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# TREATMENT OF TEXTILE EFFLUENTS BY LOW COST AGRICULTURAL WASTES: BATCH BIOSORPTION STUDY

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## ABSTRACT

The present investigation deals with the treatment of different dye containing effluents by using different agricultural waste biomasses (corncobs, sugarcane bagasse, cotton sticks, sunflower and peanut husk). Samples of textile wastewater were collected from five different textile industries of Faisalabad, Pakistan. Screening test was conducted to select the biosorbent with maximum dye removal efficiency for each of textile wastewater samples. Different process parameters like biosorbent dose, shaking speed and temperature were optimized during the study. The biosorption process using corncobs biomass was found to be good for the removal of dyes up to 79% from the one real textile wastewater sample. The biosorption efficiency of adsorbents was maximum at 0.3 g $50mL^{-1}$ of adsorbent dose with 120 rpm shaking speed and 303 K temperature. Thermodynamic study was also carried out to evaluate different parameters like free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) and biosorption process was found to be exothermic. Characterization of effluents was carried out before and after the biosorption process to check out the effect of process on the removal of Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS) and Total Suspended Solids (TSS). The results proved that agricultural wastes are good option for the removal of color and COD from real textile effluents.

**Key words:** Agricultural wastes; COD; Color; TDS; Thermodynamic study; Biosorption.

## INTRODUCTION

The textile sector enjoys a pivotal position in the exports of Pakistan. In textile industries various processes are carried out starting from fiber production to the final finishing of product (Ahmad and Hameed, 2009).The textile industry is a substantial consumer of water (Solis *et al*., 2012), dyes, surfactants and various other chemicals. Hence the amount of wastewater generated from all these processes is very high and highly contaminated (Lin and Chen, 1997).The textile wastewater contribute to high biochemical oxygen demand (BOD), suspended solids (SS), dissolved solids, color, chemical oxygen demand (COD), heat, acidity, basicity and other soluble substances (Ahn *et al*., 1999). This highly contaminated water has a high environmental impact and therefore needs to be treated before being discharged to the environment (Kumar *et al*., 2008).

A wide variety of biological, physical and chemical methods for the treatment of colored wastewater include photocatalytic degradation (Mahmoodi *et al*., 2005), coagulation (Bozdogan and Goknil, 1987) membrane filtration (Wu *et al*., 1998) and microbiological degradation (Pearce *et al*., 2003). All these methods have different color removal abilities, capital costs and operating rates (Amin *et al*., 2009). The adsorption process is preferred over other processes due its low cost, easy operation, flexibility and simplicity. Adsorption processes using activated carbons are widely used to remove color and other pollutants from wastewaters but the high cost of activated carbon makes its use limited.

Recently scientists are giving considerable attention on the use of biological-based materials and their by-products as the biosorbent for the removal of pollutants from different wastewaters because of presence of carboxyl, hydroxyl and amino groups over their surfaces (Ay *et al*., 2012). These groups are responsible for the biosorption process. Biological-based materials such as agricultural-based biomasses are cheap and easily obtainable in considerably substantial quantities. Many researchers have used agricultural-based biomasses such as cocoa shells (Meunier *et al*., 2003), grape stalks (Martinez *et al*., 2006), hazelnut and almond shells (Pehlivan *et al*., 2009), *Capsicuum annuum* seeds, (Ozcan *et al*., 2007), citrus wastes (Asgher and Bhatti, 2010), rice husk (Safa and Bhatti, 2011) and barely husk (Haq *et al*., 2011) for the removal of dyes from aqueous solution. Agricultural by products are easily available in Pakistan so the present study was designed to exploit the abundantly available agricultural wastes for the treatment of textile effluents to remove color, COD, dissolved and suspended solids. The trials were also conducted to optimize process parameters like biosorbent dose, shaking speed and temperature. However, thermodynamic study was carried out to check the feasibility of biosorption process as well.

## MATERIALS AND METHODS

**Textile wastewater:** One raw textile wastewater sample was collected from Sweety Textile and Printing Industry Faisalabad, and four were collected from the local dying houses. Samples were collected in sampling bottles and placed in icebox to preserve for analysis. These effluents were given the sample numbers as 1-5. The physico-chemical parameters such as pH, Electrical conductivity (EC), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS) and Total Suspended Solids (TSS) were estimated according to the methods prescribed in APHA (Greenberg *et al*., 1992). The removal of dyes was determined by absorbance measurements using UV-Vis spectrophotometer (Schimadzu, Japan) before and after the treatment of wastewater samples.

