langmuir isotherm model was best fitted to experimental data. The biosorption followed the pseudo-second order kinetic model suggesting a chemisorption mechanism. The positive value of $\Delta H°$ showed the endothermic nature of the process. In this research, the influence of electrolytes, heavy metals and surfactants on the removal of dyes was also examined.

Key Words:- Biosorption; Almond oil cake; cotton seed oil cake; acid dyes; modeling.

Introduction

Pigments and dyes are extensively used in the textile, paper and leather dyeing, printing, pharmaceutical, and cosmetic industries. About 10,000 different dyes are produced annually for various industrial processes, 10-15% of them are discharged by the textile industry and cause pollution [1].

Textile wastes have complex composition with variety of dyes, surfactants, bleaching agents and ionic impurities. A large amount of these dyes go into the effluent during the dyeing process as they are highly soluble in water. Most of them are toxic or even carcinogenic. Discharge of these toxic substances into water stream pollute the water and make it unfit for aquatic life. Most of the dyes are harmful to marine flora and fauna. Further, the dyes affecting the possibility for aquatic plants to perform photosynthesis. A majority of these dyes are stable to light and oxidation. Many physio-chemical methods such as adsorption, coagulation, precipitation, filtration, and oxidation have been used for the treatment of effluent containing dyes. The adsorption process has been found to be the most effective. Dyes usually have complex aromatic molecular structures. Dyes can be classified as follows: Anionic (acid, direct and reactive dyes), Cationic (basic dyes) and Nonionic (disperse dyes) dyes [2, 3].

Generally, dyes are not degraded easily. Many treatment processes have been used for the removal of dyes from waste water such as physical, chemical and biological methods. Adsorption, chemical precipitation, coagulation, chemical oxidation, ultra-filtration, reverse osmosis, photo-catalysis, dilution, ion-exchange and membrane filtration etc are incorporated in the physical and chemical treatment methods. But these methods have many disadvantages such as ineffective dye removal, costly, sludge formation and not applicable to the wide range of dye wastewaters [4, 5].

But biosorption is more promising method among all these due to its effectiveness, less costly, capacity and capability to remove dyes from industrial wastewaters on the extensive scale [6, 7].

Eriochrome Black T (EBT) and Astrazon FGGL blue are acidic dyes. EBT is poison, causes severe eye irritation or blindness. It is flammable liquid and its vapors are harmful if inhaled. Target organs in human body are kidneys, central nervous system, liver, cardiovascular system, eyes. EBT solution may be absorbed in harmful amounts through intact skin and causes skin irritation. It causes liver damage. Advanced stages may cause collapse, unconsciousness, coma and possible death due to respiratory failure. It can also cause kidney failure, vascular collapse and damage. A-FGGL blue is also toxi, it can cause necrosis, blood congestion and inflammation of skin.

The idea of using biomass in environmental cleanup has been come since the early 1900's when Arden and Lockett discovered certain types of living bacteria cultures were capable of recovering nitrogen and phosphorus from raw sewage when it was mixed in an aeration tank. There are various low cost adsorbents which are used in the biosorption process such as wheat straw [3] cotton waste, rice husk [8] maize cob, treated parthenium biomass, Almond oil cake [9].

In the present research project Almond oil cake and cotton seed oil cake are used for removal of acid dyes (EBT) and A-FGGL blue,respectively from aqueous solution. Influence of different parameters on biosorption capacity is studied.

Results and Discussion

Influence of pH

Dye biosorption is a pH dependent process. The pH of the solution influences the properties of biomass, affects the adsorption mechanisms and dissociation of the dye molecules. The effects of pH on the biosorption of EBT and A-FGGL dye on the almond and cotton seed oil biomass were studied in the pH ranging from 1-10. The results showed that the maximum biosorption of EBT and A-FGGL dyes were observed at the pH 3.0 and 2.0 respectively. At higher pH values the biosorption of dye was not effective.

A maximum uptake value of 4.846 mg/g was observed for EBT at the optimum pH 3.0. The biosorption capacity of A-FGGL dye was 3.012mg/g at pH 2.The results are depicted in Fig. 1. The pH value of the dye solution is the most important controlling factor that should not be neglected during the biosorption process. At lower pH, the biosorbent surface turned out to be positively charged and electrostatic attraction develops between the positively charged biomass and negatively charged anionic dyes. At high pH value, electrostatic repulsion appears due to the number of negatively charged sites on the biosorbent [10]. A similar behavior was observed earlier for the biosorption of acidic dyes by *Paenibacillus macerans* [11] and direct azo dyes by *Spirogyra sp.I02* [12].

Ardijani *et al*., [9] examined the effect of initial pH on the adsorption of direct Red 80 from aqueous solution onto almond shells. As pH increased from 2 to 12, the adsorption capacity decreased from 20.5 to 18.8 mg/g. Maximum uptake of dye was observed at pH 2.0.

