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International Journal of Current Research
Vol. 8, Issue, 05, pp.31324-31331, May, 2016

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

BIOSORPTION OF TEXTILE EFFLUENT USING SUGARCANE BAGASSE

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ARTICLE INFO

Article History:
Received 21st February, 2016
Received in revised form
14th March, 2016
Accepted 26th April, 2016
Published online 31st May, 2016

Key words:
Biosorption,
Sugarcane Bagasse,
Textile Effluent,
Structural Characterization.

ABSTRACT

The aim of the present study was to evaluate the effect of sugarcane bagasse adsorption capacity for textile effluent. The adsorption process was investigated in a batch mode of operation under the optimize condition of amount of adsorbent, initial concentration of dye, contact time, pH, and temperature on textile effluent. The dried sugarcane bagasse sorbent was ground and sieved into 150µm size. Further investigation of the sorption process was done using the FTIR, SEM analysis. The experiment showed that the high removal percentage at PH 6, temperature 35º C with a retention time of 100 minutes. The optimum dose amount of adsorbent was 0.3g/ ml. The results obtained in this work indicated that the potential use of sugarcane bagasse as a biosorbent is feasible method for the treatment of textile effluent.

Citation: Vigneshpriya, D. and Shanthi, E. 2016. "Biosorption of textile effluent using sugarcane bagasse", *International Journal of Current Research*, 8, (05), 31324-31331.

INTRODUCTION

Water is one of the most valuable resources on planet earth. It is the lifeline of almost all living things on earth. Although this fact is widely recognized, pollution of water resources is a common occurrence. Textile industry is one of the biggest and most established commercial industry which exhibit all around, expending 80-200m^3 of water for every ton of product and discharges 1,650m^3 of waste water every day (Gereffi, G (2002)., Ranganathan *et al.,* 2007 and Gruwez *et al.,* 1999) and it is a high consumer of water mainly as process water (90-94 %), and cooling water (6–10 %), become finally loaded with different pollutants, dyes, surfactants, acids or bases, salts, heavy metals, and suspended solids (Zaharia and Suteu 2012). Textile fabric manufacturing uses mixtures of dyes with various additives including solvents, antifoaming, whitening agents and pH conditioners. The waste water thrown out from industries is either used for irrigation purposes or it runs off into natural sources of water (Ahlawat and Kumar, 2009). In recent years, the colour of the effluent discharged into receiving water has become a serious environmental problem.

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The colour is aesthetically objectionable and it also reduces light penetration into water decreasing the efficiency of photosynthesis in aquatic plants, thereby, having adverse impact on their growth (Bhattacharya and Sarma, 1997). In addition, some of the dyes might be toxic to some organisms. Besides, being unaesthetic, these effluents are mutagenic, carcinogenic and toxic (Chung *et al.,* 1992). The carcinogenic and mutagenic nature of synthetic dyes cause many harmful effects on human beings such as kidney dysfunctions, damage to the reproductive system, central nervous system, liver and brain (Shen *et al.,* 2009). Uptake of textile effluents through food chain in aquatic organisms may cause various physiological disorders like hypertension, sporadic fever, renal damage and cramps (Karthikeyan *et al.,* 2006). Hence colour elimination in waste water is the principal problem concerning the textile industries since it is the first contaminant recognized in textile waste water and has to be removed before being discharged into the receiving water bodies. Conventional water treatment methods like ion exchange, reverse osmosis, electrodialysis, ultra filtration and chemical precipitation (Marungrueng and Pavasant 2007) can be used to remove dye from wastewater. However, these methods are not economically feasible and also are not effective for complete removal of dye. It is reported that the adsorption techniques are more efficient than other physical and chemical treatments

(Crini, 2006). With the search for new technologies involving the removal of toxic solute particles from wastewater, adsorption has emerged as an efficient and cost-effective alternative to the conventional water treatment facilities. Adsorption is defined as a process by which separation of desired components is effected by contacting a liquid or vapor, and biosorption is the property of certain inactive, dead, microbial, or natural biomass to adsorb or bind solute particles (heavy metals or dye or contaminants mainly from industrial effluents) (McCabe *et al*, 2005). For the efficient application of adsorption process, the importance should not only be given to its low cost, but prime importance should be given to the selection of adsorbents with high adsorption capacity, stability and easy availability (Crini, 2006). It can also remove certain pollutants that are not easily biodegradable. Therefore, biological treatment may be a good alternative when compared with most physical and chemical technologies.

