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Study of operational parameters and kinetics of biosorption of acid orange 7 by untreated sugarcane bagasse

Mukund Madhav, Siddharth Soni, Mayank Singhal, Chandan Kumar Gautam and Shanthi V.*

Industrial Biotechnology Division, School of Bio Sciences and Technology, VIT University, Vellore, Tamil Nadu, India

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ABSTRACT

The current work focuses on investigating the effect of the different operational parameters on the removal of Acid Orange 7 (AO7) dye from textile wastewater using natural adsorbent (untreated sugarcane bagasse) and study of the adsorption kinetics involved. The effects of operational parameters such as pH, the amount of biosorbent, initial dye concentration, rotations per minute and temperature were examined. The kinetic study shows that the process under investigation follows the Langmuir adsorption isotherm more proficiently than the Freundlich isotherm. Further investigation of the sorption process was done using the UV-Vis spectra, Fourier Transform Infrared (FTIR) spectroscopy and X-ray Diffraction (XRD). Out of several chosen parameters, the optimum conditions for efficient dye removal was found to be the dose of biosorbent (8 g), initial dye concentration (4 mg/100mL), initial pH (2.5) and temperature (30°C). This combination gave a reduction of O.D. (measured at 485 nm) by 85.42%. From the investigation sugarcane bagasse proved good biosorbent for the AO7 dye.

Keywords: sugarcane bagasse, acid Orange 7 dye, adsorption isotherm, adsorption kinetics, batch process

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INTRODUCTION

Textile effluent contains a significant amount of non-biodegradable chemical dyes. These dyes are mainly organic compounds which are classified on the basis of their structure (as anthraquinone, azo) or methods (reactive, direct, Azoic, disperse) used to fix them on the fibres [1]. Statistical data suggest that the contribution of azo dyes usage and production is 60-70% of 10000 dyes used in the industries [2]. In azo dyes the cleavage of the azo bonds leads to the formation of aromatic amines which are considered carcinogenic in nature [3]. Further they reduce the oxygen content of the water bodies leading to the death of the flora and fauna [4].

Acid orange 7 is mono azo acid dye which is currently used in industries for dyeing a variety of materials such as nylon, aluminium, detergents, cosmetics, wool and silk. It produces an allergic reaction in upper respiratory tract, bone marrow degradation and since it is carcinogenic in nature it can develop tumours, can be fatal if consumed [5]. The pre-treatment of the textile wastes with suitable adsorbent speed up the treatment process and enhances the efficiency. Several works have been done on the treatment of textile as well as sewage waste water with the agricultural bi-products. Sugarcane bagasse having high cellulosic fibre content have proved to be a better biosorbent of the textile dyes [6]. It has adsorptive sites like carbonyl, carboxylic, amine and hydroxyl groups which are able to adsorb the dyes by the ion exchange phenomena or by complex formation [7]. In the current study, the kinetics of adsorption of the Acid Orange 7 (*AO7*) dye on the sugarcane bagasse was studied. Also, the operational parameters like the amount of biosorbent used, initial dye concentration, initial pH of the dye solution, temperature and rotations per minute (RPM) were studied to infer the best combination of these parameters to obtain highest dye removal efficiency.

EXPERIMENTAL SECTION

Materials

Solid dye was obtained from textile industry (Sutlej Textiles & Industries Ltd). The instruments used are as follows: UV/Vis spectrophotometer (GE), orbital shaker (Orbitek), shaker-incubator (Orbitek), centrifuge (Remi), pH meter (Systronics) and balance with accuracy of 0.0001g.Untreated sugarcane bagasse was obtained from a nearby juice shop. It was broken into pieces. Uniform sized bagasse was chosen as biosorbent for the experiment.

Preparation of Dye Solution

A stock solution of concentration 1.0mg/mL was prepared by dissolving 1.0 g of the solid dye in a litre of distilled water. Solutions of different concentrations (2.0, 4.0, 6.0 and 8.0mg/100mL) were prepared by quantitatively diluting the stock solution in different 250mL conical flasks.