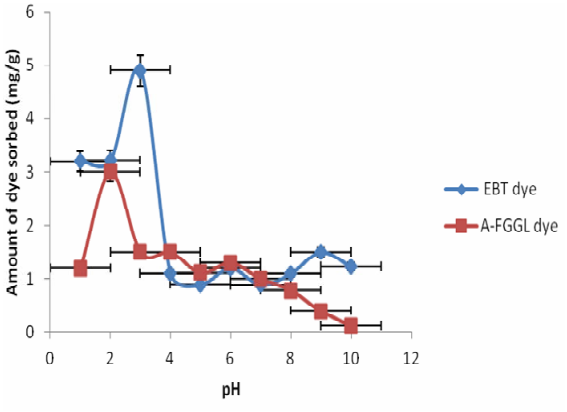

Fig.1: Effect of pH on the biosorption of Synolon Red 3HF and Synolon black HWF-FS dyes.

Similarly Dulman and Cucu-Man [13] also investigated the pH effect on the uptake of dyes by the beech wood sawdust. A maximum removal of 98.6% and 94.4% was observed for Direct Brown 2 and Direct Brown at pH 3.0 respectively.

Influence of Biosorbent Dose

The effect of biosorbent dose on the biosorption of EBT and A-FGGL dyes on the Almond and cotton seed oil cakes was evaluated by varying the biosorbent dose and results are reported in Fig. 2.

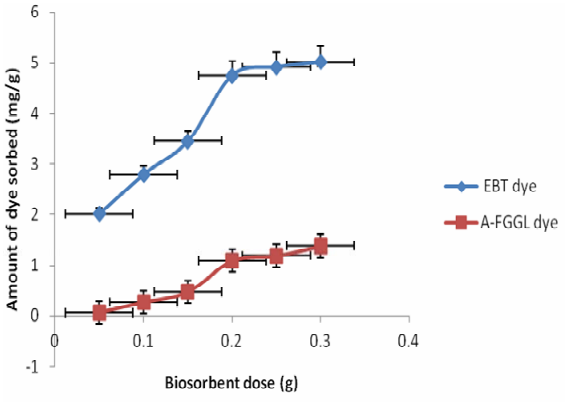

Fig. 2: Effect of particle size on the biosorption of Synolon Red 3HF and Synolon black HWF-FS dyes

The quantity of dye adsorbed decreased due to the decrease in biosorbent dose.. The maximum biosorption occurred in the present investigation at 0.3g of biosorbent dose.

Several reasons are given that the adsorption is maximum at high biosorbent dose due to the large surface area and an increase in the number of available binding sites [14]. Similar behavior regarding the biosorption of anionic dye on the Peanut hull was observed by Gong *et al*., [15]. Akhtar *et al*., [16] investigated the effect of biosorbent dose on the uptake of 2,4-dyechlorophenol. By increasing the biosorbent dose from 0.025 – 0.1g, the percentage adsorption increased fastly up to 66% and then remained constant.

Mohan *et al*., [12] reported that the adsorbent dose imparted great influence on the biosorption of direct azo dye from the aqueous media and maximum dye removal (85%) was observed with 0.5g dose. Colak *et al*., [11] also reported that biosorption of Acid Blue 225 and the Acid Blue 062 increased with an increase in the biosorbent concentration. This is due to the availability of the binding site for dyes.

Influence of Biosorbent Particle Size

The particle size of biosorbent is very important factor. The rate of dye removal increases as the particle size decreases. So, in present case adsorption occurred at smallest biosorbent particle size. Fig. 3 represents the amount of dyes adsorbed by oil cakes at different mesh sizes.

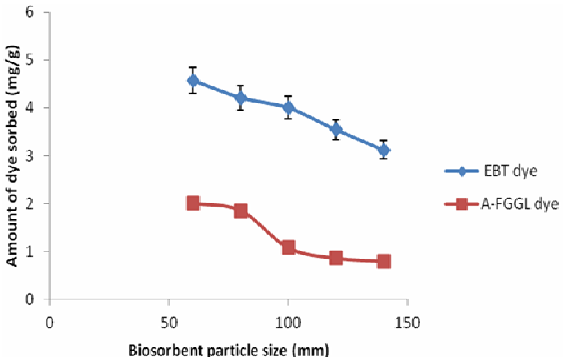

Fig.3: Effect of biosorbent dose on the biosorption of Synolon Red 3HF and Synolon black HWF-FS dyes

The results showed that the biosorption capacity of biosorbents increased with the decrease in the particle size. The maximum biosorption capacity (4.42 mg/g) was recorded at the smallest particle size (60 mesh size) for almond oil cake and (2.004mg/g) for cotton seed oil cake.