Adsorption by activated carbons prepared from biomass has been widely used for the industrial effluent treatment (Kaushik and Thakur, 2012). Since activated carbons have extended surface area, complex porous structures and high surface reactivity, it is being used as adsorbent for the removal of a wide range of pollutants dissolved in aqueous solutions (Wang *et al.,* 2007). However, the regeneration and reuse of activated carbon is not economically feasible for large scale owing to its high cost (Gupta and Ali, 2008). Low cost adsorbents are becoming the focus of many researches. These adsorbents could be produced from many raw materials such as agriculture and industrial waste (Gupta and Rastogi, 2008). A number of non-conventional low cost adsorbents used for dye removal include fruit waste, wood, waste orange peel, banana pith, maize cobs, barley husk and bagasse pith. Utilization of agricultural waste as low cost adsorbent has great significance in India where more than 200 million tonnes of agricultural residues are generated annually (Reddy, 2013). Throughout the world, much research is being conducted on the use of waste materials in order to either avert an increasing toxic threat to the environment or to streamline present waste disposal techniques by making them more affordable.

Sorption on biomaterials has been mainly attributed to the functional groups on the cell wall, which consist of various chemical groups, such as carboxyl, hydroxyl, amino and phosphate (Celekli *et al*. 2009). Each agricultural product has distinctive cell wall properties and has been proven to be effective adsorbent for the treatment of wastewater. Among the different low-cost materials, sugarcane bagasse is proven to be an efficient biosorbent for the removal of pollutants from aqueous solutions. The growth rate of the sugar cane plant is remarkably efficient. The high annual production and nature of sugarcane bagasse has increased its attractiveness for the remedy of environmental pollution in different ways (Ritter, 2007 and Arnaud, 2008). The high biosorption capacity of sugarcane bagasse is due to the presence of macromolecules in its structure along with humic and fulvic substances, cellulose, hemicelluloses, lignin, and proteins that have carbonyl, carboxylic, amine, and hydroxyl functional groups, which show the capacity to adsorb dye molecules by the ion-exchange phenomena or by complexation (Jimenez *et al*. 2005).

Keeping in view the significance of dyes and their environmental problems, the current study was undertaken with the following objectives. 1. To explore the biosorption potential of sugarcane bagasse for the removal of dyes/ pollution load from textile effluent. 2. To optimize the various parameters influencing the sorption capacity of sugarcane bagasse such as pH, temperature, contact time and adsorption dose. 3. Structural characterization of the sugarcane bagasse (FTIR and SEM).

MATERIALS AND METHODS

Preparation of biosorbent

Sugarcane bagasse after the extraction of sugarcane juice were collected from road side vendors and used as an adsorbent for textile dye removal. The collected sugarcane bagasse was washed several times to remove dust. It was then boiled in water for one hour to remove the sugar residue and rinsed several times with distilled water. The cleaned bagasse was sun dried until all the moisture evaporated. It was cut into small pieces and ground to a fine powder in an electric grinder. The powder was sieved through a mesh to get fine particles of size 150µm. The material was placed in an airtight container for further use.

Adsorbate Preparation

The effluent was collected from a small scale dyeing unit at Rayanur of Karur district, Tamilnadu. Karur is famous worldwide for its handloom textile products. Concerning its industrial location, it is one of the developing cities in Tamilnadu and textile industries are its dominating industries. The samples were collected in precleaned 5L polythene bottles from the point of discharge of the effluent from the industry and preserved in a refrigerator at 4ºC till the completion of the investigation.