Analytical Methods

Different amount of biosorbent was added in the prepared dye solution. Four different amounts of biosorbent (2.0g, 4.0g, 6.0g and 8.0g) in the various concentrations of the dye solutions were studied. Total contact time of 5 hours was provided over the orbital shaker at 100 RPM and a sample of 3.0mL was taken every hour. This sample was centrifuged at 4400 RPM for 3 min, separating any solid particles in the samples. Optical Density of these samples was measured in a UV-Visible spectrophotometer at 485nm.For measuring the effect of temperature on sorption similar procedure was followed in a shaker-incubator. Temperatures studied here were 30, 40, 50, 60 and 70 ^{0}C. For studying the effect of initial pH of the dye solution, dye solutions were treated with appropriate amounts of analytical grade NaOH or HCl with constant stirring using a pH meter. The pH studied here was in the range of 2.5 to 8.5. For studying the effect of rotations per minutes(RPM) on the sorption process, dye solutions with biosorbent material were subjected to different RPM. The different RPMs studied here were 80, 100 and 120 RPM. XRD pattern analysis of the sugarcane bagasse was done before and after the biosorption of the dye. The XRD used for evaluation had Cu Kα radiation source and a graphite monochromator. The functional group present on the biosorbent surface before and after sorption was determined by FTIR analysis using the KBr disc method.

The amount of dye uptake and efficiency of the biosorption process was calculated according to the following equation (1) and (2) [8].

$$q = (C_o - C_t)/m * V \quad (1)$$

$$\% \text{ removal} = (C_o - Ct) / C_o \quad (2)$$

Where q is dye uptake amount (mg/g), V is the volume of solution (L), m is mass of adsorbent (g), C_0 (mg/L) and C_t (mg/L) are initial and residual concentrations of dye, respectively [9].

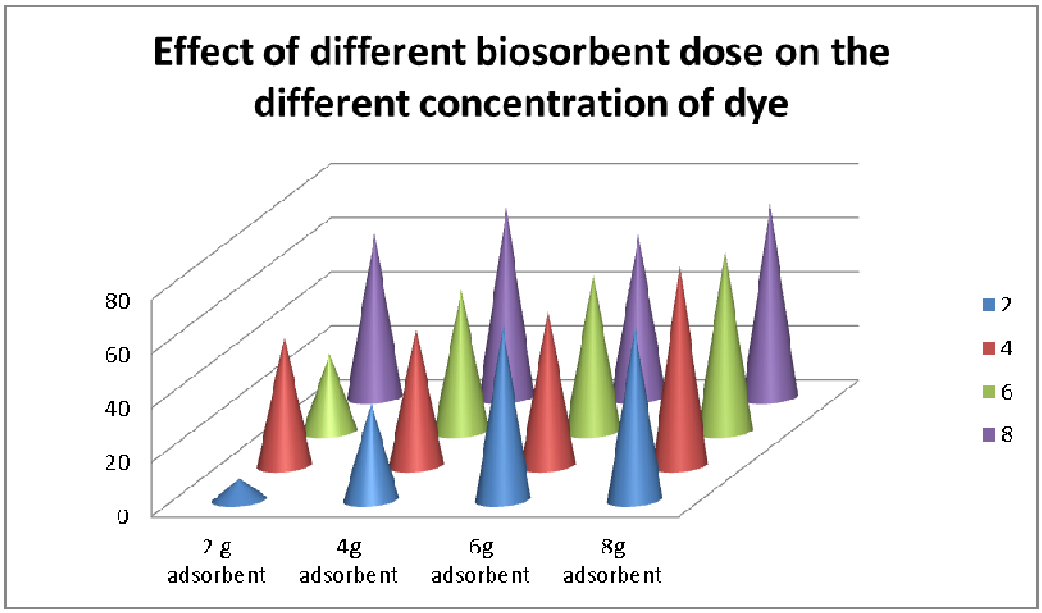
RESULTS AND DISCUSSION

Temperature of 30±1 ℃ and 100 RPM was chosen for considering the effect of all parameters on sorption process. Different combinations of the dye with the sugarcane bagasse were tested for biosorption. It was observed that the combination of 4mg/ 100mL dye and 8gm of biosorbent gave the best result. So, further analysis was carried out considering these two parameters constant.

