Removal of methylene blue dye in aqueous solution by agricultural waste

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Abstract

An experimental study investigated the potential of corn husk as a biosorbent for adsorption of methylene blue (MB) dye from dye synthetic effluent. The effects of operating parameters like, pH, contact time, initial dye concentrations and adsorbent doses on dye uptake were examined.pH of the solution was found to have most significant impact on adsorption process, and maximum dye removal was achieved at pH 6.2 within 15 minutes of contact time. The coefficient value for adsorption capacity q_{max}obtained in Langmuir isotherm was 30.33 mg/g with with significant value of regression R^2= 0.99. The value of $K_f$coefficient obtained in Freundlich isotherm was about 8.51 mg/g with a lower regression, R^2= 0.82. Kinetic study of the adsorption process followed the Pseudo second order kinetic model. Experimental results favor the adsorption process from corn husk based adsorbent.

Keywords- *Corn husk, Agricultural adsorbent, Methylene blue dye, FTIR technique*

1. Introduction

Dyes are complex chemical compounds used in various industries such as food, paper, carpets, rubbers, plastics, tanneries, cosmetic and textile to colour their products [1]. These dyes may be either natural or synthetic in origin and used frequently due to its availability and range. Synthetic dyes are mutagenic; carcinogenic in nature causes skin allergy, nausea, skin irritation, and breathing difficulties [2]. Methylene blue (MB) dye is cationic and more toxic in nature than anionic dye [3]. Deprive of harmful effect this dye is widely used in industries like textile, printing and tanning industry [4].Dyes laden wastewaters have less permeability for sunlight penetration, hence it retarded photosynthetic activity and reduce dissolved oxygen in the aquatic ecosystem. The dye-containing wastewater can be characterized by high COD (789 mg/L), BOD (275 mg/L) , TDS (5875 mg/L) content which negatively affect the life in aquatic ecosystem when they discharge into water bodies [5]. Most of the industries have less effective wastewater treatment system; hence, most of the dye residues are remained discharge in wastewater.

Recently various techniques have been employed for the removal of dyes from waste water [6] i.e. nano filtration, reverse osmosis, electrolytic coagulation, aerobic, anaerobic treatment and adsorption [7-8] by activated material. Most of these technologies have been proven ineffective for removal of synthetic textile dyes from wastewater because of the chemical stability of these pollutants [9]. Indian dye industries mostly used expensive activated carbon, which increases the cost of wastewater treatment.Researchers have shifted their interest towards the biological materials for low cost absorption process for treatment of dye containing effluent [10]. Application of waste materials such as agricultural waste, clay and microbial biomass were also used for biosorption process. These biomaterials are by-products from agricultural practice, industrial waste and porous materials [11-12]. The major advantages of biosorption methods over conventional treatment include; cost effectiveness, high efficiency, minimization of sludge and no additional requirements of further treatment [13-14]. Agricultural waste being economic and eco-friendly due to their unique chemical composition, available in abundance quantity, renewable, low cost and more efficient and are seems to be a viable option for decolourization of textile wastewater. Waste materials such as bagasse, saw dust, rice husks, tamarind fruit shell, palm fruit bunch, corn cob, barley husk, orange peel, ground nut shell, wheat bran, tree barks and barley straw [15-20] have been already observed forcolour removal of dye effluent. Agricultural wastes are mainly composed of lignocellulosic material (containing 35-36% cellulose, 25-35 % hemicelluloses, 20-30 % lignin and other components). Those have porous structure, very high free-surface volume, and lignocellulosic (plant-derived) resources. Thus, agricultural waste shows sorption characteristic for a wide range of solutes [21].

Corn husk is one of the cellulosic wasteswith no economic value in agriculture. A large quantity of corn husk is produced in India and about 8.7 Mhaareaswas under cultivation which produces 22.2 MT of maize grain during 2012-2013 [22] . It is composed of cellulose (~42%), lignin (~13%), ash (4.2%) and other material (~41%) [23].

The aim of the present study is to find out the potential of corn husk as an adsorbent for uptake of MB dye from synthetic dye wastewater. In addition to the biosorption process mechanism of biosorption process is also studied through Langmuir and Freundlich Isotherms and kinetic models are applied on experimental data to observe the kinetics behavior of biosorption process.

2. Materials and Methods

2.1 Preparationand calibration of synthetic dye wastewater

An analytical grade of Methylene blue dye (MB)was used in the preparation of synthetic dye wastewater. Stock solution of methylene blue dye was prepared (1000 mg/L) dissolving required quantity of dye in double distilled water to obtain different concentrations via dilution process (5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L, and 30 mg/L) of MB dye solution was prepared by diluting stock solution.

Synthetic wastewater was cenrtrifuged at 700 rpm for ten minutes which was then analysed for dye concentrations. Dye concentration was measured through UV-VIS spectrophotometer (Shimadzu-2450). pH of the solution in the experiment was maintained by addition of either acid/alkali 0.1 N HCl or 0.1 N NaOH) solutions. The synthetic dye wastewater was prepared and calibrated in order to find out various optical densities at various concentrations of methylene blue dye in distilled water (5, 10, 15, 20, 25, 30 mg/L). k factor was calculated by the graph (Fig 1) plotted between absorbance and concentration.