**Preparation of biosorbents:** Five different agricultural waste materials (sugarcane bagasse, peanut husk, corncobs, cotton sticks and sunflower waste biomass) were collected from different areas of Punjab, Pakistan to use as biosorbents. The biomasses were cut into small pieces and rinsed several times with distilled water to remove dust and foreign particles. The cleaned biomasses were dried in sunlight and oven dried overnight at 60 °C. The dried biomasses were ground with a food processor (Moulinex, France) and sieved using Octagon sieve (OCT-DIGITAL 4527-01) to a 300 µm mesh size and stored in air tight bottles.

**Batch experiments:** Optimization of important process parameters such as biosorbent dose, shaking speed and temperature for the maximum removal of dyes from textile effluents was carried out by using classical approach. The 250-mL conical flasks containing 50 mL of effluent with known biosorbent dose were shaken in orbital shaking incubator (PA250/25H) at 120 rpm. Screening test was performed by using 0.1 g biosorbent dose at natural pH for each wastewater sample. Blank solutions were run under same conditions except the addition of biosorbent. All the experiments were performed in triplicate and reported values are mean±SD. After certain time, the samples were taken out and centrifugation was performed at 5000 rpm for 20 min and concentration of remaining dye solution was determined by using UV-Vis spectrophotometer (Schimadzu, Japan).

The %age dye removal from each sample was calculated by using the following relationship:

$$\% \text{ Removal} = \frac{\text{Initial Abs} - \text{Final Abs}}{\text{Initial Abs}} \times 100 \quad (1)$$

**Effect of biosorbent dose:** Effect of biosorbent dose was investigated by using different biosorbent doses (0.05, 0.1, 0.15, 0.2 and 0.3 g 50 mL$^{-1}$) at 120 rpm shaking speed and 303 K temperature.

**Effect of shaking speed:** Effect of shaking speed was investigated by conducting experiments at different shaking speeds (70, 80, 90, 100, 110 and 120 rpm) at 303 K temperature under pre-optimized conditions of biosorbent dose.

**Biosorption thermodynamics:** Biosorption of dyes was investigated at different temperatures (303 to 333 K) in the orbital shaking incubator under pre-optimized conditions (biosorbent dose: 0.3 g, shaking speed: 120 rpm. Various thermodynamic parameters such as enthalpy changes (ΔH°), entropy changes (ΔS°) and Gibbs free energy changes (ΔG°) were used to determine the spontaneity of biosorption process.

## RESULTS AND DISCUSSION

**3.1 Physico-chemical characterization of textile effluents:** Each wastewater effluent was characterized before and after adsorption trials for pH, EC, COD, TDS and TSS and the values of these parameters are presented in Table 1.

**Table 1 Physico-chemical characterization of textile effluentsbefore and after the biosorption process**

| Sample No | $pH_i$ | $pH_f$ | $EC_i$ (mS) | $EC_f$ | $COD_i$ (mg L$^{-1}$) | $COD_f$ mg L$^{-1}$) | $TDS_i$ (mg L$^{-1}$) | $TDS_f$ (mg L$^{-1}$) | $TSS_i$ (mg L$^{-1}$) | $TSS_f$ (mg L$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 7.04 | 7.80 | 2.55 | 2.09 | 134 | 82 | 1955 | 1877 | 236.8 | 185.6 |
| **2** | 7.86 | 7.81 | 1.69 | 1.68 | 44 | 19 | 1700 | 1209 | 51.30 | 49.20 |
| **3** | 7.65 | 7.12 | 3.12 | 2.27 | 102 | 49 | 1902 | 1415 | 37.6 | 31.2 |
| **4** | 11.3 | 7.80 | 3.65 | 2.99 | 151 | 115 | 1812 | 1753 | 45.2 | 24.3 |
| **5** | 9.06 | 8.2 | 2.27 | 1.02 | 157 | 117 | 1721 | 1348 | 15.4 | 12.3 |

pH is an important parameter to measure the water quality. A general recommendation is that the water having pH below 6.5 and above 8.5 is not reasonable for public consumption. EC is also an important water quality parameter which reflects the soluble salts in the water (Wilcox, 1955). TDS refers to any minerals, salts, metals cation, or anion dissolved in water (Iqbal *et al*., 2012). The results indicate a decrease in COD, TDS and TSS after the treatment of textile effluents through biosorption which shows that biosorption process is effective for the treatment of textile effluents.