The increase in the biosorption capacity may be attributed to the large surface area of the smallest particle size biosorbent and large number of exchanging sites [3]. In a study performed by Tune *et al*., [17], the effect of biosorbent particle size on the removal of Remzol Black B reactive dye was investigated using various ranges of particle sizes from 75 µm to 500 µm of cotton stalk biosorbent. The results indicated that the maximum uptake (27.5 mg/g) was recorded with the smallest particle size . Gong *et al*., [15] also investigated the removal of anionic dyes by powdered peanut hull biomass increases with decrease in the biosorbent particle size.

Influence of Initial Dye Concentration

The effect of initial dye concentration of two dyes onto the biosorption capacity of the Almond and cotton seed oil cake biomasses was investigated by varying the initial concentration of dyes at the optimum biosrbent dose and other parameters. The results regarding the effect of initial concentration of dyes on the biosorption capacity of oil cake biomasses are given in the Fig. 4.

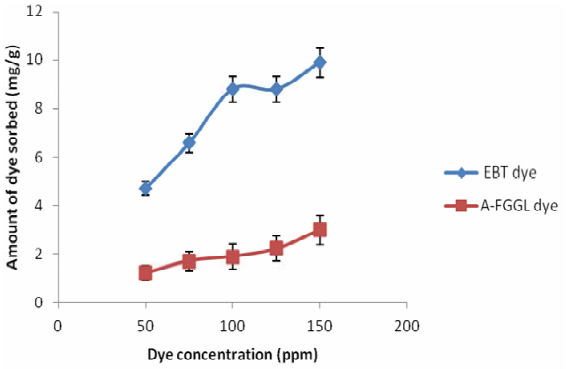

Fig. 4: Effect of dye concentration on the biosorption of Synolon Red 3HF and Synolon black HWF-FS dye.

The uptake capacity of biomass increased from 4.7 – 9.8 mg/g (for EBT) and from 1.212-2.97mg/g (for A-FGGL) with increase in the initial dye concentration, while % sorption shows the opposite trend. In the biosorption mechanism, in the start, the dye molecules adsorbed externally and the bioorption rate increased rapidly. When the external surface became saturated, the dye molecules adsorbed into the porous structure of the biomass [11]. The initial concentration of dyes provides an important driving force to overcome the mass transfer resistance of all molecules between the aqueous and

the solid phases. Bulut *et al*., [4] observed that the amount of dye sorbed per unit mass of biosorbent increased with an increase in the initial dye concentration from 50-250 mg/l. It is estimated that the binding sites of the biosorbent stays unsaturated during the biosorption .

Khaled *et al*., [14] investigated the effect of initial concentration of Direct N Blue-106 on the biosorption of orange peel carbon. The amount of dye adsorbed, q, increased with increase in the dye concentration.

Tune *et al*., [17] explained the decrease in percentage uptake of Ramazol Black B reactive dye due to the saturation of exchanging sites at higher dye concentration using cotton plant waste. The decrease in the biosorption capacity of biomass may be attributed to the hindrance in movement of dye molecules into the biosorbant Vijayaraghavan et al, [18] Another reason of unavailability of binding sites of the biosorbant is due to the shielding of gell matrix [19].

Influence of Contact Time

The biosorption efficiency was evaluated as a function of time and the results are depicted in Fig. 5.

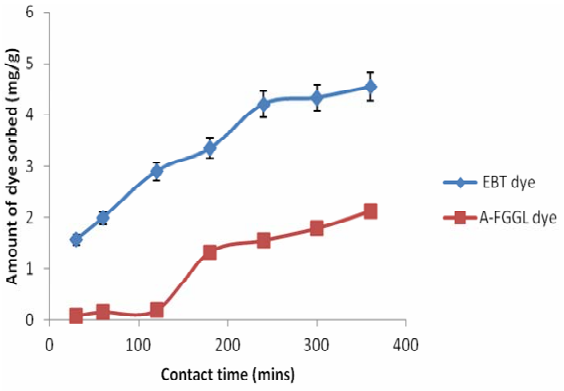

Fig.5: Effect of contact time on the biosorption of Synolon Red 3HF and Synolon black HWF-FS dyes

The amount biosorbed (mg/g) by the biosorbent increased rapidly with the increase in the contact time. When the agitation time was further increased, there was no drastic increase in the biosorption capacity of biosorbent. This increase was fast in the beginning and then slow removal was observed till equilibrium. The equilibrium was attained after 120 minutes for EBT dye and 180 minutes for A-FGGL dye.

It was generally observed that the biosorption capacity increased with time and after certain time, reached to equilibrium. In the beginning, the fast biosorption may be attributed to the presence of positive charged sites on the almond waste biosorbent surface which developed an interaction with negetively charged dye molecules. Then the biosorption began to slow down due to the slow movement of dye molecules into the interior of the bulk of the biosobent [10]. Another reason was large number of exchanging sites helped the biosorption process and then saturation occurred [20].

In another study, Ahmad *et al*., [21] observed the effect of contact time on the direct dye biosorption onto palm ash. The biosorption capacity increased steadily in the beginning and the equilibrium was attained after 129 minutes. Similarly, Akar *et al*., [22] investigated the effect of agitation time on the removal of a reactive dye from the aqueous solution. The results showed that the dye removal density (mg/g) increased with increase in time. The equilibrium was established after 40 minutes of agitation time.