Batch adsorption studies

The batch adsorption experiments were conducted to optimize the various operational parameters namely initial pH, temperature, contact time and adsorbent dose to obtain optimum colour removal from the effluent. Batch studies were conducted with fixed amounts (0.1 to 0.6g) of adsorbents which were shaken separately in a rotary orbital shaker at 150rpm in 100ml of the diluted effluent of 50% concentration at different temperatures (25,30,35,40 and 45ºC) and pH (3-10) for definite time periods (20,40,60,80,100,120 and 140 minutes). The pH was adjusted using dilute NaOH and HCl solutions. At the end of the predetermined time intervals, samples were withdrawn from the shaker and the adsorbents were separated from the solution in a centrifuge for a period of 5 minutes. The absorbance of the supernatant solution was read in a colorimeter at 340nm to estimate the final dye concentration. All experiments were carried out thrice with respect to each condition and the average values were obtained.

Colour removal efficiency was computed with the following formula:

$$\text{Removal efficiency (\%)} = \left[\frac{c_i - c_f}{c_i}\right] \times 100$$

Where c_i and c_f are the initial and final concentration of textile effluent in mg/l.

Structural characterization of the sugarcane bagasse

The structural characterization of the sugarcane bagasse was done by SEM and FTIR analysis.

RESULTS AND DISCUSSION

Effect of adsorbent dose

The effect of bisorbent dose (0.1-0.6g) on the biosorption of dyes in effluent by sugarcane bagasee was presented Figure 1. Biosorbent dose plays a very important role in the process of biosorption.

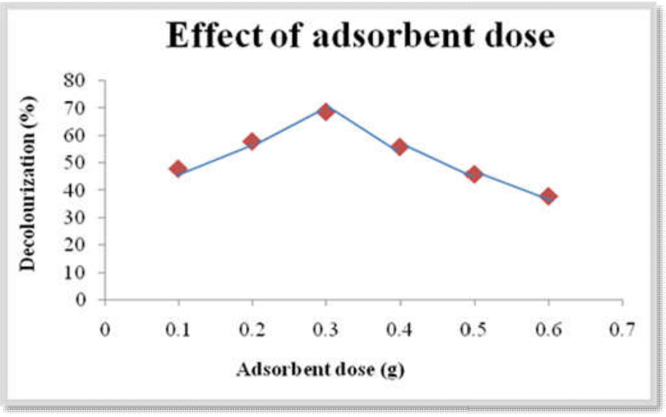


Fig.1. Effect of adsorbent dose on textile dye adsorption

The dye biosorption capacity decreased at higher biosorbent doses due to the aggregation of the biomass which results in the decrease in active sites on the surface of biosorbent available for the attachment of dye molecules. Another important factor is that at high biosorbent dose, the available dye molecules are insufficient to completely cover the available binding sites on the biosorbent, which usually results in low solute uptake (Tangaromsuk *et al.,* 2002). The maximum dye removal was observed at 0.3g (68.8%) biosorbent dose. When the biosorbent dose was further increased from 0.3 to 0.6 there was decrease in the biosorption capacity of biosorbent. At the adsorption dose of 0.6g, the per cent dye removal was 38. Adsorption efficiency decreased with increase in the biosorbent dose. The results were in accordance with the observations made by Durairaj and Durairaj (2012). They reported an optimum adsorbent dosage for maximum colour removal as 0.3g for neem leaf, orange peels, peanut hulls and coconut coir pith powders. Said *et al.* (2012) also quoted a similar adsorbent dose for sugarcane bagasse for maximum colour removal, while observing the removal of the methylene blue dye in comparison with orange II in the presence of 0.2 g adsorbent and stated that the efficient removal of methylene blue may be due to the fact that the number of available sites on the raw sugarcane bagasse modified with propionic acid (RBMPA) is active towards the adsorption of methylene blue. The removal of dye with increasing amount of bioadsorbent dose is explained by the increase in the attachment sites for the dye molecules (Mane *et al.* 2007). The decrease in removal efficiency after certain amount of biosorbent can be explained by clump formation between the particles leading to less exposure of adsorption sites for attachment (Royer *et al.,* 2009).