**3.2 Screening test:** Screening test was performed to select one biosorbent with maximum dye removal efficiency for each wastewater sample. The maximum dye removal for sample 1 and sample 2(40.4 % and 56.4 % respectively)was achieved by corncobs biomass, for sample 3 and 5, the maximum dye removal was achieved by sugarcane bagasse (43.4 % and 61.2 % respectively) and for sample 4 cotton sticks biomass depicted maximum dye removal efficiency (14.4 %).

**3.3 Effect of biosorbent dose:** During the biosorption process, the amount of biosorbent plays a very significant role. The experiments were conducted to check out the effect of biosorbent dose on the biosorption process by varying the mass of biosorbent (0.05, 0.1, 0.15, 0.2 and 0.3 g) and results are presented in Fig. 1. The results indicated that by increasing the biosorbent dose from 0.05 to 0.3 g, the dye removal also increased. The increase in biosorption of dyes by increase in biosorbent dose can be attributed due to the fact that at higher biosorbent doses, the surface area and hence the binding sites available for the attachment of dye molecules increase which results in the more efficient biosorption process (Mane and Babu, 2011). Maximum dye removal for all the samples was found to be at 0.3g/50mL sample solution except for sample 5 for which there was no appreciable dye removal above 0.15 g biosorbent dose. This might be due to aggregation of biosorbent at higher doses which leads to the blockage of binding sites on the surface of biosorbent and hence no further removal of dye molecules was achieved even at higher biosorbent doses. Similar results have been reported for the removal of color and COD from the real effluent of textile mills by Ahmad and Hameed, 2009. Patel and Vashi, 2010 also worked on the treatment of real textile effluents through adsorption and while investigating the effect of biosorbent dose, they found similar trend of increasing dye adsorption by increasing adsorbent dose.