Influence of Temperature

Wastewater from textile industry is discharged into the water stream at comparatively higher temperature. So temperature is a vital issue to study. The results in the Fig. 6 showed that the biosorption capacity of both oil cake biosorbents increased with increase in temperature from 30 ^{o}C – 60 ^{o}C. High temperature favored the biosorption of anionic dyes by oil cakes.

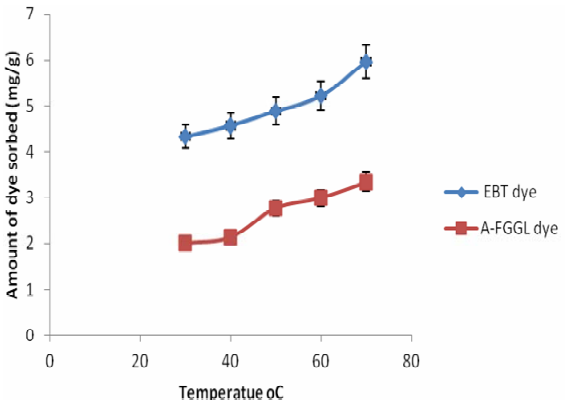

Fig.6: Effect of temperature on the biosorption of Synolon Red 3HF and Synolon black HWF-FS dyes.

The biosorption capacity of oil cake biomasses increased with increase in temperature ranging from 30^o – 70^o C indicating the endothermic nature of the process. This might be due to the increase in the number of molecules attaining the sufficient energy to undergo the chemical reaction with the biosorbent [12].

Another reason was the increase in the pore size on the biomass surface at high temperatures. The elevated temperature reduced the thickness of the outer surface of the biosorbent and increased the kinetic energy of the dye molecules, as a result the dye molecules biosorbed easily into the surface of biomass [23].

The biosorption mechanism was affected in two ways. First of all, the rate of diffusion of dye molecules into the pores of biosorbent increases with the increase in temperature. Secondly, the elevated temperature modified the biosorption capacity of biosorbent for the dye molecules [24]. The motion of dye molecules also increased with increase in the temperature [25]. Akar *et al*., [22] reported the effect of temperature on the removal of basic dye from aqueous solution onto *Pyracantha coccinea* berries using four different temperatures (15, 25, 35 and 45^oC).

The results indicated that the amount of dye adsorbed increased with increase in the temperature. This might be attributed to an increase in the kinetic energy at high temperature. The process was endothermic in nature and showed chemisorptions [22]. Tune *et al*., [17] showed the effects of various temperatures (25 – 45^oC) on the amount of Remazol Black B reactive dye adsorption from aqueous solution. The observation indicated that the amount of dye adsorbed increased from 27.5 to 30.7 mg/g for cotton stalk and from 43.3 to 45.1 mg/g in case of cotton hull, when temperature was raised from 25 to 35^oC. Then again increase in temperature up to 45^oC did not change the amount of dye adsorbed significantly.

Aksu and Tezer [6] investigated that the rate of biosorption of reactive dyes on the green algae *chlorella vulgaris* increased with increase in the temperature. Similar trend in the increase of biosorption of Ramazol Black B by *R. arrhizus* with increae in temperature was reported by Aksu and Tezer [26].

Experimental

Chemicals

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

Preparation of Oil Cake Biosorbent

Almond and cotton seed oil cakes were purchased from a local Herbals merchant. The oil cakes were washed several times with distilled hot water to remove dust, oil and other foreign particles. The cleaned biomasses were dried in sunlight for 8 hours and then for 24 hours at 60^o C in the oven. The washed dried biomasses were ground with food processor (Moulinex, France) and sieved using special sieve of various mesh sizes (60, 80,100,120 & 140 mesh sizes). The biosorbent material of different sizes was stored in plastic bottles for further use..

Preparation of Aqueous Dye Solutions

In the present investigation, both dyes were used without any further purification. Stock solutions of dyes were prepared by dissolving 0.1g of dye in 100ml of double distilled water. The experimental solutions of different concentrations from 25 to 150 mg/l were made by further dilution of stock solution. Standard curve was developed through the measurement of the dye solution absorbance by UV-Visible Spectrophotometer. The general characteristics of dyes are shown in Table-1.

Table-1: General characteristics of dyes.

Dye	Colour	λ max(nm)	Type
Eriochrome Black T	Black	400	Anionic
AstrazonFGGL blue	Blue	404	Anioinc

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 & temperature on the biosorption of dyes.Effect of salts, surfactants and heavy metals on the biosorption capacity were also studied.

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

$$q= (C_o – C_e)\ V/W$$

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 Almond biomass (g). The

%sorption was measured by using the following equation:

$$\%sorption = C_o - C_e/C_o \times 100$$

All the experiments were conducted in triplicate.