3.1 Effect of Biosorbent Dose

At a temperature of 30±1 ℃, pH of 7.0 and 100 RPM, the different dye solutions were subjected to varying doses of the biosorbent, sugarcane bagasse. As shown in the Fig. 1, an increase of biosorption efficiency was observed with the increase in biosorbent dose. The highest dye removal was obtained at 8.0mg of biosorbent dose used in the 4mg/100mL concentration of dye. The removal of dye with increasing amount of biosorbent dose is explained by the increase in the attachment sites for the dye molecules [9]. For carbonised or treated biosorbant it has been reported that, with increasing the amount of biosorbent for constant concentration of dye there is decrease in removal efficiency after certain amount of biosorbent which can be explained by the clump formation between the particles leading to less exposure of adsorption sites for attachment [10].

Fig. 1Effect of different biosorbent doses (2g, 4g, 6g, 8g) on the % reduction of different concentration of dye (2mg/100mL, 4mg/100mL, 6mg/100mL, 8mg/100mL) at p^{H} 7, temperature 30^{o}C and RPM 100



3.2 Effect of Dye Concentration

At the constant biosorbent dose of 8.0mg, temperature of 30±1 ℃, pH of 7.0 and 100 RPM, the effect of initial dye concentration was studied. As shown in theFig. 2.1, the highest efficiency obtained was at the initial dye concentration of 4.0mg/100mL.This could be possible because of the existence of a sufficient number of attachment sites on the surface of the biosorbent leading to a higher chance of interaction between the dye molecules and biosorbent surface. Lower removal efficiency of dye at higher concentration of dye could be explained by the saturation of attachment sites of the biosorbent [11].

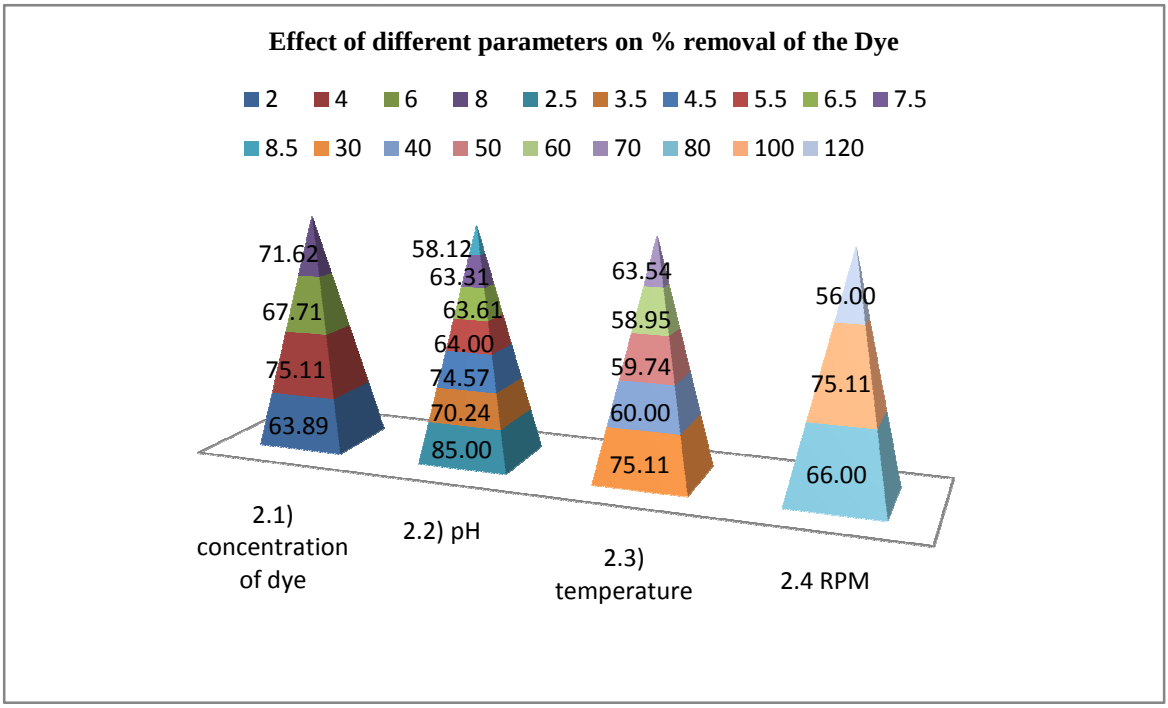
Fig.2

2.1 % removal of dye at different concentrations (2mg/100mL, 4mg/100mL, 6mg/100mL, 8mg/100mL) by constant biosorbent (8g) at pH 7, temperature 30^{o}C after 5 hours