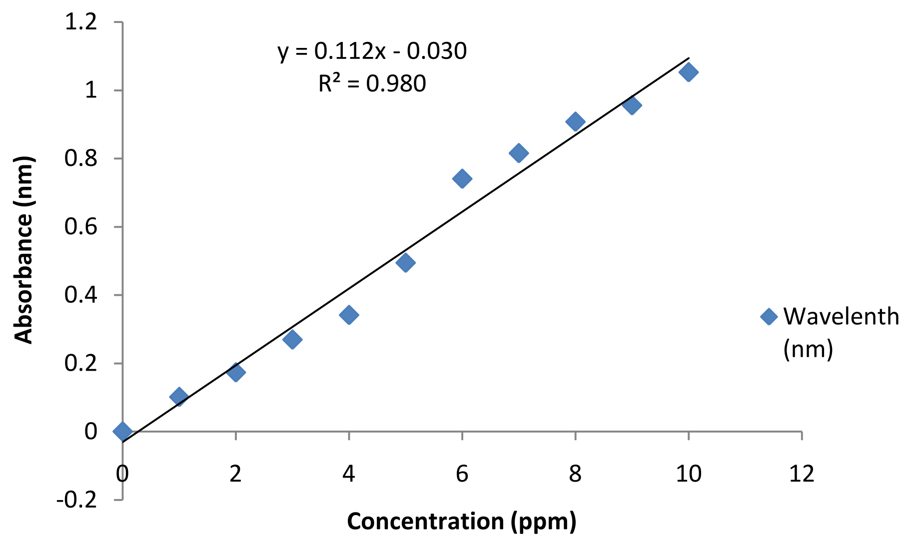

Fig 1. Calibration curve of methylene blue dyes

2.2Preparation of biosorbent

Corn husk was used as a biosorbent for removal of methylene blue dye from synthetic wastewater. The material was collected from the local markets of Lucknow, Uttar Pradesh, India. The corn husk biomass was washed withdistilled water many times to remove the dust impurity. After washing, the material was grinded with mixer grinder. The powdered material was again dried in an oven at 105 ºC for 24 hours and stored in an air tight plastic container for adsorbent study. .

2.3 Analysis of colour removal efficiency of corn husk

Colour removal efficiency was determined for each concentration of wastewater at fixed time interval (contact time). The percentage colour removal at equilibrium was calculated by the following formula.

$$Decolorization(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$Dyeadsorptioncapacity(q_e) = \frac{C_o - C_e}{m} \times V \quad (2)$$

Where, C_o and C_e are the liquid-phase dye concentration at initial stage and equilibrium stage respectively (mg/L); V is the volume of dye solution (L) and m is the mass of adsorbent (g).

2.4 Adsorption equilibrium studies

Batch equilibrium adsorption studies were carried out in laboratory by containing 250 mL of dye solutions of different initial concentrations of 5, 10, 15, 20, 25 and 30 mg/L with 0.25 g of dried fine powdered corn husk in 500 mL conical flasks for a period of 2 h. The adsorption process was performed at selected temperature (25-28 ºC), and different pH of dye wastewater to observe the effective adsorption process.

2.5 Isotherm Study

The equilibrium adsorption isotherm is applied to understand the design and significance of adsorption system. Langmuir and Freundlich are two important adsorption isothermwere used in this study. Isotherm models are generally used to evaluate the sorption capacity shown by biomass in sorption system and mathematical relationship between the quantity of adsorbate and concentration remaining in the system [24].

2.6 Langmuir Isotherm

It is usually used for monolayer adsorption process and expressed as follows:

$$q_e = \frac{q_{max}\, bC_e}{1+bC_e} (3)$$

where, q_e is the amount of metal sorbed at equilibrium (mg/g), q_{max} is the monolayer sorption capacity (mg/g), b is the Langmuir constant, C_e is concentration of metal ions in solution at equilibrium.

The linear form of Langmuir model is as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b\,q_{max}} (4)$$

There must be a straight line with slope of ($1/q_{max}$) and an intercept of ($1/bq_{max}$) when a plot of (C_e/q_e) verses C_e is drawn.

2.7 Freundlichisotherm

The Freundlich equation is basically empirical but is often useful as a means for data description and representing the equilibrium on heterogeneous surfaces and does not assume monolayer coverage [25-26].

. The Freundlich model in its linear form is express as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e (5)$$

Where C_e is the equilibrium concentration (mg/g); q_e is the adsorbed amount at equilibrium (mg/g); 1/n and k_f and n are experimentally calculated by plotting the function (equation. 3)

2.8 Kinetic study

Adsorption kinetic describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at solid-solution interface [27]. The most commonly models used for adsorption kinetics are Pseudo-first order and Pseudo-second order kinetic models.

2.9 Pseudo first order

Lagergren first-order rate expression based on solid capacity is generally showed as follows [28]:

$$\frac{dt}{dq} = k_1(q_e - \mathrm{q}) \quad (6)$$

where q and q_e are amounts of dye adsorbed (mg/g) at time, t (min) and at equilibrium, respectively, k1 is the rate constant of adsorption (l min^{-1}).

It is mathematically can also expressed as follows:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (7)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \quad (8)$$

Where, k_1 is first order constant; q_e(mg/g) is the amount of adsorbate adsorbed at equilibrium and at anytime; q_t is the amount of adsorbate adsorbed at time time t. The value of $q_e$and k_1 can be obtained from the non-linear curve fitting of experimental data q_t verses t.

2.10 Pseudo-second order

Pseudo-second order is mathematically expresses as follow:

$$q_t = \frac{k_2 q_e 2}{1 + k_2\ q_e \mathrm{t}} \quad (9)$$

where, k_2 ((g/mg)/h) is the second order constants q_e (mg/g) and q_t(mg/g) the amount at adsorbed at equilibrium at any time.

3. Results and Discussion

3.1 Effect of pH

pHas a key factor was found to have played important role in adsorption of MB dyes from the synthetic dye wastewater. The maximum adsorption of MB dyes (90 %) onto corn husk powder was achieved at pH 6.2 (slightly acidic; Fig. 2). Maximum dye sequestration from the aqueous solution of MB dye achieved within 15 minutes after start of the experiment at all studied concentrations. At pH 6.2, the adsorbent surface is negatively charged that provides more electrostatic attraction between corn husk and MB dye which cause increase the adsorption capacity. Above this pH, adsorption process decreased due to weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent [29].

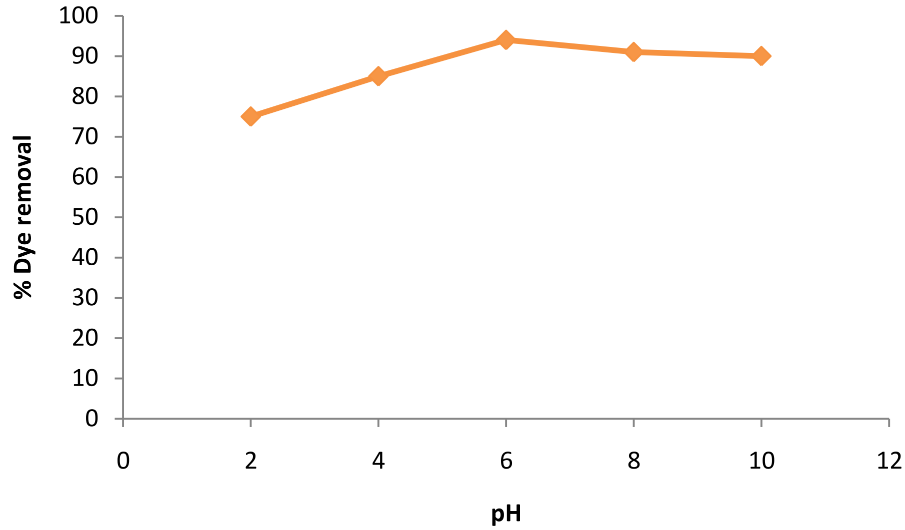

Figure 2: Effect of pH on MB dye adsorption (dye concentarion= 10 mg/L, adsorbent dose= 0.25 gm/250 ml and time= 2 h)