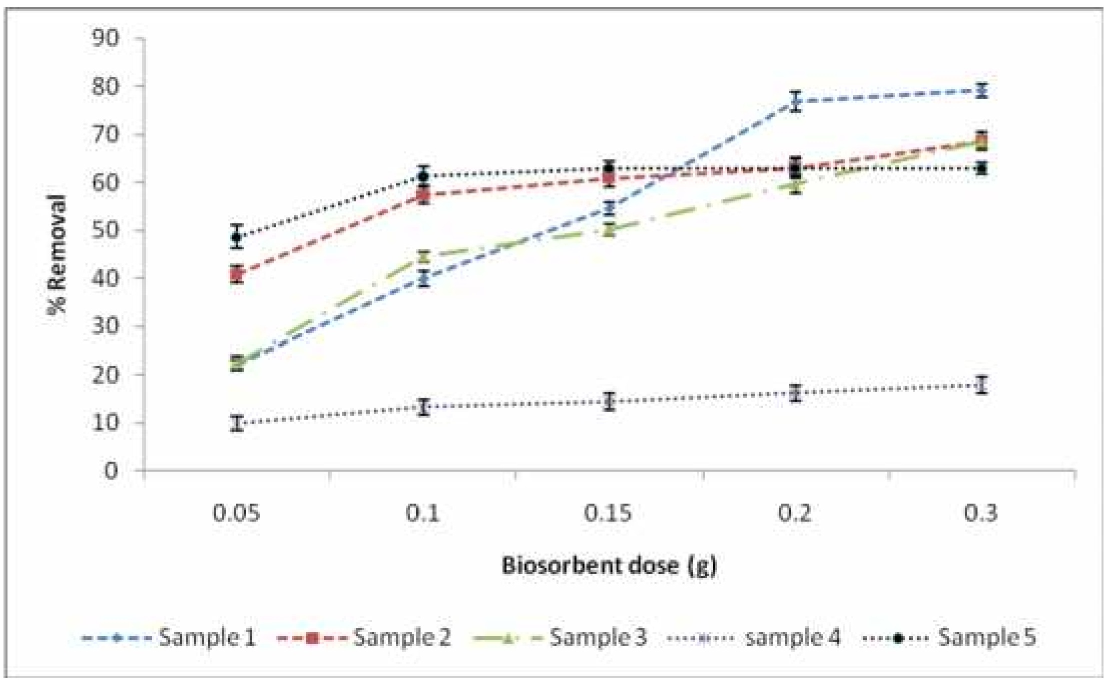


**Fig. 1: Effect of biosorbent dose on the adsorptive removal of dyes from different effluents**

**Effect of shaking speed:** The shaking speed is among one of the mass transfer parameters which influence the biosorption process. So the effect of shaking speed on the removal of dye containing wastewater was explored by changing the shaking speed from 70, 80, 90, 100, 110 and 120 rpm and the results are presented in Fig. 2. The results clearly demonstrate that by increasing the agitation speed, the biosorption of dyes from all the five samples increased. This fact can be explained as in actual the biosorption process depends on various stages which include (i) migration of adsorbate molecules from the bulk solution to the surface of the biosorbent; (ii) diffusion through the boundary layer to the surface of biosorbent; (iii) biosorption at a site; and (iv) intraparticle diffusion into the interior of the biosorbent. This is because with low agitation speed the greater contact time is required to attend the equilibrium. With increasing the agitation speed, the rate of diffusion of dye molecules from bulk liquid to the liquid boundary layer surrounding the particle become higher because of an enhancement of turbulence and a decrease of thickness of the liquid boundary layer (Patil *et al*., 2012).Al-Qodah, (2000) worked on the removal of dyes by using adsorption process onto shale oil ash and the results indicated increased adsorption at higher shaking speed.

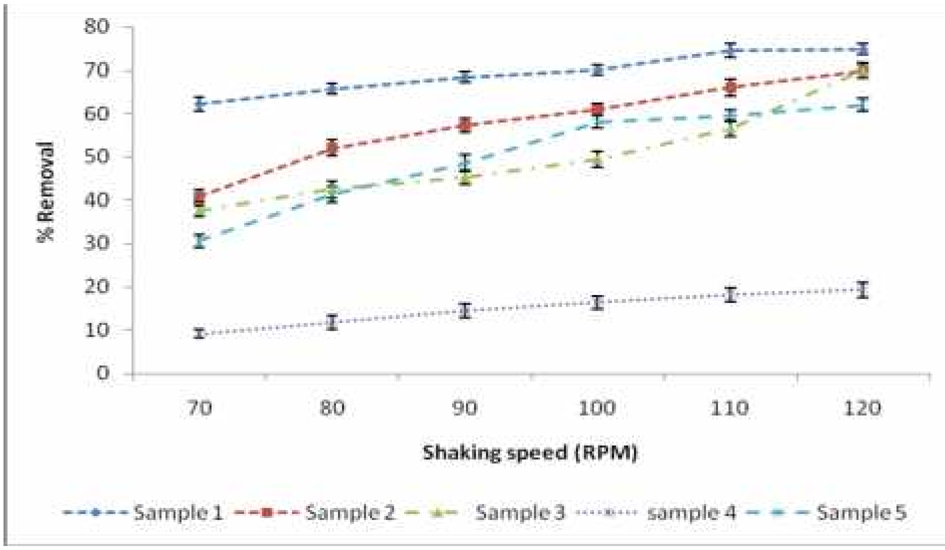


**Fig. 2. Effect of shaking speed on the adsorptive removal of dyes from different effluents**

**Effect of temperature:** Mostly the textile effluents are released at higher temperatures so temperature can be an important process parameter which affects the biosorption process. To check out the effect of temperature on the biosorption of dyes, the temperature was varied from 303-343 K and results are shown in Fig 3. The results depicted that with the increase in temperature biosorption efficiency of biosorbent declined. Higher dye removals were achieved at lower temperatures. All the five different textile wastewater samples showed the similar result. This fact can be explained due to the fact that in the process of biosorption, weak interaction forces (Van der Waals forces and hydrogen bonding) are involved and increase in temperature results in breakdown of adsorptive forces which result in decrease in dye removal at higher temperatures (Chatterjee *et al*., 2009). Asgher and Bhatti, (2012) also found a decrease in biosorption of dyes with the increase in temperature.