2.2 Effect of different pH on the % reduction in dye conc. (at initial dye conc. 4mg/100mL, biosorbent (8g), temperature 30^{o}C, after 5 hours)

2.3 Effect of different temperature on the % reduction of dye conc. (at initial dye conc. 4mg/100mL, biosorbent (8g), pH 7 after 5 hours)

2.4 Effect of different RPM on the % reduction of conc. of dye (at initial dye conc. 4mg/100mL, biosorbent (8g), pH 7, temperature 30^{o}C after 5 hours)



3.3 Effect of Initial pH of Dye Solution

At the biosorbent dose of 8g, initial dye concentration of 4 mg/100mL, temperature of 30 ± 1^0C and 100RPM, the effect of initial pH on the biosorption was studied. The most appreciable biosorption was obtained at an acidic pH of 2.5, as shown in the Fig. 2.2.

This may be possible due to higher electrostatic attraction between the surface and dye. Under acidic condition, the dye uptake for acidic dye is higher as compared to the basic and neutral conditions [12]. The development of the charge due to different functional group on the surface of biosorbent and ionic state of dye are two conditions playing a significant role in the colour removal in the case of pH[13]. Dye attachments are inhibited due to aqua complex formation by clumping of increasing hydroxyl and hydrogen ion attributed at less acidic (more basic) pH range [14].

3.4 Effect of Temperature

Evaluation of temperature effect on the process is essential for industries. The industrial effluents (including unused dyes) come out at slightly higher temperature than the normal temperature of the surrounding [11]. The effect of temperature for biosorption was studied at the constant biosorbent dose of 8.0mg, dye concentration of 4.0mg/100mL and 100 RPM. As shown in the Fig. 2.3, the highest efficiency of biosorption was observed at 30^0C.

3.5 Effects of Rotations per Minute (RPM)

Agitation is responsible here for the proper exposure and even interaction of the dye molecules with biosorbent. So it's an important parameter for investigation of the sorption process. The study of the effect of RPM on the biosorption process was studied at the constant biosorbent dose of 8.0mg, dye concentration of 4.0mg/100mL and temperature of 30^0C. Biosorption process was most appreciable at 100 RPM under the given conditions as shown in the Fig. 2.4**.**

At 80 RPM, the reduction in O.D. (at 485 nm) was sharp initially but reduction declined with time. At 120 RPM, it was expected that proper movement of the biosorbent material would occur in the dye solution resulting in an appreciable reduction in O.D. (at 485 nm). However this was not observed as the reduction efficiency was lower than 100 RPM. This could probably mean that the dye molecules are getting separated out or could not properly attach to the biosorbent sites of the sugarcane bagasse at this higher speed of rotation.

3.6 Equilibrium Adsorption Isotherms

The study of adsorption isotherm plays a vital role in determining the industrial application of the biosorption process. As the maximum removal level could be attained at the equilibrium concentration, the information about the parameter of the isotherm helps to predict the extent of the solute removal [15].

Isotherms figures are analysed by setting them to different isotherm model. Here, Langmuir and Freundlich adsorption isotherm methods were taken into consideration to check the favourableness of the adsorption process. The Langmuir adsorption theory suggests the assumption of the covering of the homogeneous adsorbent surface of the monolayer of the adsorbate [16]. The different data were fitted into this mathematical equation (5) for analysis of the Langmuir isotherm [17].

$$C_e/ q_e= 1/Q_o b+C_e/q_e \quad (3)$$

Here in this equation (3), C_e = concentration at equilibrium (mg/L), q_e= equilibrium adsorbed amount (mg/g), Q_o = capacity of adsorption (mg/g) and b = adsorption energy (Langmuir constant) (l/mg). The value of b and $Q_o$were obtained from the intercept and slope of graph plotted between C_e/q_e and C_e. The obtained results are tabulated inTable 1**.**