3.2 Effect of contact time

The effect of contact time on the adsorption of MB dye in aqueous solution by corn husk powder was studiedfor all concentrations varied from 5-30 mg/L. The result is presented in Fig.3 which indicates a maximum (> 90%) dye uptake reached within 15 minutes. Doses of dye adsorption, increases with increasing contact time. At initial state, the rate of dye uptake was higher in the beginning time due to the presence of active sites on the adsorbent. The rate of adsorption gradually become slower and quantitatively insignificant.

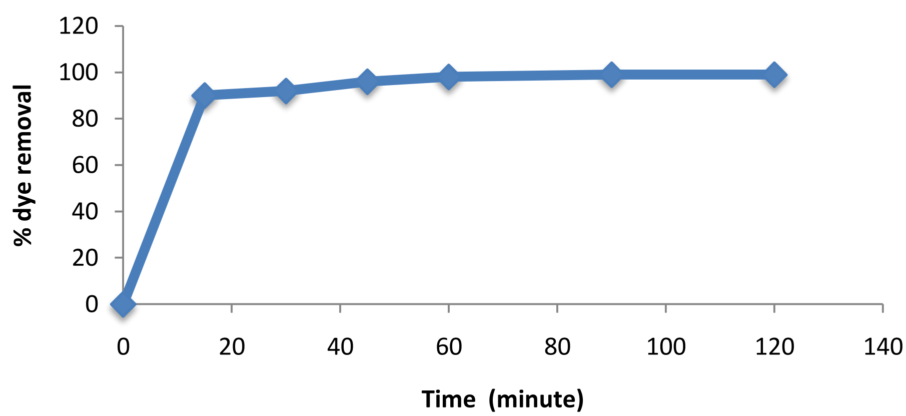

Figure: 3 Effect of contact time on MB dye adsorption (dye concentration= 10 mg/L, adsorbent dose= 0.25 gm/250 ml and time= 2 h)

3.3 Effect of adsorbent doses

The adsorption of MB on corn husk powder was studied by varying the amount of corn husk and biosorbent ranging from 1-25 gm/l at room temperature (25 °C); and solution concentration was 10 mg/L for all experiments. The percent adsorption was increased with increase in doses (Fig. 4) due to increased surface area and availability of more binding sites [30]. The maximum adsorption was observed least for higher amount of doses [31]. However, the increase concentrations of doses lead to decrease adsorption with increasing adsorbent dose. This decrease may be due to unsaturation of adsorption sites [32].

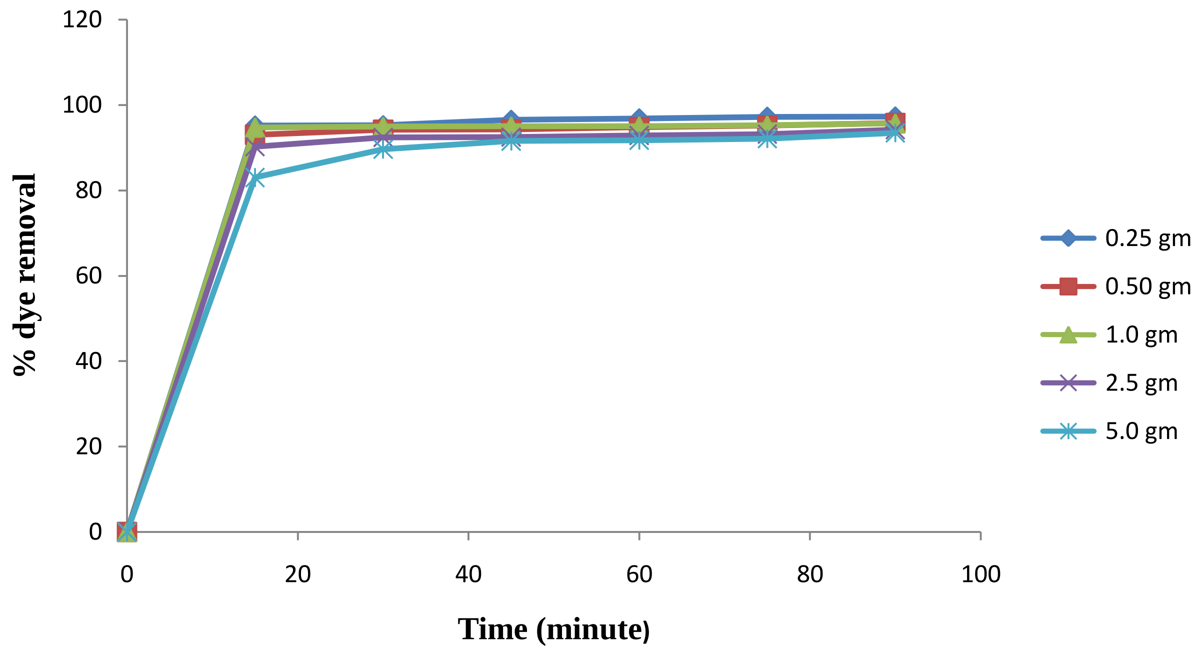

Figure 4 : Effect of adsorbent dose on MB dye adsorption (dye concentration= 10 mg/L, /250 ml and time= 2 h)

3.4 Effect of initial concentrations

In sorption process, the effect of contact time was investigated at different MB dye concentrations (5, 10, 15, 20, 25, and 30 mg/L) onto corn husk adsorbent at a fixed adsorbent dose (0.25 gm/250 ml) in test solution. The experiments were carried out at different time intervals (15, 30, 45, 60, 90 and 120 minutes). The MB dye uptake range was found from 83-97 percent at all studied concentrations (Fig. 5). The maximum dye removal was shown by adsorbent was shown by adsorbent dose 0.25 gm/250 ml at 10 mg/L concentrations. These observations were found similar with observations reported by other researchers [33]. The dye removal rate was decreased at as increase dye concentrations from 5-30 mg/L. The reason behind it was the less availability of binding sites in aqueous dye solutions.