Effect of pH

The effect of pH on textile dye adsorption on sugarcane bagasse was presented in Figure 2. The effect of pH was studied by varying the pH from 3.00 to 10.00. At pH 3.0 the minimum adsorption of 25.00% was observed. With further increase in pH, a gradual increase in adsorption was observed, with 36.00% at pH 4.00 and 49.08% at pH 5.00, which recorded a maximum of 64.40 at pH 6.00. pH 7.00 recorded a slight decrease in adsorption (62.00). Above pH 7 the adsorption percentage was gradually decreased and recorded 45.00% at pH 10.00. The above results indicate that the dye adsorption considerably increased when pH was raised from 3.00 to 6.00. At pH 3.00, per cent dye removal was very low which increased as pH was raised to 6.00. Slightly acidic pH favours dye adsorption. Similar observation was reported by Ashoka and Inamdar (2010) and they stated that the adsorption efficiency was greatly affected by pH variation and for formaldehyde treated bagasse the dye adsorption considerably increased as pH was varied from 2 to 6. Sayed *et al.* (2013) also reported that the dye adsorbed by sugarcane stalks was lower at lower pH and the maximum was attained at pH values higher than 4.5 indicating optimum pH as slightly acidic or neutral.

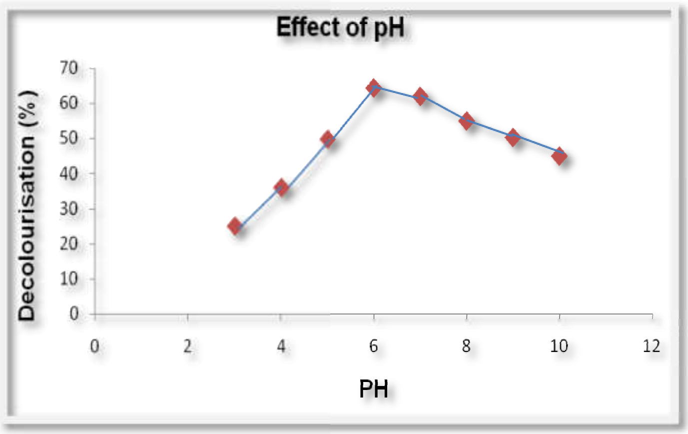


Fig. 2. Effect of pH on textile dye adsorption

Similarly for the sulphuric acid treated bagasse the dyes adsorption significantly change over the pH value of 4 to 7 (Azhar *et al.,* 2005). Several reasons may be attributed to dye adsorption behavior of the adsorbent relative to solution pH. The electrostatic attraction as well as the organic properties of the adsorbent and structure of dye molecules could play important roles in dye adsorption. Adsorbent's surface is positively charged at acidic pH. This causes competition between protons and dye cations for adsorption locations. Under acidic condition the dye uptake for acidic dye (anionic dye) is higher as compared to the basic and neutral conditions. When pH is raised a negative charge is present on the surface of the adsorbents causing better dye cation adsorption through electrostatic attraction. A negatively charged site on the adsorbent does not favour the adsorption of anionic dye molecules due to electrostatic repulsion (Chiou, 2002; Hamdaoui, 2006; Thinakaran *et al.,* 2008).

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 (Mittal, 2006, Zaheer *et al.,* 2014). Thus the pH value of the solution is an important process controlling parameter in the adsorption of dye. The initial pH values of the dye solutions affect the surface charge of the adsorbent and thus the adsorption of charged dye groups on it. At an acidic pH condition, the hydroxyl and carboxyl groups on the surface of sugarcane bagasse are protonated and they inhibit the binding of the dye cation and promote the binding of dye anion. With an increasing pH of the dye solution, the surface groups will be deprotonated resulting in an increase of negatively charged sites that favour sorption of the cationic dye. In the present study, slightly acidic condition (pH 6) favours dyes adsorption from the textile effluent. Therefore, it is suggested that the optimum pH for the removal of different dyes is around 6.00.