Table 1 Values of Langmuir isotherm constants and correlation coefficient at different temperature for AO-7 dye adsorption on sugarcane bagasse at pH 7, dye conc. (4mg/100mL), biosorbent (8g)

S.NO	Temperature(°C)	Q_0 (mg/g)	B (1/mg)	R^2
1	30	28.01	4.103	.9999
2	40	16.77	1.413	.9997
3	50	14.00	1.126	1
4	60	19.01	1.696	1
5	70	22.12	2.226	.9960

The correlation coefficients (R^2) works as deciding factor in comparing the different adsorption models and their applicability [17]. The value of R^2 from table 1 suggests that Langmuir isotherm might be suitable due to higher correlation coefficient in comparison to the other model used. The value of adsorption capacity increased from 14 mg/g to 22.12 mg/g when the temperature was raised from 40°c to 70°c. This may be indicative of creation of new adsorption or active sites in biosorbent with increased temperature. There are chances of abrupt decrease in the adsorption capacity value at too high temperature [18]. Independence of kinetic energy of the dye was shown by the absence of linearity in the values of Langmuir constant *b* .The prediction of the favourableness or unfavourableness of Langmuir was checked by putting the values of "*b*"(Langmuir constant) and "*c*"(initial concentration of the dye) in the expression of the dimensionless separation factor "*r*" [19].

$$r = 1/(1+bc) \quad (4)$$

The condition for the favourability of Langmuir is $0<r<1$, which is fulfilled at all the temperature, as all the values of "r" lied below 0.05.

Heterogeneous surface energies using the multilayer adsorption is described by the Freundlich isotherm and expressed as [20]

$$q_e = K_f C_e^{1/n} \quad (5)$$

The logarithmic form of equation of the Freundlich isotherm can be represented as follows:-

$$Log\ q_e = log\ K_f + 1/n\ log C_e \quad (6)$$

Both K_f (capacity of adsorption) and *n* (adsorption intensity) are also known as the Freundlich constants. The graph plotted between log q_e and logC_e gives slope $=1/n$ and intercept =log K_f. The value of *n* lying in 1 to 10 range is a sign of good adsorption potential [17]. The closeness of R^2 value to unity indicates the well fitness of the data with the Langmuir isotherm. The different values of constants at different temperatures are represented below in Table 2.

Table 2 Values ofthe Freundlich isotherm constant and correlation coefficient at different temperature for*AO7* dye adsorption on sugarcane bagasse at pH 7, dye conc. (4mg/100mL), biosorbent (8g)

S.NO	Temperature (°C)	k_f (mg/g)(mL/mg)^n	*N*	R^2
1	30	37.896	2.997	0.9993
2	40	44.442	1.210	0.9996
3	50	42.481	1.333	1
4	60	82.110	0.448	1
5	70	39.120	1.792	0.994

3.7 Adsorption Kinetics

To understand the mechanism involved in adsorption processes and for scalability, the studies of various adsorption kinetic parameters are necessary [8]. The biosorption process is dependent on the physical and chemical characteristic of adsorbent [17]. For investigating the adsorption processes 3 kinetic models pseudo- first, pseudo-second and intra-particle diffusion was taken into consideration at different condition of temperature, pH, dye concentration and adsorbent amount.

The most preferred equation for the less concentrated solute is pseudo-first order [21].

The pseudo-first order equation is represented as follows [22]:

$$Log\ (q_e - q_t) = log\ q_e - k_1 t/2.303 \quad (7)$$

Here q_e= equilibrium adsorption dye amount (mg/g), q = amount of dye adsorbed at time t (hr) (mg/g) and k_1 = rate constant (hr^{-1}). The values of k_1 and q_e were obtained from the slope and intercept of the graph plotted between log (q_e-q) and time (t).

The pseudo - second order reaction rate varies with the quantity of adsorbed dye at biosorbent surface at equilibrium [21]. The pseudo - second order equation is expressed as

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (8)$$

Where t= time (hr), k_2= rate constant ($g \cdot mg^{-1}\ hr^{-1}$),q_e = equilibrium adsorption dye amount (mg/g).The graph plot t/q_e vs. Time (t) gave the value of $k_2$and q_s from its slope and intercept.