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 [27] and Freundlich [28] isotherm models. Analysis of adsorption data is necessary for the development of biosorption isotherms and biosorption kinetics models. These models are used for optimization of design parameters. The interaction between biosorbent and sorbate can be determined by biosorption isotherm models. There are different isotherms which are used to describe the biosoption equilibrium data. In this present study, two isotherms, named as Langmuir and Freundlich isotherm models were investigated.

Langmuir Isotherm

The Langmuir adsorption isotherm is frequently applied for the biosorption of organic and inorganic pollutants from aqueous solution. This model suggests that the biosorption onto the adsorbent surface is homogenous in nature. According to Langmuir isotherm, the biosorption of solute from aqueous solution onto the biosorbent surface is occurred as monolayer biosorption on the homogeneous number of exchanging sites. This phenomenon describes the uniform biosorption energy on the biosorbent surface [29].

The Langmuir isotherm can be presented by the following equation:

$$C_e/q_e = C_e/q_m + 1/K_a\, q_m$$

where C_e is the concentration of dye solution (mg/l) at equilibrium and q_e is the amount of dye biosorbed on the biomass (mg/g) at equilibrium. The value of q_m signifies the maximum biosorption capacity describing a complete monolayer adsorption (mg/g) and K_a is the adsorption equilibrium constant (l/mg) that is related to free energy of biosorption. The values of Langmuir parameters for both dyes onto two different biosorbents are shown in Table-2.

Freundlich Isotherm

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

$$\ln q_e = \ln K_f + 1/n \ln C_e$$

where K_f is the Freundlich isotherm constant related to the bonding energy. K_f is defined as the distribution coefficient and suggests the amount of dye sorbed on the biosorbent for unit equilibrium concentration. q_e is the amount adsorbed per unit mass of adsorbent (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/l). The value of n indicates whether the biosorption process is favorable or not. The value of n for favorable adsorption should be greater than 1 [30] The values of Freundlich constants are given in Table-2. From the values given in Table-2 it can be concluded that the biosorption of Eriochrome Black-T and A-FGGL dye is best fitted to the Langmuir isotherm model with R^2 value of 0.9082 and respectively

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

Isotherm models	EBT dye	A-FGGL dye
Langmuir		
R_L	0.11	0.118
R^2	0.9082	0.891
q_m	6.002	3.543
Freundlich		
K_F	4.576	2.065
R^2	0.8745	0.834
n	1.618	0.891

Adsorption Kinetics Studies

The transient behavior of dyes onto the Almond and cotton seed oil cake biomass was analyzed using the pseudo-first order [31] and pseudo second order [32] kinetic models. Kinetic studies are necessary to optimize different operating conditions for the biosorption. The rate of biosorption process depends upon 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.

In this study, Pseudo-first-order and Pseudo-second-order models are used to study the adsorption

kinetics. The applicability of these kinetic models was determined by the correlation coefficients R^2.

Pseudo-First-Order Kinetic Model

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:

$$dq_t/d_t = K_1(q_e-q_t)$$

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:

$$\log (q_e/q_e-q_t) = (K_1/2.303)t$$

By rearranging the above equation following linear form is obtained:

$$\log (q_e-q_t) = \log q_e – (K_1/2.303)t$$

The values of q_e experimental, q_e calculated, R^2 and K_1 of both dyes are given in Table-3.

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

Kinetic models	EBT dye	A-FGGL dye
Pseudo-first-order		
K_1 (1/min)	0.00737	0.00691
q_e (experimental)	7.131	1.985
q_e (calculated)	2.128	7.107
R^2	0.4977	0.247
Pseudo-second-order		
K_2 (g/mg min) 10^{-3}	4.543	0.031
q_e (experimental)	7.131	1.985
q_e (calculated)	8.403	5.672
R^2	0.991	0.889

This Table shows that in pseudo-first-order kinetics the experimental and calculated value of q_e does not match each other and R^2 value is also not satisfactorily. Mostly, the first order kinetic model is not fitted good for whole data range of contact time [33]. This suggested that the biosorption of present acid dyes is not likely to follow the first order kinetic model.

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:

$$dq_t/d_t = K_2(q_e-q_t)^2$$

where K_2 (g/mg min) is the second order rate constant for the biosorption process, qe 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.

$$t/q_t = 1/K_2q_e^2 + 1/q_e\ (t)$$

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 was more than the pseudo-first order kinetic model.

Bulut and Aydin, [34] investigated the adsorption of Methylene Blue using wheat shells and they found that the values of constants for the pseudo-first order and pseudo-second order models were increased with increasing temperature and the R^2 value for the pseudo-second order model was greater than 0.999 indicating the second order nature of adsorption process.

Ponnusami *et al*., [35] studied the use of guava leaf powder for the adsorption of Methylene Blue. 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 pseudo-second order model were 0.999, indicating the conformity of the second order model.

