

# Effect of Ph on Decolorization of Azo Dyes by Corn Cob Residues

Anmoljit Kour Sodhi, Gurinder Singh, RitulJayara and Ajay Kumar\*

School of Bioengineering and Biosciences, Lovely Professional University, Phagwara, Punjab 144411, India

\*Corresponding Author E-mail: [kumarajaybiotech@gmail.com](mailto:kumarajaybiotech@gmail.com)

## Abstract

All the toxic dyes that are released into the water bodies should be treated before releasing them as it has various harmful effects on humans as well as the aquatic life. In the present study absorbent used is easily available waste corn cob, that has been used to remove dyes from water. The corncob used was treated with NaOH and its adsorption of dye (malachite green) was tested at different pH range (2-9) and same was done with untreated corncob, the dyes used were malachite green, Congo red. The dyes used in the study are azo dyes. pH is one of the most important parameters around which the study revolves. Standard solution of both Congo red and malachite green was prepared. The concentration for Congo red was 20 mg/L and the concentration for malachite green was 20 mg/L. Moreover, the experiment performed was in the form of batch and various parameters such as contact time and pH were evaluated. Characterization of both untreated corncob as well as NaOH treated corncob was done using Fourier transform infrared (FTIR) and Scanning electron microscopy (SEM). It was noted that as the pH shifted from acidic to basic the percentage removal i.e. the amount of dye removed increased.

**Keywords:** toxic dyes, concentration, adsorption, Congo red, malachite green.

## Introduction

Pollution is the presence of any unwanted substance into a natural environment that may lead to adverse effects and changes. Pollution is of different type like water pollution, noise pollution, air pollution, soil pollution. Water pollution is the spoliation of water bodies due to human liveliness; the textile and dyeing industry is the major manufacturer of synthetic dyes producing thousands of different chemical dyes. small volume of these dyes can affect water bodies in dreadful ways because of the presence of harmful characteristics they can affect the visibility and stop sunlight from passing inside the water, it is not environment friendly because of its toxic nature [4], this polluted water can be carcinogenic[17]. Malachite green comes in the category of azo dye. It has various destructive features which unhealthy for humans as well as aquatic fauna. It also causes focal necrosis in liver, damages mitochondria and causes nuclear alterations. Removal of these dyes from the water Is a big provocation. The food chain is also affected by these contaminations which indirectly cause harm to human's other harmful effects include, increased heart rate, vomiting, jaundice, diarrhea, and tissue necrosis [1]. In this "Pollutant Removal Age," many technological developments have been made to reduce contaminant outflow into the environment [10]. Dyes usually have complex aromatic molecular structures due to the reason they are firmer and are difficult to degrade, many types of dye that are being used in the textile industries are direct, reactive, acid and basic dyes. Numerous dyes that are being used at industrial level are

carcinogenic and toxic because of which many methods and techniques that are used for taking out of the dyes from effluent and to minimize the amount of pollutants, such as membrane filtration, ion-exchange, precipitation, reverse osmosis, evaporation, adsorption, coagulation-flocculation, liquid-liquid extraction, electrolytic recovery, etc.[13]. However, most of the methods that are being used are expensive. Therefore, it is necessary to generate an ultra-efficient environmentally safe method for the taking out dyes from industrial effluent [12].

Physical treatment like adsorption is a very convenient method for taking out harmful compounds from effluent, if the adsorbents are easily accessible and commercial [19]. Some of the biomasses commonly used are, Coconut shell fiber [2], olive fruit residue [5], bagasse [14], rice bran [9], hazelnut shell [3], and neem leaf [16].

Several studies are carried out on the activated carbon from many low-price sources like coconut husk, coconut shell, bamboo ash etc. for taking out toxic level of water [4]. In this study we are using corncob as adsorbent for taking out azo dyes from the effluent.

Agricultural wastes come into notice for adsorption of dyes from damp solution. Several agricultural wastes show finest performance, as they are inexpensive, they are present in huge quantity naturally, highly accessible, nature friendly[11].