Effect of temperature

The effect of temperature on dye biosorption was presented in Figure 3. The effect of temperature was studied in the range from 25°C to 45°C. The percentage of dye removal was increased from 28.57 to 48.28 for the rise in temperature from 25°C to 35°C. Further increase in temperature from 35°C to 45°C could not increase dye removal, rather a decrease was observed from 48.28 % to 44.06 %. Therefore, the maximum removal of dye from effluent was achieved at 35°C. This was achieved because as temperature increase from 25°C to 35°C, a slight increase in surface area of the adsorbent could be possible but further increase in temperature could result in the loss of active surface area resulting from prolonged exposure to high temperatures. Hence, the adsorption was slow at high temperatures. The optimum temperature was 35°C at which the adsorption was very effective and the present study shows the exothermic nature of adsorption.

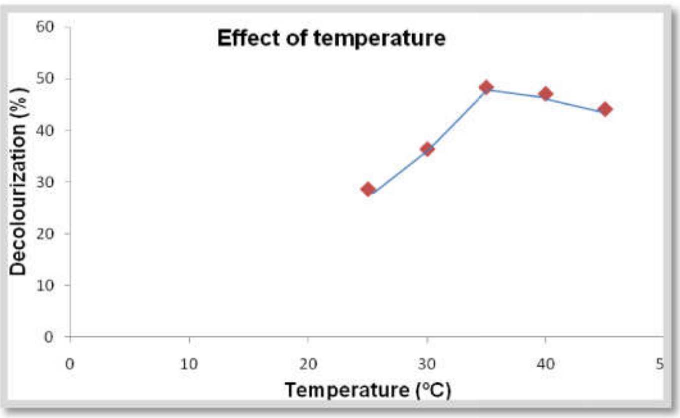


Fig. 3. Effect of temperature on textile dye adsorption

The results of the present investigation are in accordance with Carpenter *et al*. (2013) who observed that the optimum temperature was 35°C at which the adsorption was very effective and stated that the study was exothermic in nature. Madhav *et al*. (2013) also reported highest efficiency of biosorption at 30ºC with decrease in biosorption beyond 30ºC. This increase in adsorption may be due to increase in number of adsorption sites caused by breaking of some of the internal bonds near the edge of the active surface sites of the adsorbents as suggested by Kanawade and Gaikwad (2011). According to Durairaj and Durairaj (2012) increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles owing to the decrease in the viscosity of the solution. An increased number of molecules may acquire sufficient energy to undergo an interaction with active sites at the surface.

The decrease in biosorption of dyes at high temperatures may be due to the weakening of adsorptive forces responsible for the adsorption of dye molecules on the surface of biosorbents. This can also be due to the fact that deactivation of biosorbent active sites takes place, which leads to the decreased biosorption at higher temperatures (Asgher and Bhatti, 2012). Thus temperature is one of the most important controlling parameter in adsorption. Adsorption is normally exothermic in nature and the rate of adsorption in most cases decreases with increase in temperature of the system. Some of the adsorption studies show increased adsorption with increasing temperature and found to be an example of endothermic adsorption.

Effect of contact time

The effect of temperature on dye biosorption was presented in Figure 4. The effect of contact time on colour removal was observed from 20 to 140 minutes and the result was presented in table 4 and figure 8. From the figure, the plot reveals that the uptake of dye was rapid in the first 60 minutes and after 120 minutes the amount of dye removal was almost constant.