Ozacar and Sengil [36] suggested that the removal of reactive dyes onto calicinated alunite obeyed the second order kinetic model. Ncibi *et al*., [1] and Acemioglu [37] reported that the removal of textile metal complexed dye by *Posidonia oceanica* (L) leaf sheaths and uptake of Congo red fro aqueous

solution by calcium rich fly ash followed pseudo-second order kinetics.

Influence 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 and NaOH was investigated in this study. The salt concentrations range from 0.1 – 1.0 was used to investigate the effect on the dye removal. Fig. 7, 8 shows that the amount of dye sorbed of EBT and A-FGGL onto almond and cotton seed oil cake biomasses decreased with increase in the concentration of electrolytes.

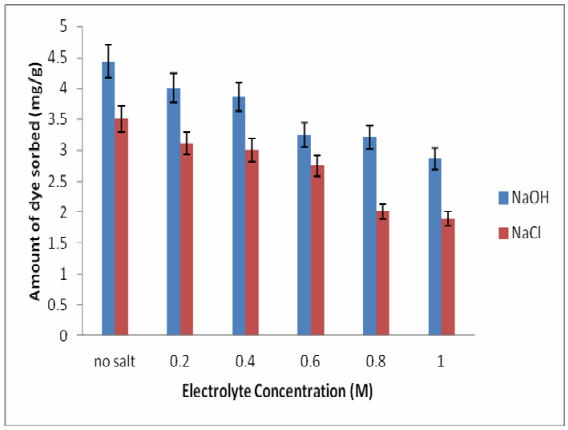

Fig. 7: Effect of electrolytes conc on the biosorption of Synolon Red 3HF dye.

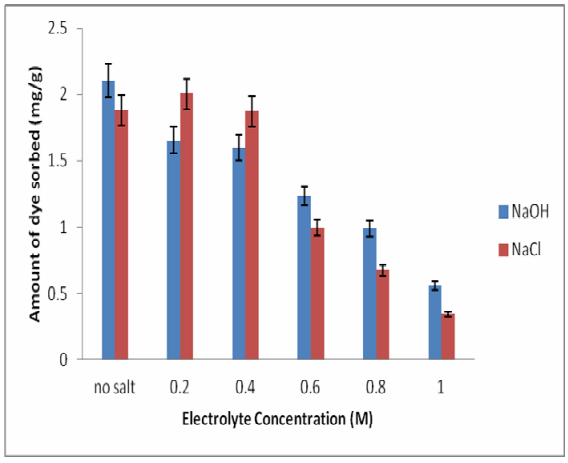

Fig.8: Effect of electrolytes conc on the biosorption of Synolon black HWF-FS dye.

This may be due to masking effect of Na^+ ion on the biomass surface and decreased the biosorption of dyes onto the oil cakes [38].

Janos *et al*. [39] investigated that the biosorption of acidic dye increased with increase in the concentration of salts by 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 [40].

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 depicted in Figs. 9,10.

The biosorption capacity of dyes enhanced in case of $Hg^{2+}$and Pb^2. 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 [41]. Other reason is the addition of metals produced the aggregation and flocculation of biomass and increased the biosorption capacity. Pb^{2+} caused great aggregation than any other metal [42].

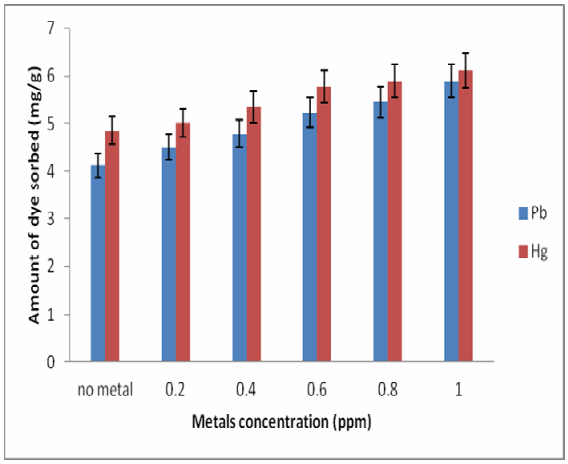

Fig.9: Effect of metals conc on the biosorption of Synolon Red 3HF dye.

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, 12.

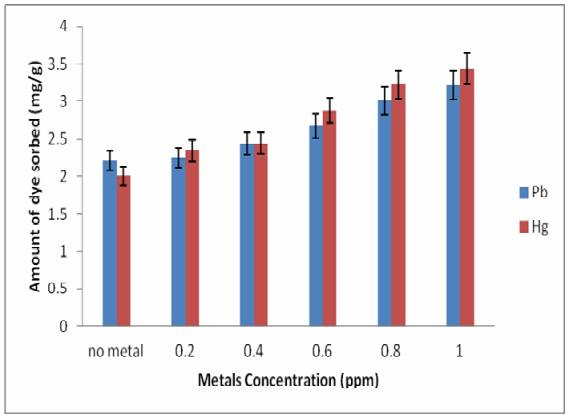

Fig. 10: Effect of metals conc on the biosorption of Synolon black HWF-FS dye.