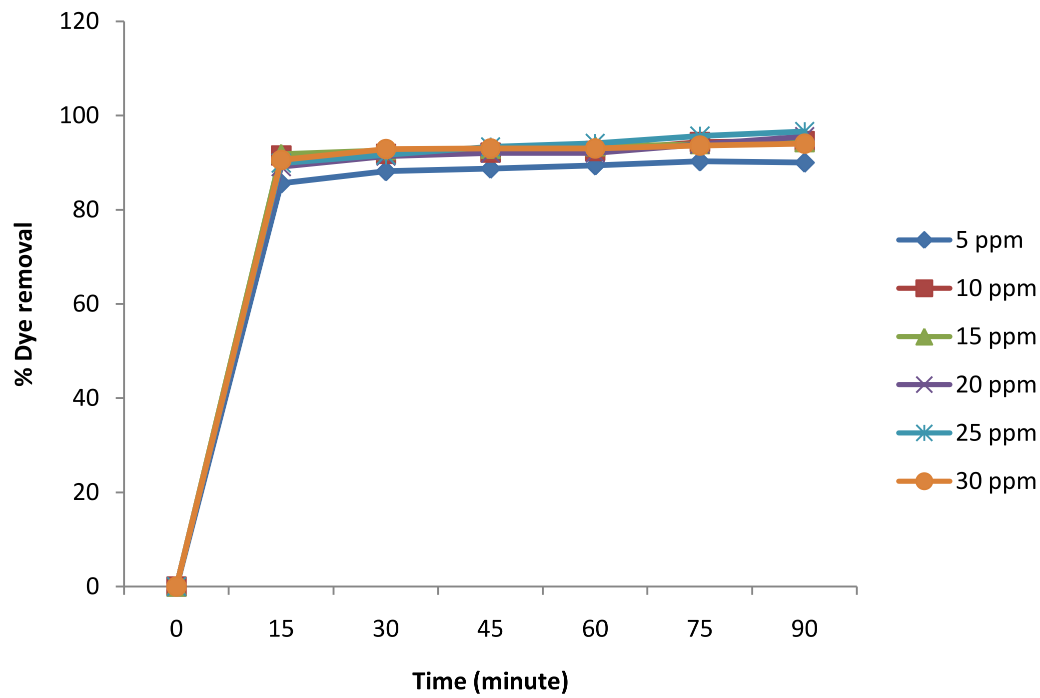

Figure 5: Effect of initial concentrations on MB dye adsorption (adsorbent dose= 0.25 gm/250 ml and time= 2 h)

3.5 Adsorption Isotherm studies

The values of Langmuir and Freundlich constants for MB dye uptake on corn husk are given in Table 1. The values of K_F and n were obtained by the plot of log qevs log Ce (Table 1). The R^2 values of Langmuir constant was 0.9487 which was higher than R^2 value of Freundlich (0.8268), this means that Langmuir data fitted well than Freundlich data in adsorption process (Fig 6 & 7).

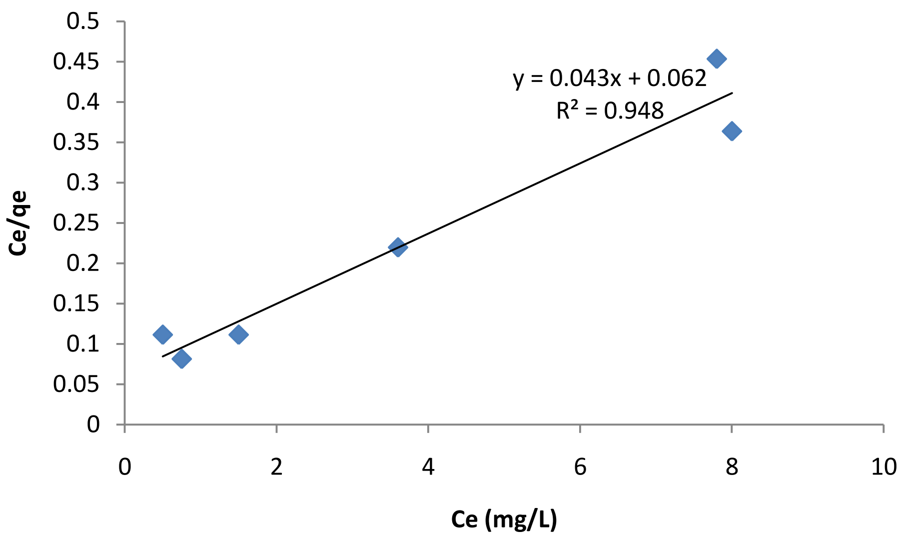

Fig. 6 Langmiur plot of Ce/qevsCe for dye adsorption

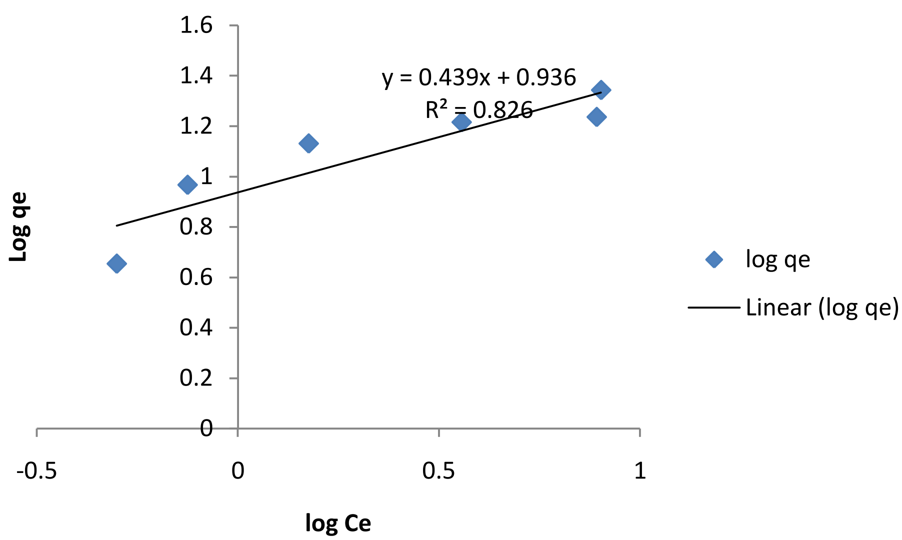

Fig 7 Freundlich plot for MB dye removal by using corn peel

Table 1 Equilibrium model parameters for the removal of MB onto corn husk powder

Langmuir constant			Freundlich constant		
Q_{max}(mg/g)	B (L/mg)	R^2	n	K_F(mg/g)	R^2
30.30	0.003	0.9487	2.27	8.51	0.8268