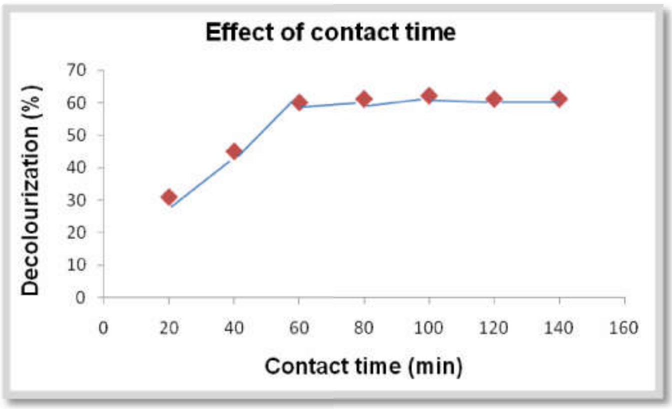
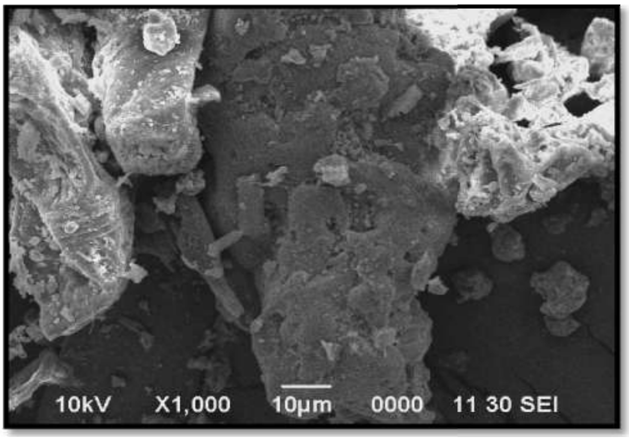


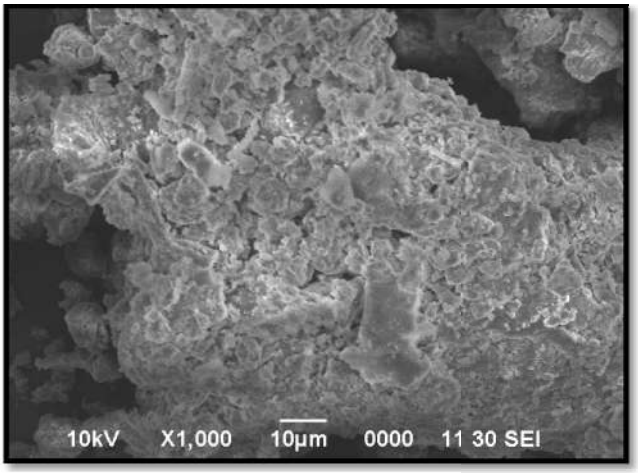
Fig.4. Effect of contact time on textile dye adsorption

The curve on contact time was found to be smooth and continuous leading to saturation indicating monolayer coverage of dye on adsorbent surface. Sorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. In the later stage, the sorption is likely an attachment controlled process due to less available sorption sites. Similar results have been reported in literature for adsorption of Malachite green dye over sea shell powder

(Chowdhury and Saha, 2010). At the beginning the dye is adsorbed by the exterior surface of the adsorbent and the adsorption rate is fast. When the exterior adsorption surface saturate the dye enters into the pores of the adsorbent and is adsorbed by the interior surface of the particles. The first rapid uptake can be rationalized as a rapid attachment of dyes to the biosorbent surface or due to the large number of vacant sites available at the initial stage. In the process of dye adsorption, the dye molecules have to first encounter the boundary layer effect, then adsorbed from the surface and, finally, they have to diffuse into the porous structure of the adsorbent (Malik, 2003).