Over the past few years research centers are looking for low cost adsorbents, for the adsorption method to take place properly choosing of proper adsorbent is the key. Corncob is easily available material with no cost. Corn is a major crop many-sided over the globe. Annually corn is produced about  $520 \times 10^9$  kg [18]. Nowadays, corn is second most ample crop globally [6-7] and is anticipated to exceed both wheat and rice to become the number one grain at global scale by 2020 [20] Corncob is a waste from the corn field or different industries dealing with corn. Cobs is the integral hard, thick, central core of maize. They are made up of 44–45% cellulose, 31–40% hemicellulose, and 8–15% lignin [21]. This waste can be utilized for adsorption of various dyes from the waste water. This study is focused to test its effectiveness for taking out of azo dyes such as Congo red from the aqueous solution [8], also, the effect of pH, temperature, rpm on the absorbance of the dye from the aqueous solution was also looked over. In the present workchecks the potential of corncob in taking out Congo red from the aqueous solution, the dye is brownish red in color [8].

## **Material and methodology**

The corn cob used in the research is collected from a private agriculture field of district Kangra of state Himachal Pradesh, India, the corn cob used was dried and then grinded. The dyes used in the study are azo dyes (Congo red and Malachite green).

### **Preparation of dye solution**

The methylene blue and Congo red dye used in this study was prepared in the form stock solution of 20mg/l. The experiment was carried in the form of triplets.

### **Preparation of malachite green and NaOH treated corncob**

30 gm of corn cob was taken and dried under sunlight for 5-7 days. It was mixed with 300 mL of  $0.5 \text{ mol L}^{-1}$  NaOH and was kept in orbital shaker for 30 mins. The treated sample was exposed to 4 % (v/v) acetic acid in order to remove excess base, proceeded by washing with distilled water until the neutral pH was achieved. As the pH became neutral all the excess water was removed by keeping it in hot air oven at  $100^\circ\text{C}$  for 1 hour [15]. The dye solution of

malachite green was also prepared using 20 mg of dye in 1000ml of distilled water. The samples were taken in the form of triplets and the pH was set ranging between (2-9). The amount of corn cob (adsorbent) was taken 1gm in 50 ml of the solution. The following graphs represent the relation between percent removal and contact time, the experiments were carried using the NaOH treated corn cob.

**Batch adsorption studies**

The batch experiment for Congo red and malachite green was conducted by mixing 2mg of the dye in 50 ml of water in the blue cap bottles, with the measured amount of corn cob poured in them samples were set at different pH and were put in the shaker, the rpm of the shaker was set at 100, for one hour. The range of the pH was set between (2-9) sampling of the samples with different pH was done after every hour and this was repeated for four hours. The pH was maintained with the help the hydrochloric acid and sodium hydroxide solution of 1M. The mixture was sieved and the filtrate was analyzed for its dye content using spectrophotometer.

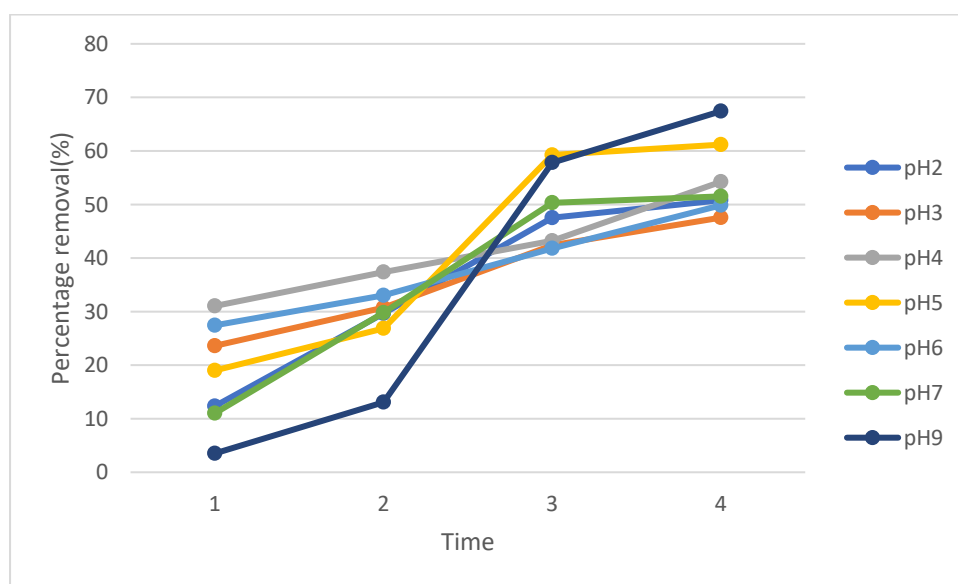
The dye adsorbed was calculated by using equation 1.

$$Q_e = \frac{C_0 - C_e}{C_0} \times \frac{V}{m} \text{----- (1)}$$

where C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium adsorbate concentrations(mg/L) , V is the volume of adsorbate(L) , and m is the mass of adsorbent(g).