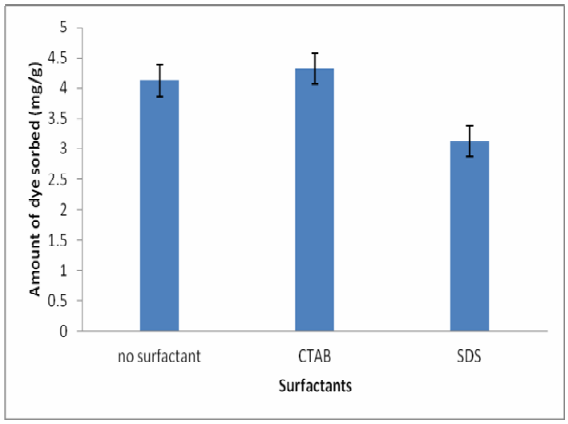

Fig. 11: Effect of surfactants on the biosorption of Synolon Red 3HF dye.

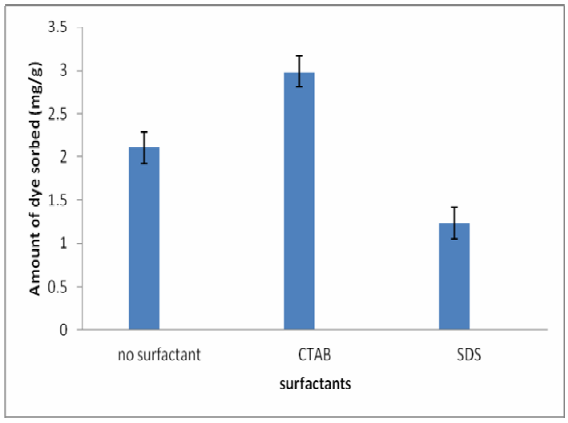

Fig. 12: Effect of surfactants on the biosorption of Synolon black HWF-FS dye.

Cationic surfactant, CTAB (cetyltrimethyl ammonium bromide), increased the biosorption of two direct dyes. This may be due to impregnation of cationic surface gives positive charge on the biomass surface and attracted strongly toward the negatively charged direct dyes [43].

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 [44].

Conclusion

The results obtained from investigation indicated that the Almond and cotton seed oil cakes are very efficient and promising biosorbents for the removal of EBT and A-FGGL dyes from aqueous solution. The biosorption was influenced by the dye solution pH, biosorbent particle size, biosorbent dose, initial dye concentration, contact time and temperature. Adsorption capacity of biomass was found to decrease with increase in pH. The adsorption of present acidic dyes is primarily influenced by the surface charge of the adsorbent particles which in turn is influenced by the solution pH. The availability of positively charged groups at the adsorbent surface is necessary for the adsorption of anionic dye. As pH increased, more negatively charged surface was available, which decreased the availability of positively charged sites, which in turn hindered the adsorption of dye. The biosorption capacity was found to be increase with decrease in the biosorbent particle size. The maximum biosorption capacity was recorded at the smallest particle size (60 Mesh Size). The increase in biosorption capacity may be attributed to the large surface area of the smallest particle size of biosorbent and large number of exchanging sites. The quantity of dye adsorbed decreased with the decrease in biosorbent dose. Maximum biosorption occurred at 0.3g of biosorbent dose. This is due to increase in the number of available binding sites. The uptake capacity of biomass increased with increase in the initial dye concentration. It suggests that the available sites on the biosorbent are the limiting factor for the dye removal. Optimum contact time for equilibrium to achieve was found to be 120 and 180 minutes for EBT and A-FGGL dyes. The amount of dye biosorbed increased rapidly with increase in contact time, but there was no drastic increase in biosorption capacity with further increase in agitation time. It is due to the slow movement of dye molecules into the

interior of the bulk of the biosorbent after the saturation of exterior exchanging sites. Biosorption of dyes is best fitted to the Langmuir Isotherm and pseudo-second order kinetic models.

