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METHYLENE BLUE DYE REMOVAL FROM AQUEOUS SOLUTION BY UTILIZATION OF GROUNDNUT SHELL ACTIVATED CARBON

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Abstract - *Activated carbons are extensively used as efficient and versatile adsorbents for purification of water, air and many chemical and natural products. Groundnut shell were used as the adsorbent of this research work. Groundnut shells are the leftover product obtained after the removal of groundnut seed from its pod. This is the abundant agro-industrial waste product which has a very slow degradation rate under natural conditions. Methylene blue is a commonly used cationic dye for colouring, this can also because eye burns in humans and animals. According to batch studies it was concluded that adsorption depend on contact time, adsorbate concentration, pH & also adsorbent AC dose. Main observation in this study was increase in the % removal leads to decrease in the Qe (mg/g) (dye adsorbed on AC) & vise–versa. Sulphuric acid treated Activated Groundnut shell carbon results shows 95-99% of adsorption. When adsorbate conc. increases, accordingly adsorbent AC want to be increased. (100ppm=0.3g, 800ppm=1.0g, 1500ppm=2.0g). CT of 60 min and pH of 8 was considered as optimum. Adsorption followed by Freundlich isotherm where R2= 0.992***.**

Key Words: Groundnut Shell, Methylene Blue, Activated Carbon, Adsorption, pH, Contact Time.

1. INTRODUCTION

The coloured effluents reaching natural water currents and pollute them heavily. The dyes interfere in photosynthetic activity by absorbing sunlight in aquatic plants and effects ecosystem. To overcome this difficulty dyes which are toxic should convert into non-toxic type before discharging into water bodies. Since time immoral many traditional methods have been used for treatment of effluent. The traditional methods like flocculation, coagulation, activated carbon adsorption, membrane separation methods used to reduce the effluent properties and colour removal efficiency. One of the best method of efficient is nothing but the process of the absorption for the purpose of removal of the dyes. Give some of the important advantages for the process of the absorption hence the activated carbon is most popularly used as one of the compound which comes as an organic extracted from the solution which is very diluted. Groundnut shell which is considered as an carbonaceous and also as well as solid waste which is fibrous in nature. And also it creates one of the major problem of the disposal which is having a certain fuel value. From this product we can also generate some of the important activated carbon also by using one of the important product like groundnut shell. Some of the major influencing parameters which are considered as contact time and also as those of the absorbent include in the initial dye and its proper concentration along with some of the parameter like temperature and also as well as pH value are taken for the research. important methodology absorption Kinetic is been applied for the pseudo first order and also as well as second order which comes under important models. Some of the important analysis consider for the equilibrium data using one of the important models which are given by Langmuir and Freundlich isotherm. The evaluation also done important parameters of thermodynamic of the adsorption.

The main Objective of this study:

1. To prepare Groundnut shell activated carbon (GSAC).
2. To investigate Methylene blue Dye removal efficiency using Batch method along with efficiency of colour removal.
3. To study the influence of adsorption parameters such as contact time, adsorbent dose, initial dye concentration, temperature and pH.
4. To evaluate Adsorption kinetic by applying the Langmuir and Freundlich isotherms

2. MATERIALS

2.1 GROUNDNUT SHELLS

Groundnut shell product is available most widely in the agro. Based Industrial waste product consideration and also the degradation level is very slow. When compared to that of the natural condition of the degradation. Groundnut shell an agricultural product is used has adsorbent in this study, a healthy halve shells are collected and it is cleaned to remove the dirt & soil and it is sun dried for 72 hrs. Dried Groundnut shell powder was crushed to the powder and it is sieved in 300 microns. Then the powder is used for the activation process.

Fig. 1: Dried Groundnut shell powder and sieve

2.2 METHYLENE BLUE DYE

MB belongs to the group of cationic dye. It was a Heterocyclic & Aromatic compound with chemical formula of C_16 H_18 N_3 SCL & its MFW is 319.85 g/mol and its absorption wavelength is 665 MB was first examined by Heinrich Caro a German chemist in 1876. In the room temperature it was in form of solid, dark green powder, odourless & it will turn to blue when it mixed in the water.

Fig. 2: Structure of Methylene Blue dye

2.3 GSAC PREPARATION

Groundnut shell Activated Carbon is prepared by following steps. Activation is done by using conc. H2SO4 which is called chemical activation process. Concentrated sulphuric acid is added to the powdered groundnut shell in ratio 1:1.5 (W:V) then it is kept in a hot air oven for 12 hrs at 120 C°. It was washed till the acid is removed and its pH should come around 6.0 then it is soaked with 1% of sodium bi carbonate solution over night to remove free acids and washed it many times and kept in oven for 24 hrs at 105 C and is stored in a zip lock cover.