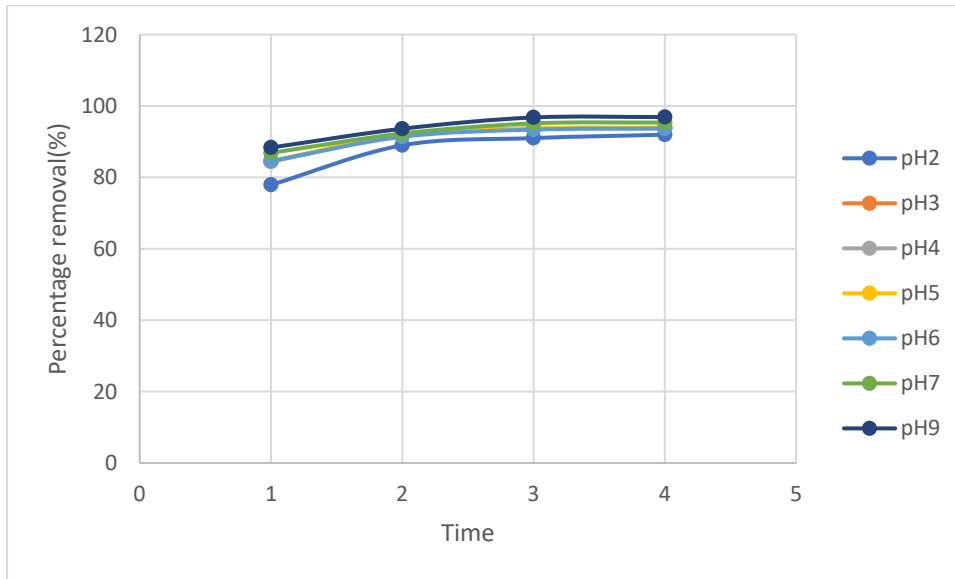
**Result and discussion**

**Graphical analysis**



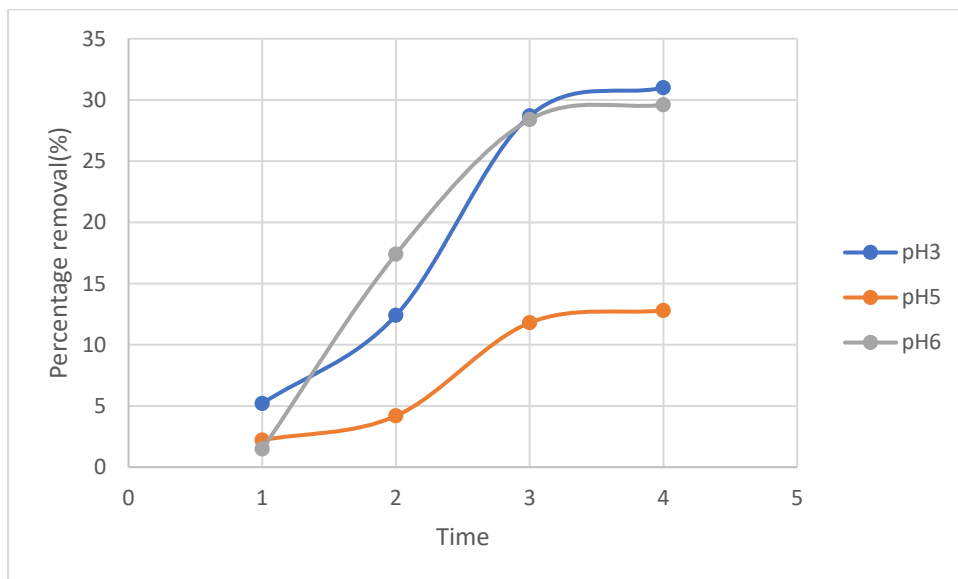
**Fig 1.1: plot between time and percentage removal for raw corn cob and malachite green**

The graph shows percentage removal of different Ph (1,2,3,4,5,6,7,9). As the fig 1.1 shows that as the time times and pH changes to basic from acidic there is increment in the percentage removal.eg., for pH2 the percentage removal after one hour is 12.35after two hours the percentage removal changes to 29.65 after three hours it is 47.53 and after 4 hours it increases to 50.53.In such way the percentage removal for all the Ph increases.