References

1. M. C. Ncibi, B. Mahjoub, A. M. Ben Hamissa, R. Ben Mansour and M. Seffen, *Desalination*, **243**, 109 (2009).
2. G. Mishra and M. Tripathy, *Colourage*, **40**, 35 (1933).
3. T. Robinson, T. B. Chandran and P. Nigam, *Water Resource*, **36**, 2824 (2002).
4. Y. Bulut, N. Gozubenli and H. Aydin, *Journal of Hazardous Material*, **144**, 300 (2007).
5. G. Crini, *Bioresource Technology*, **97**, 1061 (2006).
6. Z. Aksu, Z and S. Tezer, *Journal of Process Biochemistry*, **40**, 1347 (2005).
7. H. N. Bhatti and Y. Safa, *Desalination and Water Treatment,* **48**, 267 (2012).
8. Y. Safa and H. N.Bhatti, *African Journal of Biotechnology*, **10**, 3128 (2011).
9. F. D. Ardejani, K. Badii, N. Y. Limaee, S. Z. Shafaei and A. R. Mirhabibi, *Journal of Hazardous Material*, **151**, 730 (2008).
10. A. El-Nemr, O. Abdelwahab, A. El-Sikaily and A Khaled, *Journal of Hazardous Material*, **161**, 102 (2009).
11. F. Colak, N. Atar and A. Olgum, *Journal of Chemical Engineering*, **150,** 120 (2009).
12. S. V. Mohan, S. V. Ramanaiah and P. N. Sarma, *Journal of Chemical Engineering*, **38**, 61 (2008).
13. V. Dulman and S. M. Cucu-Man, *Journal of Hazardous Material*, **162**, 1457 (2009).
14. A. Khaled, A. El-Nemr, A. EI-Sikaily and O. Abdelwahab, *Journal of Hazardous Material*, **165,** 100 (2009).
15. R. Gong, Y. Ding, M. L. I. C. Yang, H. Liu and Y. Sun, *Dyes Pigments*, **64,** 187 (2005).
16. M. Akhtar, M. I. Bhanger, S. Iqbal and S. M. Hasany, *Journal of Hazardous Material*, **128,** 44 (2006).
17. O. Tune, H. Tanaei and Z. Aksu, *Journal of Hazardous Material*, **163**, 187 (2009).
18. K. Vijayaraghavan, M. H. Han, S. C. Choi and Y. S. Yun, *Chemosphere*, **68**, 1838 (2007).
19. R. Gourdon, E. Rus, S. Bhende and S. S. Sofer, *Journal of Environmental Science and Health*, **25**, 1019 (1990).
20. V. Vadivelan, and K. V. Kumar, *Journal of Colloid and Interface Science*, **286,** 90 (2005).
21. A. A. Ahmad, B. H. Hameed and N. Aziz, *Journal of Hazardous Material*, **141**, 70 (2007).
22. T. Akar, B. Anilan, A. Gorgulu and S. T. Akar, *Journal of Hazardous Material*, **168**, 1302 (2009).
23. Z. Aksu, A. I. Tatli and O.Tnc, *Journal of Chemical Engineering*, **142**, 23 (2008).
24. N. Cancer, I. Kiran, S. Ilhan and C.F. Iscen, *Journal of Hazardous Material*, **165**, 279 (2009).
25. G. Bayramoglu and M. Y. Arica, *Journal of Hazardous Material*, **143**, 135 (2007).
26. Z. Aksu and S. Tezer, *Journal of Process Biochemistry*, **36**, 431 (2000).
27. T. Langmuir, *Journal of American Society for Chemistry*, **38**, 2221 (2000).
28. H. M. F. Freundlich, *Journal of Physical Chemistry*, **57**, 385 (1906).
29. M. Dogan, M. Alkan and Y. Onganer, *Water, Ai, Soil and Pollution*, **120**, 229 (2000).
30. O. Anjaneya, M. Santoshkumar, S. N. Anand and T. B. Karegoudar, *International Biodeterioration and Biodegradation*, **63**, 782 (2009).
31. S. Lagergren, *Handlingar*, **24**, 1 (1898).
32. Y. S. Ho, G. McKay, D. A. J. Wase and C. F. Foster, *Adsorption Science Technology*, **18**, 639 (2000).
33. Z, Aksu and D. Donmez, *Chemosphere*, **50**, 1075 (2003).
34. Y. Bulut and H. Aydin, *Desalination*, **194**, 259 (2006).
35. V. Ponnusami, S. Vikram and S. N. Srivastavam, *Journal of Hazardous Material*, **152**, 276 (2008).
36. M. Ozacar and I. A. Sengil, *Journal of Hazardous Material*, **40,** 1 (2003).
37. B. Acemioglu,. *Journal of Colloid and Interface Science*, **274**, 371 (2004).
38. Q. H. Tao and H. X. Tang, *Journal of Environental Science China*, **24**, 3890 (2004).
39. P. Janos, S. Coskun, V. Pilarova and J. Rejnek, *Bioresour Technology,* **100**, 1450 (2009).
40. E. L. Grabowska and G. Gryglewicz, *Dyes and Pigments*, **74**, 34 (2007).
41. Z. Aksu, S. Ertugrul and G. Donmez, *Journal of Hazardous Materials,* **168**, 310 (2009).
42. R. X. Liu, X. M. Liu and H. X. Tang, *Journal of Colloidal and Interface Science,* **239**, 475 (2001).
43. B. C. Oei, S. Ibrahim, S. Wang and H. M. Ang, *Bioresour.Technology,* **100**, 4292 (2009).
44. C. Kartal and H. Akbas, *Dyes Pigments,* **65**, 191 (2005).