a. Before adsorption



b. After adsorption

Fig. 5. SEM photographs of sugarcane bagasse

Kavitha and Namasivayam (2007) explained that the initial rapid phase may be due to the increased number of vacant sites available at the initial stage. Consequently there exists an increased concentration gradient between the adsorbate in solution and the adsorbate in the adsorbent. Bansal *et al*. (2009) described that initially for adsorption, large number of vacant sites are available, which slowed down later due to exhaustion of remaining surface sites and repulsive force between surface molecules and bulk phase. Similar observations of rapid rise, gradual increase and constant phase were reported by earlier investigators. Dezhampanah *et al*. (2014) reported that the high rate of adsorption onto sugarcane bagasse occurred within the first 20 minutes of the process and the equilibrium state was reached after 80min. Said *et al*. (2013) stated that the uptake of dyes was rapid in the first 20 minutes and after 75 minutes the amount of dyes removal was almost constant. It was reported that the optimum contact time for colour removal was 75 minutes for neem leaf, orange peels, peanut hulls and coconut coir pith (Sivakumar and Shankar, 2012). The equilibrium time for the removal of the dye was 90 minutes for immobilized form of biosorbent (Zaheer *et al.,* 2014).

The adsorption of dye was faster and attained the equilibrium after 60 minutes (Said *et al.,* 2012). Aksu and Isoglu (2006) reported that a contact time ranging from 2-4 hours was sufficient to achieve equilibrium for the removal of direct dye by waste sugar beet pulp. Thus the contact time between dyes and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of dyes and establishment of equilibrium in short period signifies the efficiency of the adsorbent for its use in wastewater treatment. From the optimization studies it may be concluded that the most efficient operational parameters in the current study were found to be; pH of 6, temperature of 35ºC, contact time of 100 minutes and adsorbent dose of 0.3g for the treatment of textile effluent of 50% dilution using sugarcane bagasse as an adsorbent.

Structural Characterization of Biomass

Sem Analysis

The surface features and morphological characteristics of the biosorbent were studied using SEM analysis. The study was useful in determining the particle shape and porous structure of the sugarcane biomass.

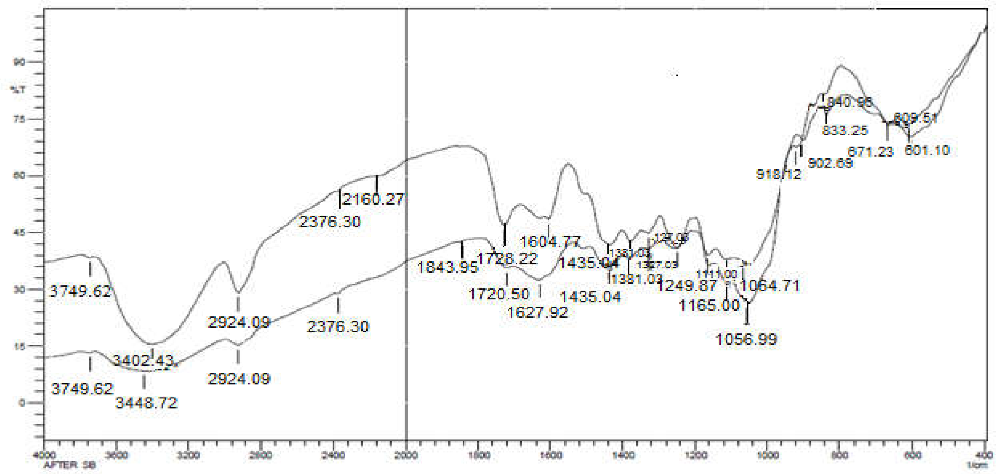


Fig.6. FT-IR spectra of sugarcane bagasse particles before and after adsorption

SEM micrographs of the free sugarcane biomass and textile dye loaded biomass in 1000X magnification are presented in Fig. 5-a and 5-b respectively. The photographs indicate the porous and fibrous texture of the biosorbent with high heterogeneity that could contribute to the biosorption of the dyes. The presence of macropores in sugarcane bagasse was demonstrated by Ribeiro *et al.,* 2001. It was suggested by Guo *et al.,* 2008, Tseng *et al.,* 2003 that the adsorbents with micropores have high surface area in contrast to macropores and are more efficient in adsorption process. This indicates the relative disadvantage of the physical nature of the sugarcane bagasse. However, it was observed that some adsorbents which have low surface area and macropores, are also capable of interacting with pollutants in an aqueous medium (Yurtsever and Sengil, 2009; Ribeiro *et al.,* 2011). These interactions occur due to the presence of chemical groups of the adsorbents and not only to the deposition of the pollutants molecules on pores. These functional groups bind with the pollutants through hydrogen bond, electrostatic, hydrophobic and Van der walls interactions.