The essential parameter of the Langmuir isotherm can be expressed in terms of an equilibrium parameter, R_L, [34] (Eq.10 which is defined as below:-

R_L=1/(1+bC_0)(10)

Where, C_0 is the initial dye concentration (mg/L) and b is the Langmuir constant. The value of R_L for the present study at different concentrations were found to be ranges between 0 to 1 (Table 1) which confirms the favourable state of dye uptake.

R_L values indicate the Langmuir isotherm suitable condition,unfavourable (R_L>1), linear (R_L=1), favourable (0< R_L<1) and irreversible (R_L=0) [35].

In Freundlich data, if value shows the degree of non linearity between methylene blue dye concentrated and adsorption as follows, if n=1, then adsorption is linear, if n<1; then adsorption is a chemical process, if n>1; then adsorption is a physical process. In the present work, n value was found to be 2.27 (Table 1). The value of n ranges from 1-10 represent good adsorption process [36-37].

3.6 Adsorption kinetic studies

The kinetic plots, pseudo first order and pseudo second order wereshown in Table 2; those were toused to calculate the maximum adsorption capacity (mg/g) and the rate constants. The theoretical maximum adsorption capacity (30.333 mg/g) inferred from the pseudo second order equation was closer to observed experimental value (30.30 mg/g). The pseudo second order kinetic model was based on the premise that the sorption rate was controlled by chemical sorption [38] .

In present study, the applicability of pseudo first order (Eq. 6) and pseudo second order model (Eq. 7) was tested for the sequestration of MB dye from aqueous media. For the pseudo first order model straight- line plots of log(qe-qt) against time were analyzed. For pseudo second order t/qt was plotted against time
Slopes and intercepts of pseudo first order and pseudo second order model are given in Table (2) (Fig.8 & 9); those were to calculate the maximum metal uptake capacity (mg/g) and the rate constants. The theoretical maximum adsorption capacity (30.333 mg/g) inferred from the pseudo second order equation was closer to observed experimental value (30.30 mg/g). The pseudo second order kinetic model was based on the factor that the sorption rate was controlled by chemical sorption [38]. On the bases of correlation factor, it was found that Pseudo second order (R^2=0.99) fitted well than Pseudo second order (R^2=0.88) with the adsorption experiment.

Table 2. Comparison between adsorption of Lagergren pseudo first order and pseudo second order

Initial dye concentration (mg/L)	First order model			Second order model		
	K_1 (×10^{-3}/min)	Q_e(mg/g)	R^2	K_2 (×10^{-3}g/mg/min)	Q_e(mg/g)	R^2
5	0.0345	0.630	0.90	0.048	4.545	0.99
10	0.0396	0.933	0.74	0.011	9.523	0.99
15	0.033	0.807	0.95	0.004	16.666	0.99
20	0.014	1.288	0.75	0.002	20.0	0.99
25	0.019	1.678	0.70	0.002	25.0	0.99
30	0.028	1.111	0.88	0.001	33.333	0.99