**Fig 1.2: plot between time and percentage removal for NaOH corn cob and malachite green.**

The graph shows percentage removal of different Ph (1,2,3,4,5,6,7,9). As the fig 1.2 shows that as the time times and pH changes to basic from acidic there is increment in the percentage removal.eg., for pH2 the percentage removal after one hour is 77.9,after two hours the percentage removal changes to 88.99, after three hours it is 91.01 and after 4 hours it increases to 91.96.on comparing the percentage removal of raw corn cob with NaOH corn cob we can see increases in percentage removal for NaOH treated corn cobs.



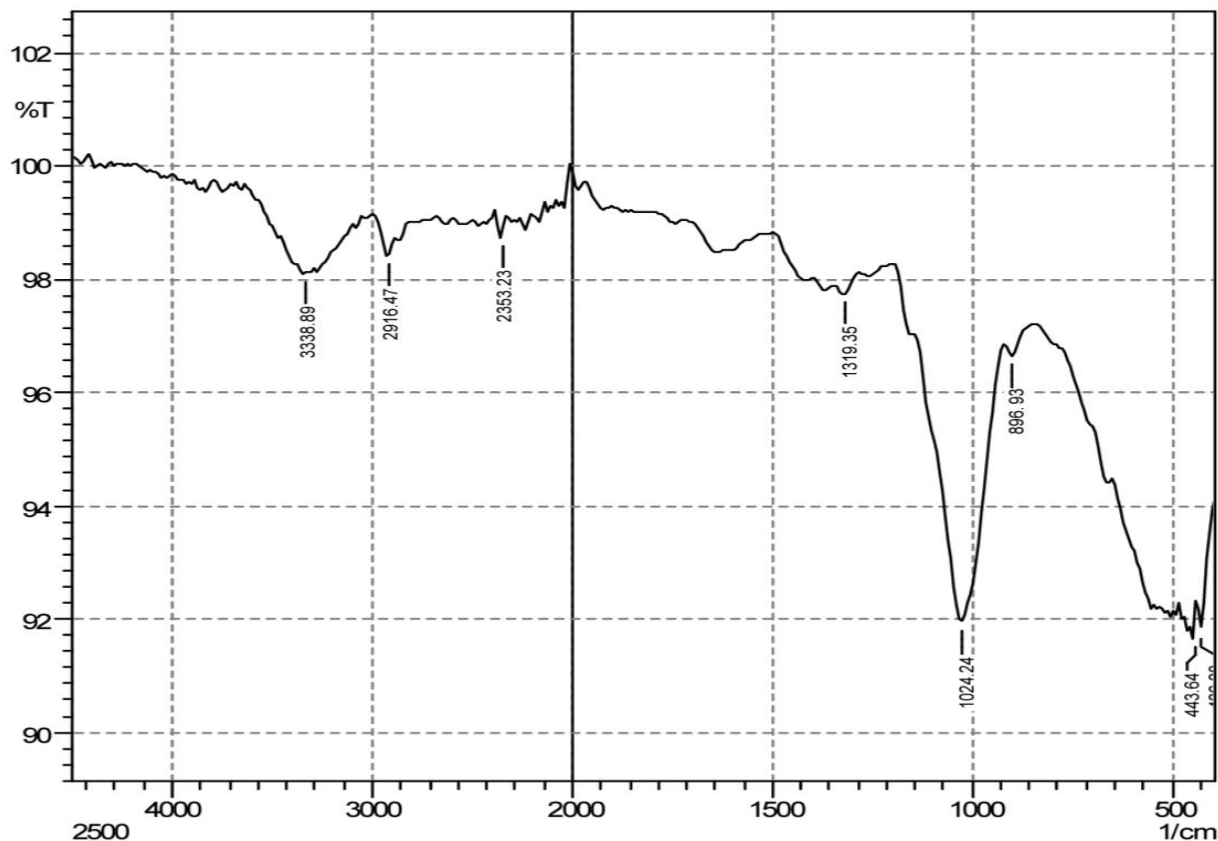
**Fig 1.3 plot between time and percentage removal for Congo red at pH 3,5,7.**

The graph shows percentage removal of different Ph (3,5,7). As the fig 1.3 shows that as the time times and pH changes to basic from acidic there is rise in the percentage removal.eg., for pH3 the percentage removal after one hour is 5.2 ,after two hours the percentage removal changes to 12.4, after three hours it is 28.7 and after 4 hours it increases to 31.In such way the percentage removal for all the Ph 5 and 7 also increases.