The initial sorption rate= h (mg/g min) is demarcated as [22]

$$h = k_2 q_e^{\ 2} \tag{9}$$

Intra-particle diffusion can also explain the adsorption process. Here, the film's resistance plays a crucial role in the transport of the solute thus making the intra-particle diffusion as the rate limiting factor. According to Morris-Weber adsorption varies with the square root of time [23], so for the calculation of the intra-particle diffusion; Morris-Weber equation is used in the following manner [3].

$$q_t = k_i t^{1/2} + C \tag{10}$$

Where k_i= rate constant for the intra-particle diffusion (mg. $^{g\text{-}1}hr^{-1/2}$) and is obtained by the slope of the plot between q_t and $t^{1/2}$. The film thickness of the boundary can be obtained from the intercept C [24]. All the values calculated using the equation 7, 8, 9 and 10 are tabulated in the table 3, 4 and 5.Biosorption kinetics was carefully observed for various parameters such as concentration of dye, amount of biosorbent and pH. From the various data it was found that pseudo-second order kinetics is followed in temperature (30 - 70^{o}C) and at biosorbent amount in the range 2 - 8g. At lower concentrations of dye (2mg/100mL) intra- particle diffusion was followed. Pseudo-first order kinetics was best fitted at pH of 8.5 and at rest pH values, the pseudo-second order kinetics was followed.

Table 3 Values of Kinetic constants and correlation coefficient of pseudo-first, pseudo-second and intra-particle diffusion for *AO7*dye biosorption on sugarcane bagasse at different concentration of the dye, biosorbent (8g), pH 7, temperature 30^{o}C

Conc. of dye	Pseudo- first order		Pseudo-second order			Intra-particle diffusion	
mg/100mL	K_1 (hr^{-1})	R^2	K_2 ($g \cdot mg^{-1}\ hr^{-1}$)	R^2	h (mg/g hr)	K_i ($mg.^{g\text{-}1}hr^{-1/2}$)	R^2
2	2.042	0.843	.00763	0.916	32.649	39.334	0.942
4	1.351	0.803	.0222	0.983	113.41	18.916	0.932
6	1.528	0.889	.0342	0.992	133.33	13.347	0.961
8	0.628	0.853	.0263	0.992	131.554	15.37	0.956

Table 4Values of Kinetic constants and correlation of pseudo-first, pseudo-second and intra-particle diffusion coefficient for *AO 7* dye biosorption on sugarcane bagasse at different amount of biosorbent, Dye conc. (4mg/100mL), pH 7, temperature 30^{o}C

amount of biosorbent	pseudo-first order		pseudo-second order			Intra-particle diffusion	
(g)	K_1 (hr^{-1})	R^2	K_2 ($g \cdot mg^{-1}\ hr^{-1}$)	R^2	h (mg/g hr)	K_i ($mg.^{g\text{-}1}hr^{1/2}$)	R^2
2	1.210	0.955	0.0489	0.984	302.981	7.637	0.580
4	1.764	0.857	0.0339	0.987	40.151	12.28	0.971
6	0.647	0.972	0.0272	0.994	34.721	14.467	0.953
8	1.680	0.794	0.0450	0.985	57.471	9.311	0.933

Table 5 Values ofKinetic constants and correlation coefficient of pseudo-first, pseudo-second and intra-particle diffusion for *AO7*dye biosorption on sugarcane bagasse at different pH and dye conc. (4mg/100mL), biosorbent (8g),temperature 30^{o}C

p^H	pseudo-first order		pseudo-second order			Intra-particle diffusion	
	K_1 (hr^{-1})	R^2	K_2 ($g \cdot mg^{-1}\ hr^{-1}$)	R^2	h (mg/g hr)	K_i ($mg.^{g\text{-}1}hr^{-1/2}$)	R^2
2.5	2.106	0.953	0.0659	0.997	138.88	9.101	0.801
3.5	1.122	0.961	0.0573	0.998	78.12	8.966	0.828
4.5	1.114	0.932	0.0476	0.993	67.11	10.387	0.784
5.5	0.630	0.967	0.102	0.999	114.94	4.615	0.982
6.5	0.450	0.990	0.0587	0.996	65.78	6.840	0.989
7.5	0.926	0.952	0.0753	0.997	76.92	5.987	0.934
8.5	1.403	0.997	0.0279	0.940	28.23	13.369	0.767

3.8 FTIR Analysis

FT-IR analysis of the biosorbent sample was done to investigate the functional groups present on surface via the KBr Disc method before and after the biosorption. These functional groups available on the surface are responsible for attachment of dye to the surface.