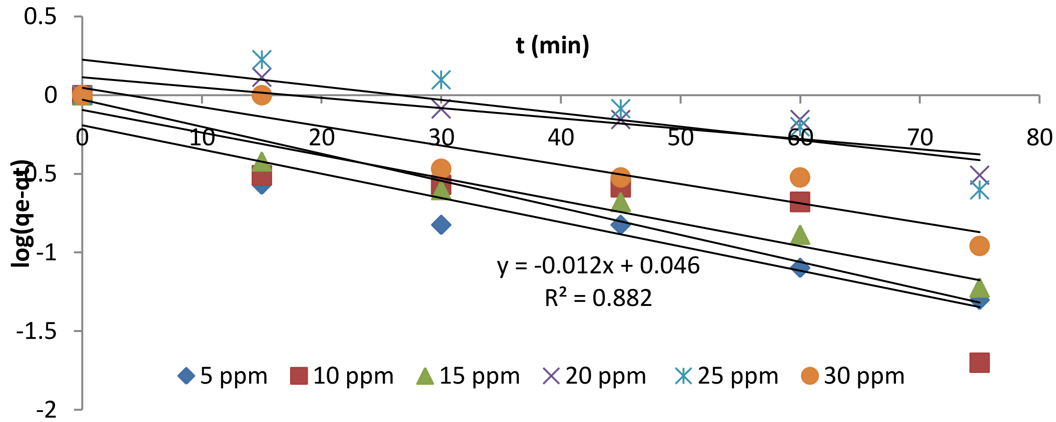

Fig 8 Lagergren pseudo first order kinetic order model

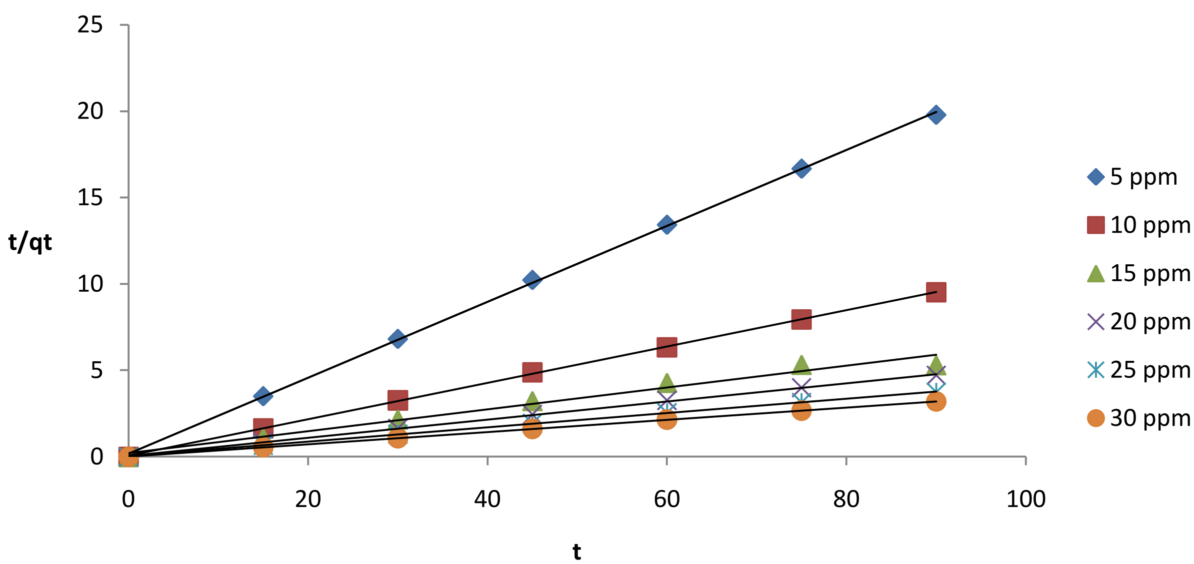

Figure. 9: Ho's pseudo second order kinetic model

3.7 Comparison of corn husk methylene blue uptake with other adsorbents

Table 3 represents a comparative evaluation of locally available adsorbents for methylene blue dye removal. It was observed that corn husk is better than other reported adsorbents. Therefore, corn husk is efficient adsorbents in terms of adsorption capacity.

Table 3. Comparison of methylene blue dye uptake with other adsorbents

Adsorbent	Adsorption capacity (mg/g)	References
Neem saw dust	3.62	[39]
Beer brewery waste	4.92	[40]
Cow dung ash	5.31	[41]
Coir pith carbon	5.87	[42]
Orange peel	20.50	[43]
Activated olive stones	22.1	[44]
Cogongrass	27.40	[45]
Banana peel	29.94	[43]
Corn husk	30.33	present study

3.8 FTIR Analysis of corn husk

FTIR (Fourier Transform Infrared) spectra were analyzed by Shimadzu-8400S instrument before and after sorption of methylene blue dye in order to identify the vibrational groups in the corn husk.

Figure 10, denotes the FTIR spectra of corn husk prior to adsorption of methylene blue dye. The peaks at 3987 cm^{-1} and 3734 cm^{-1} were characteristic of OH band stretching. The peak at 2154 cm^{-1} is due to C≡C group. The peaks at 1674 cm^{-1} is assigned to ketonic C=O stretching frequency. The peak at 1537 cm^{-1} indicate the presence of C=C stretching vibration of the aromatic rings. The relatively intense band at 1389 cm^{-1} can be assigned to CH aliphatic bending. The peak around 1331 cm^{-1} corresponds to the CH bending.

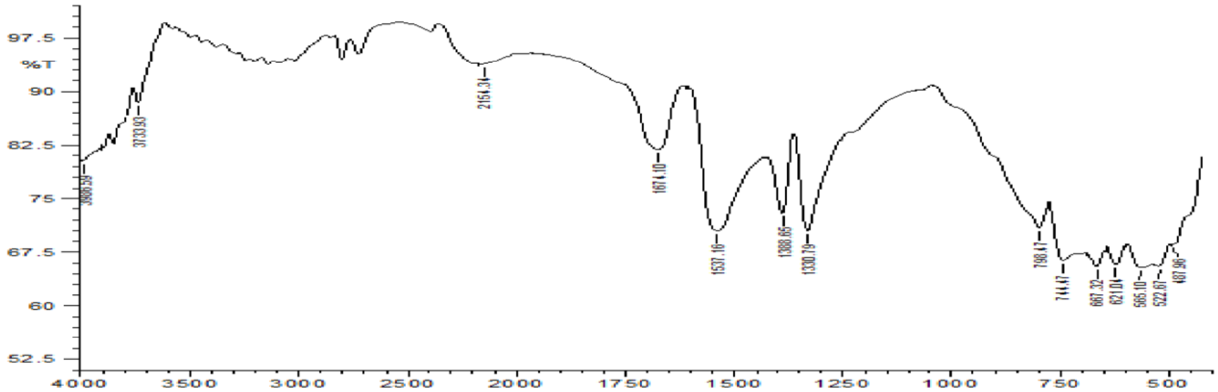

Fig.10 FTIR spectra of corn husk before adsorption

In Fig 11, the bands in the region of 3917-3684 cm^{-1} are attributed to the OH groups of alcohols and carboxylic acids. The bands at 2947 cm^{-1} can be associated with CH groups. The peaks at 2827, 2729 and 2702 cm^{-1} are assigned to CH stretching vibration of aldehyde group. The peak at 2679 cm^{-1} indicates the presence of NH_2 symmetric ring. The peaks at 2588 cm^{-1} are due to SH stretching vibrations. The two peaks at 2473 cm^{-1} and 2359 $cm^{-1}$are assigned to C=O stretching. The peak at 2332 cm^{-1} and 1626 cm^{-1} indicates the presence of Si-H and C=O groups, respectively. The strong peak at 1362 cm^{-1} are due to presence of aliphatic stretch.