### FTIR analysis

FTIR analysis for raw as well alkali (NaOH) treated corncob was done.

The FTIR analysis show following peaks(fig 2.1) for untreated corn cob at 3346.61  $\text{cm}^{-1}$ , 2924.18  $\text{cm}^{-1}$ , 2856.67  $\text{cm}^{-1}$ , 2395.67  $\text{cm}^{-1}$ , 2283.79  $\text{cm}^{-1}$ , 2108.27  $\text{cm}^{-1}$ , 1730.21  $\text{cm}^{-1}$ , 1620.26  $\text{cm}^{-1}$ , 1450.52  $\text{cm}^{-1}$ , 1365.65  $\text{cm}^{-1}$ , 1240.27  $\text{cm}^{-1}$ , 1159.26  $\text{cm}^{-1}$ , 1031.95  $\text{cm}^{-1}$ , 715.61  $\text{cm}^{-1}$ , 538.16  $\text{cm}^{-1}$ , 443.64  $\text{cm}^{-1}$  are representing following functional groups O-H, C-H, C-H, O-H, O-H, C=C, C=O, C=O, C-H(CH<sub>3</sub>), N=O,C-O, C-O, C-O, C-Cl, C-Cl-C-Cl.



**Fig2.2: FTIR spectra of NaOH treated corn cob.**

The FTIR show following peaks fig(2.2) for NaOH treated corn cob at  $3338.89\text{cm}^{-1}$ ,  $2915.47\text{ cm}^{-1}$ ,  $2353.23\text{ cm}^{-1}$ ,  $1319.35\text{ cm}^{-1}$ ,  $1024.24\text{ cm}^{-1}$ ,  $896.93\text{ cm}^{-1}$ ,  $443.64\text{ cm}^{-1}$ ,  $426.28\text{ cm}^{-1}$  .and they represent the following functional groups N-H O-H ,C-H,C-O,C-O,C-O,C-Cl ,C-Cl , C-Cl.

**SEM analysis**

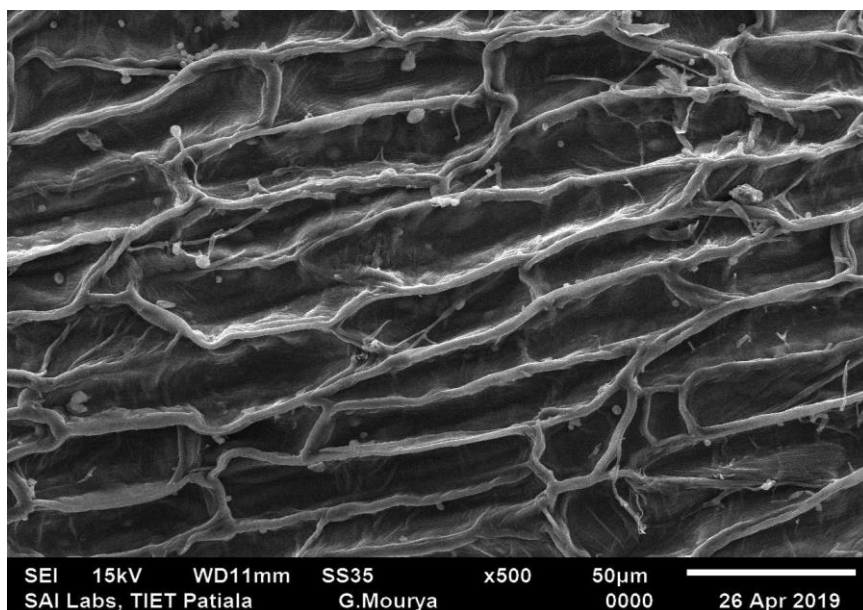


Fig 3.1:Raw corncob before adsorption of malachite green(500x)