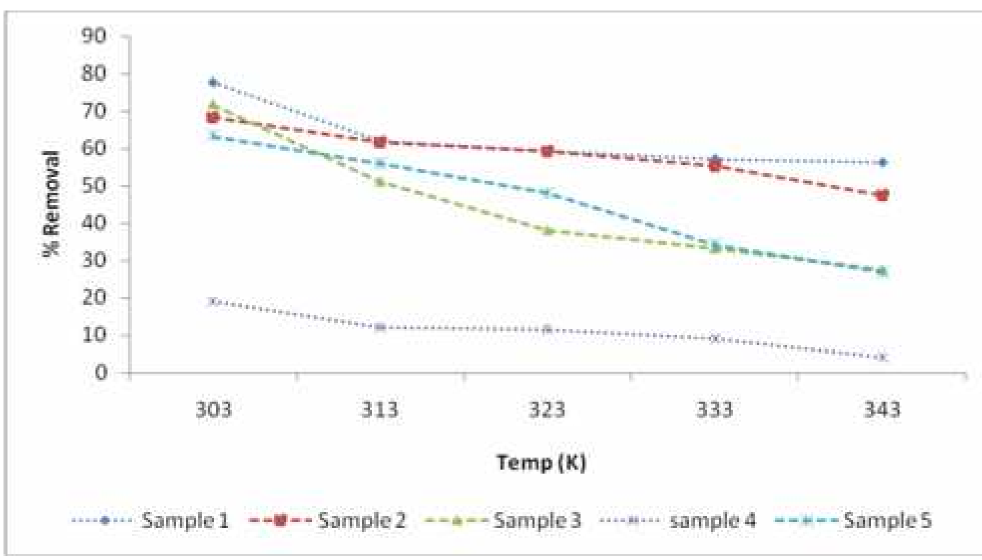


**Fig. 3. Effect of temperature on the adsorptive removal of dyes from different effluents**

**Thermodynamic study:** The thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) have a significant role to define the feasibility, spontaneity and heat change for the biosorption process. The thermodynamic parameters can be calculated using the following equations:

$$\Delta G^\circ - \Delta H^\circ \quad T\Delta S^\circ \qquad (2)$$

$$\Delta G^\circ = \quad RT ln K_d \qquad (3)$$

Where $K_d$=qe/Ce

R is the gas constant (8.314 J $mol^{-1}$ $K^{-1}$) and T is the absolute temperature. so it can also be written as

$$ln(K_d) = \frac{\Delta S^\circ}{R} \quad \frac{\Delta H^\circ}{R} \times \frac{1}{T}$$

The values of ΔG°, ΔH° and ΔS° are presented in Table 2. The magnitude of ΔG° gives an idea about the type of sorption. The results indicated that with the increase in temperature, the ΔG° values also increase which indicate the non-spontaneity of biosorption process at higher temperatures. The values of ΔH° are found to be negative for all the samples which prove that biosorption reaction was exothermic in nature.The biosorption process was also accompanied by decrease in entropy (negative entropy values). This behavior signifies the ordering of system as biosorption proceeds. Asgher and Bhatti, (2012) performed the thermodynamic study for the biosorption of reactive dyes using *Citrus sinensis*and reported that biosorption of reactive dyes onto citrus waste biomass was an exothermic reaction. Deniz and Saygideger, (2011) also worked on the biosorption of basic dyes by using princess tree leaf biomass and evaluated the thermodynamic parameters. They found the biosorption process exothermic in nature and reported the similar results.

**Table 2 Thermodynamic study for the biosorption process of different wastewater effluents**

| Sample No. | ΔH° (kJ $mol^{-1}$) | ΔS° ($JK^{-1}$ $mol^{-1}$) | ΔG°(kJ $mol^{-1}$) 303 K | 313 K | 323 K | 333 K | 343 K |
|---|---|---|---|---|---|---|---|
| **1** | -1.84 | -0.027 | 2.21 | 2.34 | 2.62 | 2.85 | 2.95 |
| **2** | -7.54 | -0.088 | 1.53 | 3.41 | 3.82 | 4.38 | 5.43 |
| **3** | -14.05 | -0.016 | 1.13 | 4.54 | 6.04 | 6.97 | 7.89 |
| **4** | -39.37 | 0.015 | 7.1 | 9.8 | 10.2 | 11.3 | 14.07 |
| **5** | -12.66 | -0.145 | 2.1 | 4.06 | 5.05 | 6.8 | 7.96 |

**Conclusion:** Sugarcane bagasse, corncobs and cotton stick biomass showed maximum removal efficiency for dyes from textile wastewater. Different parameters were optimized during the study and best removal was obtained with 0.03g $50mL^{-1}$ biomass dose at 30 °C with shaking speed of 120 rpm. Thermodynamic study showed exothermic nature of biosorption process. Agricultural wastes such as sugarcane bagasse, corncobs and cotton stick biomass could be used as best option for the treatment of textile effluents.

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