FT-IR Analysis

Each adsorbent has different binding capacity for each dye molecules. Adsorption capacity is not only affected by the textural or porous structure of adsorbents but also strongly influenced by the chemical structures of the surface. The cell surface consist of various polysaccharides, proteins, and lipid containing various functional groups such as amino, hydroxyl, carboxyl, carbonyl, sulphonate, sulfhydryl, and phosphate, which can act as binding sites for dye molecules. FT-IR spectra of sugarcane bagasse particles before and after adsorption of textile dyes in the effluent were analyzed to determine the vibration frequency changes in their functional groups within the range of 4000 to 500 cm-1. Sugarcane bagasse particle is a lingocellulosic compound and is generally considered as structures built by cellulose molecules, organized in microfibrils and surrounded by hemicellulosic materials, lignin and pectin along with small amounts of protein (Asheh *et al.,* 1997). According to Meza *et al*. (2006), cellulose, hemicelluloses and lignin contents occur in varying proportions depending on soil properties and plant's development stage.

The absorbance at 3749.62, 3402.43, 2924.09, 2376.30, 1728.22, 1604.77, 1435.04, 1381.03, 1327.03, 1249.87, 1056.99, 918.12, 840.96 and 601.73 cm-1 are seen in the spectrum of sugarcane bagasse particles before adsorption (Fig. 11a). The major peaks are at 3402.43, 2924.09, 1728.22, 1249.87 and 1056.99 cm-1. The peak at 3402.43 cm-1 indicates the presence of free and intermolecular bonded hydroxyl (-OH) of cellulose, hemicellulose and pectin (Kannan and Sundaram, 2001). The peak at 2924.09 cm-1 indicates the occurrence of CH3. The peak at 1728.22 cm-1 reveals the existence of C=O from esters probably of lignin and hemicellulose (Brigida *et al.,* 2010). The peak at 1249.87 cm-1 is due to C-O stretching. The peak at 1056.99 cm-1 shows the tertiary amine (-C-N stretch) and alkyl substituted ether (C-O) stretch (Coates, 2000) due to the presence of cellulose, hemicellulose and lignin (Sun *et al*., 2001). The following vibration frequency changes were observed in the spectrum after dye adsorption. (Fig.11b) shows 1. Peak shift from 3402.43 cm-1 to a greater frequency of 3448.22 cm-1. 2. Peak reduction at 2924.09 cm-1. 3. Peak reduction and peak shift from 1728.22 cm-1 to a lower frequency of 1720.20 cm-1. 4. Peak reduction at 1249.87 cm-1. 5. Peak shift from 1056.99 cm-1 to a greater frequency of 1064.71 cm-1. Shifts in band position to either lower or higher frequency and change in shape or band intensity indicate the involvement of functional groups in biosorption (Sharma and Nandi, 2013). In the present study major functional groups involved in biosorption process were found to be hydroxyl, methyl, carbonyl and amine groups. Thus the complexation interactions are the main driving force for adsorption and represent the chemical adsorption mechanism.

Conclusion

In the present study, sugarcane bagasse material generated in the sugar industry was used successfully, as a low cost and effective adsorbing surface for the removal of dyes and pollution load from textile effluent which could be used for textile waste water treatment at industrial scale. From the study it could be concluded that the studied textile effluent has high pollution potential and warrants an urgent need to follow adequate effluent treatment methods before discharge into surface water for reducing potential environmental hazards. It is also evident that the sugarcane bagasse as an adsorbent may provide a promising approach towards textile waste water treatment.

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