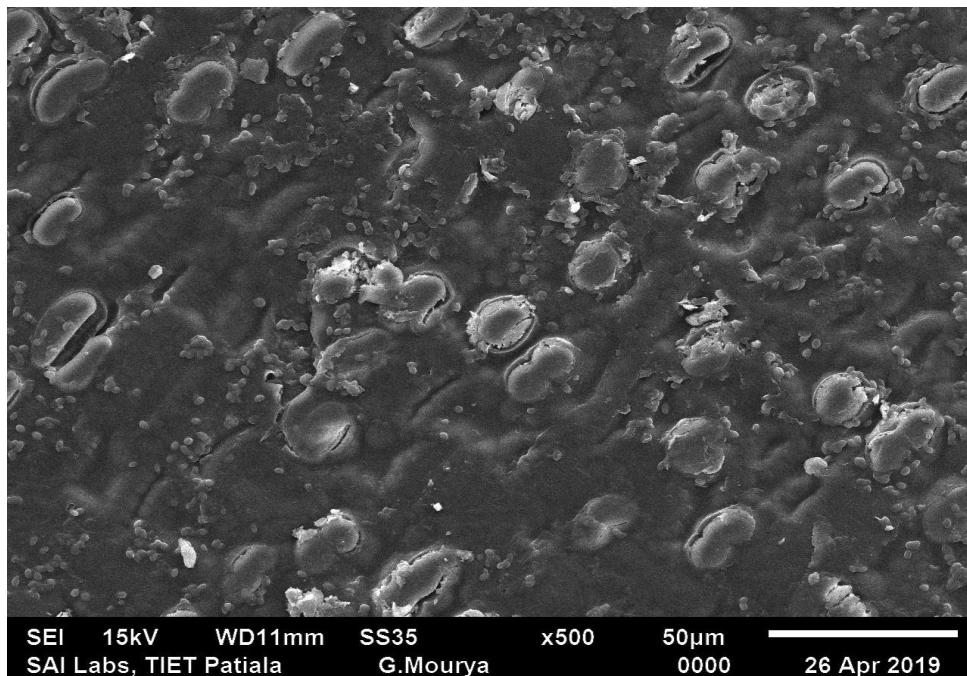


Fig 3.2: untreated corncob after the adsorption of malachite green(500x)

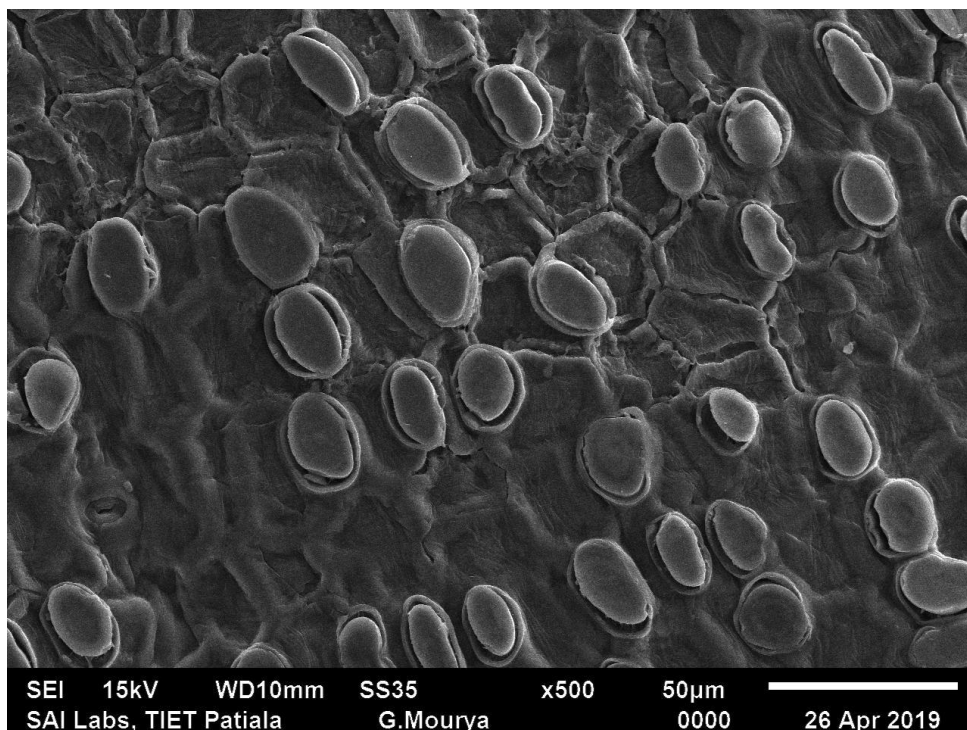
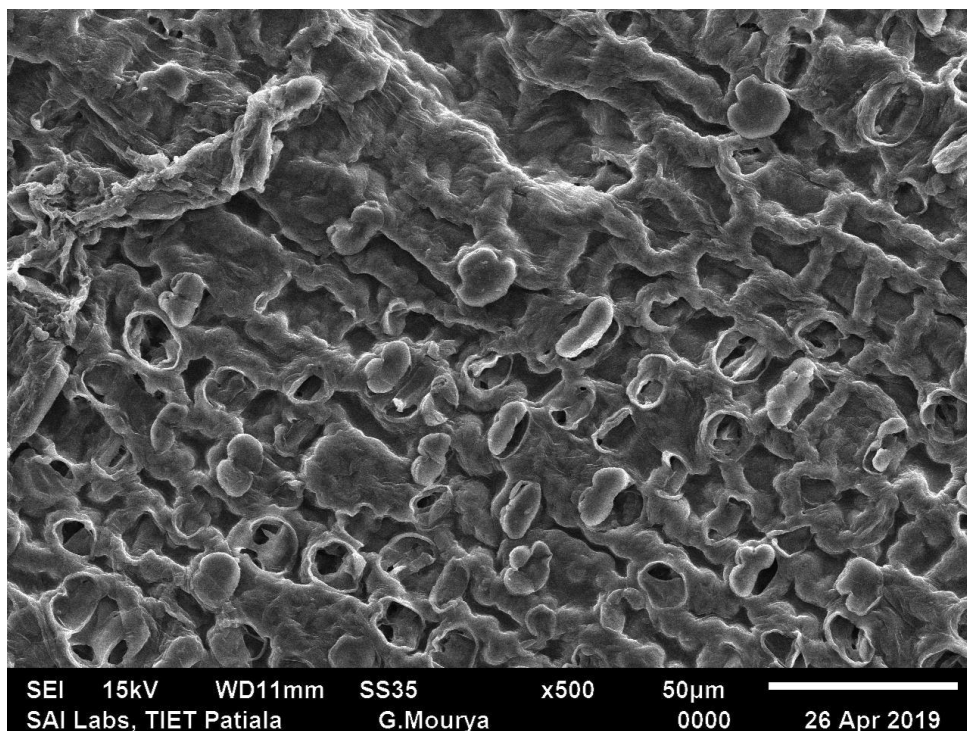