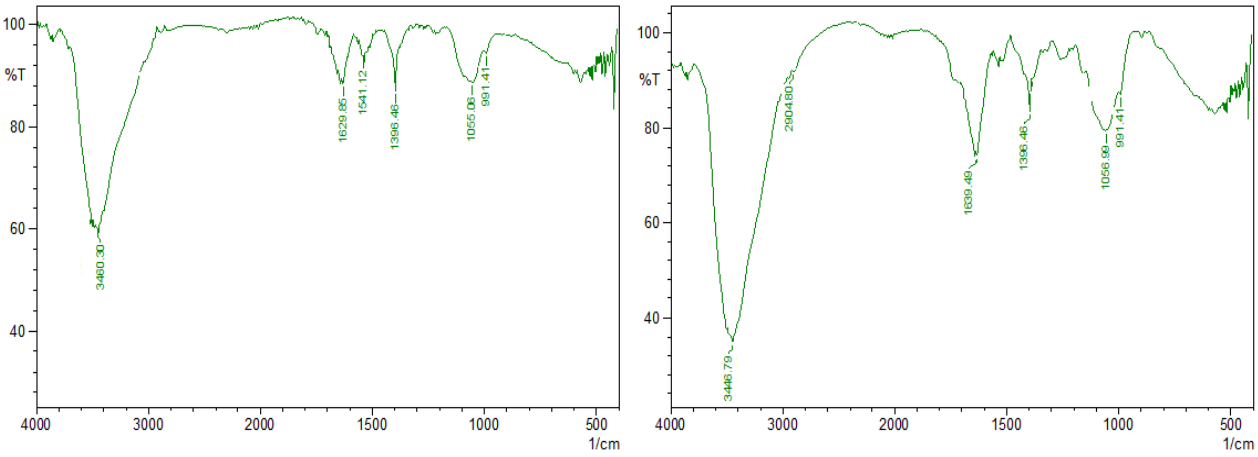
The Fig. 3 is shown below in which, 3.1 shows dye bounded biosorbent and 3.2 shows biosorbent. The spectral peak displayed at 3446.79 and 3480.30 cm^{-1} refers to the hydroxyl group (-OH stretch) due to the presence of the lignin and carbohydrate [24]. The peak at 1639.84 cm^{-1}, 1629.85 cm^{-1} attribute to the (c=c stretch) and different types of amines. The (c=c stretch) are most common in the lignin structure. The presence of the phenol group or tertiary

alcohol and carboxylate ion was predicted by the spectral peak at 1396.46 cm^{-1}. The peak at 1056.99 cm^{-1}, 1055.06 cm^{-1} shows the tertiary amine (-C-N stretch) and alkyl substituted ether (C-O stretch) respectively [25].

Fig. 3

3.1 : (FTIR spectral plot for the dye bounded biosorbent)

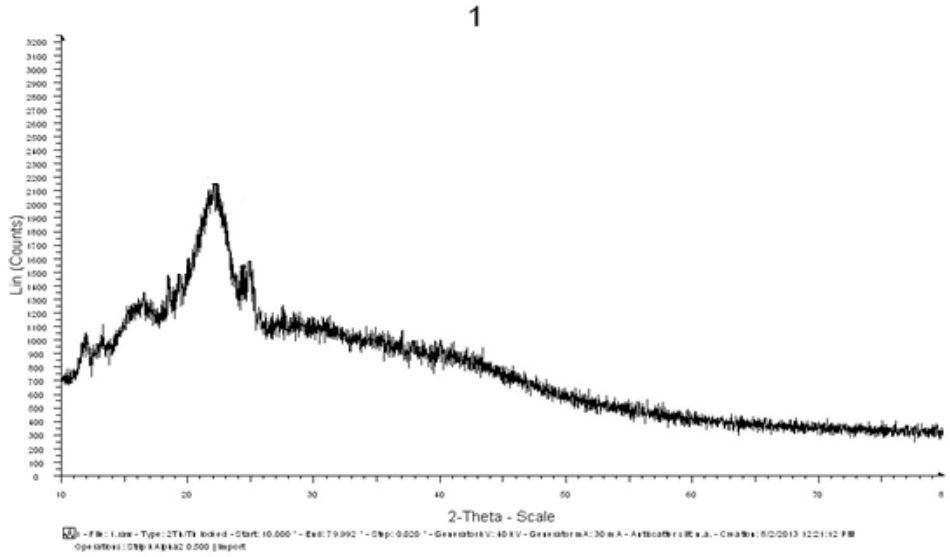
3.2: (FTIR spectral plot for the biosorbent)