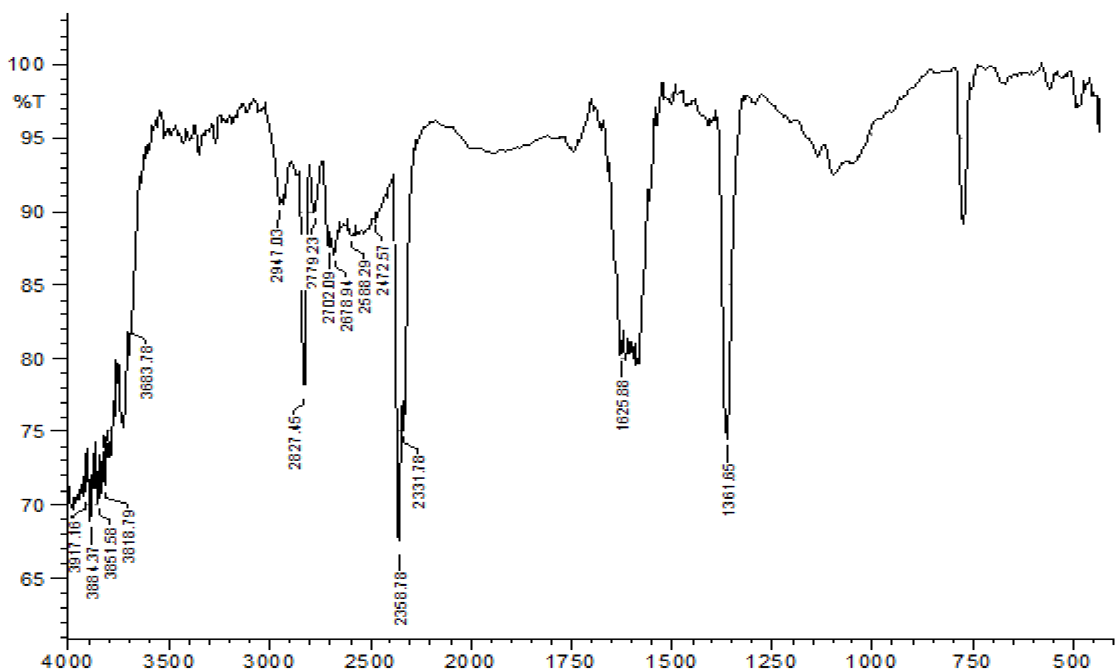

Fig .11 FTIR spectra of corn husk after adsorption

4. Conclusion

The adsorption of methylene blue dye onto corn husk was explored under different conditions. The adsorption process was examined under parameters such as pH, contact time, initial metal concentrations and adsorbent doses. The maximum dye removal occurred at pH 6.2 within 15 minutes time intervals. The experimental data fitted well with Langmuir isotherm data than Freundlich isotherm which shows the monolayer adsorption. The Langmuir constant, R_L, and Freundlich constant, n, both favoured the adsorption system. Maximum monolayer adsorption capacity was found to be 30.30 mg/g. The adsorption kinetic followed the pseudo-second order model which confirms physisorption as well as chemisorption mechanism. Corn husk could be employed as a low cost adsorbent for the efficient removal of methylene blue dye.

Conflict of Interest

The authors have declared no conflict of interest.

References

[1] Doğan, M., Abak, H. and Alkan, M. (2008) Biosorption of methylene blue from aqueous solutions by hazelnut shells: Equilibrium, Parameters and Isotherms. *Water Air Soil Pollution* Vol. 192, pp.141-153

[2] Yogub, M.T., Sen, T.K. and Ang, H.M. (2012) Equilibrium, kinetics and thermodynamics of methylene blue adsorption by pine tree leaves.*Water Air and Soil Pollution*, Vol. 223, No. 8, pp.5267-5287

[3] Hao, J.O., Kim, H. and Chiang, P.C. (2000) Decolourization of wastewater. *Critical Review in Environmental Science and Technology*, Vol.30, pp.449-550

[4] Gupta, V., Suhas, Ali, I. and Saini, V. (2004) Removal of rhodamine B, fast green, and methylene blue from wastewater using redmud, an aluminium industry waste. *Industrial and Engineering Chemical Research*, Vol. 43, pp.1740-1747

[5] Prasad, P. and Rao, V.B.R. (2011) Physico chemical analysis of Textile effluent and decolorization of Textile azo dye by *Bacillus endophyticus*strain VITABR13. *Research:Bioremediation,* Vol.2, No.2, pp.55-62

[6] Nigam, P., Armour, G., Banat, I.M., Singh, D. and Marchant. R. (2000) Physical removal of textile dyes & solid state fermentation of dye-adsorbed agricultural residues.*Bioresource Technology,* 72, No. 3, pp.219-226

[7] Binupriya, A.R., Sathishkumar, M., Kavitha, D., Swaminathan, K., Yun, S.E. andMun, S.P. (2007) Experimental and Isothermal Studies on Sorption ofCongo Red by Modified Mycelial Biomass of Wood Rotting Fungus.*Clean Soil Air Water*, Vol. 35,No.2, pp.143:150

[8] Malik, D.S., Jain C.K., and Yadav AK (2016) Removal of heavy metals from emerging cellulosic low-cost adsorbents: a review. Applied Water Science, DOI 10.1007/s13201-016-0401-8.

[9]Thinakaran, N., Baskaralingam, P., Thiruvengada, Ravi, K.V., Panneerselvam, P. and Sinavesan, S. (2008) Adsorptive Removal of Acid Blue: Equilibrium and Kinetic Study. *Clean Soil and Air Water,* Vol. 36, No. 9, pp.798–804

[10] Forgacs, E., Cserhati, T. and Oros, G. (2004) Removal of synthetic dyes from wastewaters: a review. *Environment International*, Vol. 30,No.7, pp.953-971

[11] Cemil, I.S., lek, A.S. and Ilgaz, A. (2008) Investigation of Biosorption Behavior of MethyleneBlue on Pleurotusostreatus (Jacq.) *P. Kumm*. *Clean Soil Air Water*, Vol.36, No.4, pp.387 – 392

[12] Vijayakumar, G., Dharmendirakumar, M., Renganathan, S., Sivanesan, S., Baskar, G. and Elango, K.P. (2009) Removal of Congo Red fromAqueous Solutions by Perlite. *Clean Soil Air Water, Vol*.37, No.4-5, pp.355-364

[13] Jain CK, Malik DS, Yadav AK (2016) Applicability of plant based biosorbents in the removal of heavy metal: a review. Environ Process. Vol 3(2):495-523

[14] Crini G (2003) Dye removal from aqueous solution by adsorption on treated saw dust, BioresourTechnol 89:121-124

[15] Garg, V.K., Gupta, R., Yadav, A.B. and Kumar, R. (2003) Dye removal from aqueous solution by adsorption on treated saw dust. *Bioresource Technology* Vol. 89, No. 2, pp.121-124

[16] Chowdhury, A.K., Sarkar, A.D. and Bandyopadhyay, A. (2009) Rice Husk Ash as a Low Cost Adsorbent for theRemoval of Methylene Blue and Congo Red inAqueous Phases. *Clean Soil Air Water* Vol.37, No. 7, pp.581 – 591.