Fig 3.3 :NaOH treated corncob (500x)



**Fig 3.4:NaOH treated corncob after adsorption of malachite green(500x)**

Scanning electron microscopy was done to testify the surface structure of raw as well as treated corncob. In case of raw corn cobs there is no binding in the pores. Huge number of open pores present or in other words we can say that there were huge amount of active sites as shown in fig 3.1, while after the addition of malachite green the porosity decreases and there was binding between the pores and dye or in simple words we can say that the active sites which were open got bonded by the dye, as shown in fig 3.2. Once the raw corncob was treated with NaOH we can see the difference there are less number of pores and its surface has been modified as compared to the raw corncob as shown in fig 3.3. Fig 3.4 shows that there is binding of the dye with NaOH treated corncob a smaller number of active sites are present. We can also see that the binding in NaOH treated corncob is more as compared to raw corncob after the adsorption of malachite green.

### Conclusions

The result of the study concluded that corn cob residue is efficient material for the elimination of azo dyes and when the corn cob residue is treated with NaOH its efficiency to remove dye increases. pH and contact time are important parameters of this study, these parameters are directly proportional to the amount of dye adsorbed. Thus, from the study it was concluded that treated corn cob residue can be used as an alternative for the removal of azo dyes from the water.

### Reference

1. A.A.said., El-Wahab, M. A., Soliman, S. A., & Aly, A. A. M, Potential application of propionic acid modified sugarcane bagasse for removal of basic and acid dyes from industrial wastewater. In 2010 International Conference on Environmental Engineering and Applications, pp. 154-156, sep.2010.