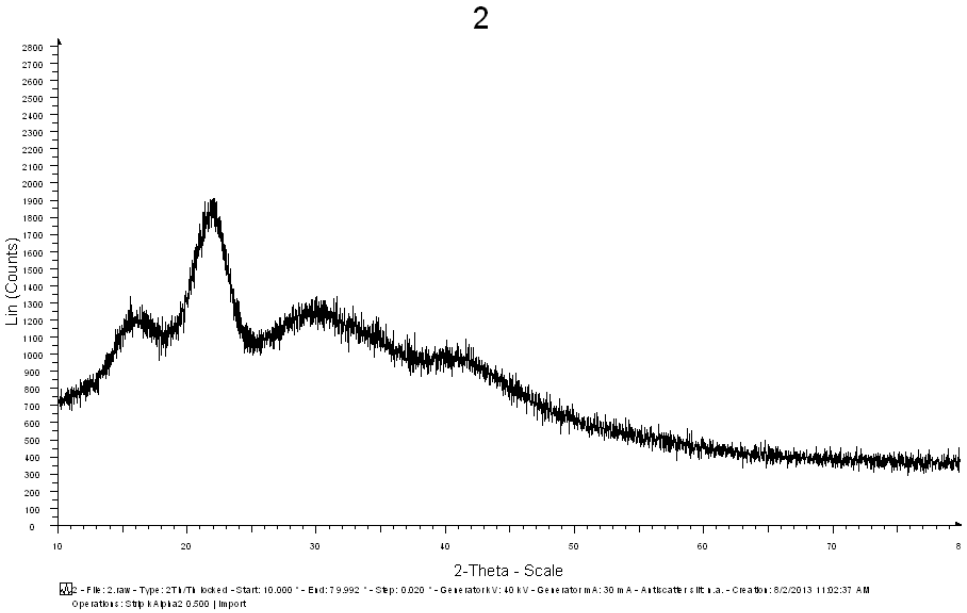
3.9 XRD Analysis

The crystalline nature of a substance is mainly detected by X-Ray Diffraction[26]. The shape, position and width of peak provide the information about its structure. The graph with the clear and well-defined peak is the denotation of the crystalline compound whereas the dispersed peak marks the presence of amorphous substances [27]. The XRD pattern of biomass without biosorption showed the major peak at 22^{o}, which is in the correspondence with the cellulosic crystallographic planes [28]. The XRD pattern after loading of the biosorbent with *AO7* dye resulted in diffused peaks which may be attributed to the conversion of the crystalline structures into amorphous. The above observation can be concluded from the fig. 4.

Fig. 4 XRD pattern of sugarcane bagasses



4.1. before sorption of the acid orange 7 dye



4.2. after sorption of the acid orange 7 dye

CONCLUSION

From this study, it was inferred that even untreated sugarcane bagasse can be used to efficiently remove the Acid orange 7 dye from the textile waste water by optimizing the operation parameters. The most efficient operational parameters in the current study was found to be; for the biosorption of the acid orange dye were (for the dye solution concentration of 4.0mg/100mL), a biosorbent dose of 8.0mg, temperature of 30^0C and rotations per minute of 100 RPM (85.42%). The reaction followed the Langmuir isotherm model as well as the Frendulich model and the order of the reaction was observed to be mostly of the pseudo-second order. The FTIR and XRD analysis has further proven the successful removal of dye molecules by untreated sugarcane bagasse. Optimization of the biosorption parameters and a better understanding of the adsorption kinetics will help in achieving better efficiency and reduction in operational cost of the dye removal process from the textile industrial wastewater.

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