[17] Saha, P. (2010) Assessment on removal of methylene blue dye using tamarind fruit shell as biosorbent. *Water Air and Soil Pollution,* Vol. 213, No. 1, p.287-299

[18] Malik, R., Romteke, D.S. and Wate, S.R. (2007) Adsorption of malachite green on ground nut shell waste based powdered activated carbon. *Waste Management* Vol. 27, pp.1129-1138

[19] Hamdaoui, O. and China, M. (2007) Removal of methylene blue from aqueous solution by wheat bran. *ActaChimicaSlovenica* Vol. 54, No.2, pp.407-418

[20] Ibrahim, S., Shaobin, W. and Ang, H.M. (2010) Removal of emulsified oil from oily wastewater using agricultural waste barley straw. *Biochemical Engineering Journal*, Vol. 49,No.1, pp.78-83

[21] Bhattacharyya, K.G. and Sharma, A. (2005) Kinetics and thermodynamics of Methylene blue adsorption on Neem (Azadirachtaindica) leaf powder. *Dyes and Pigments* Vol. 65,No.1, pp.51-59

[22] Kumar, R., Srinivas, K., Boiroju, N.K. and Gedan P.C. (2014) Production performance of maize in India: Approaching an inflection point. *International Journal of Agricultural Statistical Sciences*, Vol. 10, No. 1, pp.241-248

[23] Huda, S. and Yang, Y. (2008) Chemically extracted corn husk fibers as reinforcement in light-weight poly(propylene) properties. *Macromolecular Science and Engineering*, Vol. 293, No. 3, pp.235-243

[24] Pehlivan, E., Altun, T., Cetin, S. and Bhanger, M.I. (2009) Lead sorption by waste biomass of hazelnut and almond shell. *Journal of Hazardous Materials* Vol. 167, pp.1203–2128

[25] Vankar, P.S., Sarswat, R. and Malik, D.S. (2010) Biosorption of lead and cadmium ions from aqueous solutions onto natural dye waste of *Hibiscus rosasinensis*. *Environmental Progress & Sustainable Energy* Vol. 29, No. 4, pp.421-427

[26] Kaya, K., Pehlivan, E., Schmidt, C. and Bahadir, M. (2014) Use of modified wheat bran for the removal of chromium(VI) from aqueous solutions. *Food Chemistry* Vol.158, No.1, pp.112–117

[27] Reddy, D.H.K., Seshaiah, K., Reddy, A.V.R., Rao, M.M. and Wang, M.C. (2010) Biosorption of Pb^{2+} from aqueous solutions by Moringaoleifera bark: Equilibrium and kinetic studies. *Journal of Hazardous Materials,* Vol.174, No. 1-3, pp.831-838

[28]Lagergren, S. (1898) About the theory of so-called adsorption of soluble substances. *Kung Svenska Vet Hand*. Vol. 24, pp.1–39

[29] Baral, S.S., Das, S.N. and Rath, P. (2006) Hexavalent chromium removal from aqueous by adsorption on treated saw dust. *Biochemical Engineering Journal* Vol. 31, No.3pp.216-222

[30] Lata, H., Garg, V.K. and Gupta, R.K. (2007) Removal of a basic dye from aqueous solution by adsorption using *Partheniumhysterophorous*: an agricultural waste. *Dyes and Pigments* Vol. 74, No. 3, pp.653-658

[31] Garg, V.K., Amita, M., Kumar, R. and Gupta, R. (2004) Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian rose wood saw dust: a timber industry waste. *Dyes and Pigments*, Vol. 63, No. 3, pp. 243-250

[32] Yu, L.J., Shukla, S.S., Dorris, K.L., Shukla, A. and Margrave, J.L. (2003) Adsorption of chromium from aqueous solutions by maple saw dust. Journal of Hazardous Material Vol. B100, pp.3-63

[33] Grag, V.K., Gupta, R., Yadav, A.B. and Kumar, R. (2003) Dye removal from aqueous solution by adsorption on treated saw dust. *Bioresource Technology* Vol. 89, No.2, pp.121-124

[34] Malik, P.K. (2004) Dye removal from wastewater using activated carbon developed from sawdust adsorption equilibrium and kinetics. *Journal Hazard Mater* Vol. 113, No. 1-3, pp.81-88

[35] Doke, M.K., Khan, E.M. (2012) Equilibrium, kinetics and diffusion mechanism of Cr(VI) adsorption onto activated carbon derived from wood apple shell. Arabian Journal of Chemistry. (article in press) doi:10.1016/j.arabjc.2012.07.031

[36] Mittal, A., Kurup, L., Mittal, J. (2007) Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tatrazine from aqueous solutions using hen feathers. *Journal of Hazardous Materials*, Vol. 146, No.1-2, pp.243-248

[37] Desta, B.M. (2013) Batch sorption experiments:Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto teff straw (*Eragrastistef*) agricultural waste. *Journal of Thermodynamics* 1-6

[38] Ding, Y., Jing, D., Gong, H., Zhou, L. and Yang, X. (2012) Biosorption of aquatic cadmium (II) by unmodified rice straw. *Bioresource Technology* Vol. 114, pp.20-25

[39] Khattri, S.D. and Singh, M.K. (2000) Colour removal from synthetic dye wastewater using a biosorbent. *Water Air and Soil Pollution*, Vol. 120 No. 3, pp.283-294

[40] Tsai, W.T., Hsu, H.C., Su, T.Y., Lin, K.Y. and Lin, C.M. (2008) Removal of basic dye (methylene blue) from wastewater utilizing beer brewery waste. *Journal of Hazard Materials* Vol. 154, No. 1-3, pp.73-78

[41] Ozdemir, F.A., Demirata, B. and Apak, R. (2009) Adsorptive removal of methylene blue from simulated dyeing wastewater with melanine-formaldehyde-urea resin. *Journal of Applied Polymer Science*, Vol. 112, No.6, pp.3442-3448

[42] Kavitha, D. and Namasivayam, C. (2007) Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. *Bioresource Technology*, Vol. 98, No.1, pp.14-21

[43] Annadurai, G., Juang, S.R. and Lee, J.D. (2002) Use of cellulose based waste for adsorption of dyes from aqueous solution. *Journal of Hazardous Materials* Vol.B92, pp.263-274

[44] Alaya, M.N., Hourish M.A., Youssef, A.M. and El-Sejariah, F. (2000) Adsorption properties of activated carbons prepared from olive stones by chemical and physical activation. *Adsorption Science & Technology* Vol.18, No.1, pp.27-42

[45] Su, X.-H.C., Teng, T.T., Alkarkhi, A.F.M. and Low, L.W. (2014) *Imperatacylindrica* (Cogongrass) as an adsorbent for methylene blue dye removal: Process optimization. *Water Air and Soil Pollution*, Vol. 225, pp.1941.