2. A.C.A de Lima, R.F Nascimento, F.F de Sousa, M. Josue Filho, & A.C Oliveira, Modified coconut shell fibers: a green and economical sorbent for the removal of anions from aqueous solutions. *Chemical Engineering Journal* vol ED 185, pp.274-284, March.2012. .
3. B. Zhao, X. Xu, S. Xu, X. Chen, H. Li, & F. Zeng, Surface characteristics and potential ecological risk evaluation of heavy metals in the bio-char produced by co-pyrolysis from municipal sewage sludge and hazelnut shell with zinc chloride. *Bioresource technology*, vol ED 243,pp. 375-383, November.2017
4. C.N Arenas,A.Vasco, M.Betancur, J.D Martinez, Removal of indigo carmine (IC) from aqueous solution by adsorption through abrasive spherical materials made of rice husk ash (RHA). – *Process Safety and Environmental Protection*, vol ED 106, pp. 224– 238, Feb.2017
5. D.Obregón-Valencia& D.R M. Sun-Kou,Comparativecadmiumadsorption study on activated carbon prepared from aguaje (*Mauritia flexuosa*) and olive fruit stones (*Olea europaea* L.) *Journal of Environmental ChemicalEngineering*,vol ED 2, pp.2280–2288, December.2014
6. D.R Ort, & S.P. Long, Limits on yields in the cornbelt. *Science*,vol ED 344(6183), pp.484-485, may.2014.
7. F. Gong, X. Wu, H. Zhang, Y. Chen, &W. Wang, (2015). Making better maize plants for sustainable grain production in a changing climate. *Frontiers in plant science*, vol ED 6,pp.835, October. 2015.
8. F.Haghseresht&G.Q Lu, (1998). Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. *Energy & Fuels*, vol ED 12(6), 1100-1107, September. 1998
9. G.B Hong, &Y.K Wang, Synthesis of low-cost adsorbentfrom rice bran for the removal of reactive dye based on the response surface methodology. *Applied Surface Science*, vol ED 423, pp. 800–809, November.2017.
10. G.Crini ,PM.Badot (eds)orption process and pollution: An introduction PUFC, Besancon, France,2010.
11. G.L Dotto, S.K Sharma, & L.A Pinto, Biosorption of organic dyes: Research opportunities and challenges. *Green chemistry for dyes removal from wastewater: Research trends and applications*, pp.295-329.march.2015.
12. H. Singh, G. Chauhan, A.K Jain, &S.K Sharma, Adsorptive potential of agricultural wastes for removal of dyes from aqueous solutions. *Journal of Environmental Chemical Engineering*, vol ED 5(1), pp.122-135, February.2017.

13. H.C Tao, H.R Zhang, J.B Li, W.Y Ding, Biomass based activated carbon obtained from sludge and sugarcane bagasse for removing lead ion from wastewater. *Bioresour Technol*, vol ED 192, pp.611–617, September.2015
14. H.Demiral& C.Güngör, Adsorption of copper (II) from aqueous solutions on activated carbon prepared from grape bagasse. *Journal of Cleaner Production*, vol ED 124(2016), pp.103–113, June. 2016.
15. H.I Chieng, L.B Lim, & N. Priyantha, Enhancing adsorption capacity of toxic malachite green dye through chemically modified breadnut peel: equilibrium, thermodynamics, kinetics and regeneration studies. *Environmental technology*, vol ED 36(1), pp.86-97, July.2014.
16. M.S Podder& C. B Majumder, Study of the kinetics of arsenic removal from wastewater using *Bacillus arsenicus* biofilms supported on a neem leaves/MnFe<sub>2</sub>O<sub>4</sub> composite. *Ecological Engineering*, vol ED 88, pp.195–216, March. 2016
17. M.Vakili, M.Rafatullah, B.Salamatinia, A.Z. Abdullah, M.H. Ibrahim, K.B.Tan, Z.Gholami, P.Amouzgar, Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: a review. – *Carbohydrate Polymers*, vol ED 113, pp.115–130, November.2014.
18. Q.Cao, K.C.Xie, Lv, Y. K., & Bao, W. R, Process effects on activated carbon with large specific surface area from corn cob. *Bioresource Technology*, vol ED 97(1), pp.110-115, January.2006.
19. S.Banerjee, S.Barman, G.Halder, Sorptive elucidation of rice husk ash derived synthetic zeolite towards deionization of coalmine waste water: A comparative study. – *Groundwater for Sustainable Development*, vol ED 5, pp. 137–151, September.2017
20. T.J. Jones, Maize tissue culture and transformation: the first 20 years in *Molecular Genetic Approaches to Maize Improvement*, (Heidelberg: Springer), pp. 7 – 27, 2009.
21. T.Robinson, B. Chandran, & P. Nigam, Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. *Environment International*, vol ED 28(1-2), pp.29-33, April.2002.