Fig. 3: Blast furnace burnt groundnut shell powder with sulphuric acid

2.4 ADSORBATE PREPARATION

The stock solution of MB dye was prepared with adding 1.5g powdered MB in 1 litre of water, concentration of 1500 ppm was prepared. And different concentration was prepared by series of dilution using RO water, synthetic sample was prepared and 50 ml of working solution is taken for analysis. The adsorbate is prepared by using N1*V1=N2*V2formula for different concentration. The chemicals used for this study were of Analytical-grade reagents. For preparing all of the solutions and reagents Double-distilled water was used. 0.1 M HCl or NaOH was used for initial pH.

3. METHODOLOGY

3.1 ADSORPTION ISOTHERMS

The Adsorption isotherm is a functional expression for the variation of adsorption with conc of adsorbate in bulk solution. Equations which express the experimental isotherm data were;

1. Langmuir equation
2. Freundlich equation

The linearized form of the Langmuir equation is as follows (Eq 1).

$$\frac{Ce}{Qe} = \frac{1}{k_L Q_m} + \frac{Ce}{Q_m} \quad \ldots\ldots\ldots (1)$$

Where;
Ce is the equilibrium concentration (mg L-1),
Qe is the amount adsorbed at equilibrium
(mg g-1),
Qm (mg g-1) and KL (L mg-1) are Langmuir constants.
(Fig 5.5) Shows the linear graph plotted between Ce/Qe vs Ce.
Qm and KL were tabulated from slop and intercept of the linear plot of Ce/Qe vs. Ce.

Linearized form of the Freundlich equation is as follows (Eq 2).
The slope 1/n ranging between 0 and 1, graph of log (Qe) vs. log (Ce) was plotted where the values of KF and 1/n are tabulated from the intercept and slope of the linear regressions.

$$\text{Log } Qe = \log Kf + 1/n \log Ce \quad \ldots\ldots\ldots\ldots\ldots(2)$$

3.2 RESPONSE SURFACE METHODOLOGY

In Minitab RSM is powerful statistical tool in optimizing and it is a mathematical technique useful for developing of optimization process and had advantage on other methods used normally in the case of large variables, it is very practical, economical and useful tool. The Box-Behnken method of design of experiment which gives maximum efficiency for an response surface methodology which mainly contain three factors pH, initial concentration, adsorbent dosage and sometime temperature and contact time also, which predict the number of trails by knowing the three levels (low, medium, high) and the number of runs is less compared to central composite design . Mainly Box –Behnken method has various applications in many fields like Spectro analytical method in optimization of chromatographic method and in capillary electrophoresis and electroanalytical method and so on.

3.3 ADSORPTION STUDY

Adsorption study was carried out according to the runs given by BBD. So Adsorbate MB dye stock solution was prepared and pH is varied with respect to design of experiment. (50 ml) from prepared stock was drawn in to 250 ml conically shaped flask. AC of groundnut shell was added according to the design and covered with cling foil paper. The mixture was kept in a shaker at temperature of 27 C and speed at 150 rpm with constant time of 1 hour. Then it was filtered and tested in spectrophotometer under wavelength of 665nm, observing the variations in optical density and concentration of samples and experimental conditions were noted and same of three trails were conducted.

Batch studies was govern to know the influence of the adsorbent by varying the dosage of AC from 0.1g to 2.5g at different concentrations by constant time and pH, and also the influence of CT also examined by varying the CT from 30min to 120min by constant adsorbent dosage and pH, variation of pH was examined and altering the pH from 6 to 12 by constant time and adsorbent by varying the pH by adding 0.1 M HCl and 0.1 M NaOH solutions. Also influence of adsorbate also examined by altering its concentration and other components kept constant. By knowing optimum results of above experimental conditions, further test was carried according to Box-Behnken design. A 2D contour plot and 3D surface plots were plotted to get clear idea of response w.r.t other factors. In the design the Adsorbate concentration varies from 100 ppm to 1500 ppm where middle term is given as 800 ppm and Adsorbent dosage is varies from 0.3 gram to 2.0 grams where 1.15 grams is considered as middle factor and pH is varies from 7 to 12 middle value is 9.5 and 13 runs is carried in three trails.

4. RESULTS & DISCUSSIONS

4.1 EFFECT OF pH

pH of the any media includes & controls the magnitude of the electrostatic charges. MB is a basic cationic dye so the rise in the pH leads to rise in % of adsorption slightly. Experimental study is carried from pH 6 to 12, basic dye gives positive charge when it dissolved in the water and in the acidic range positive charge surface of adsorbent tend to oppose the adsorption. So, the pH 8 is considered as optimum pH for further studies.

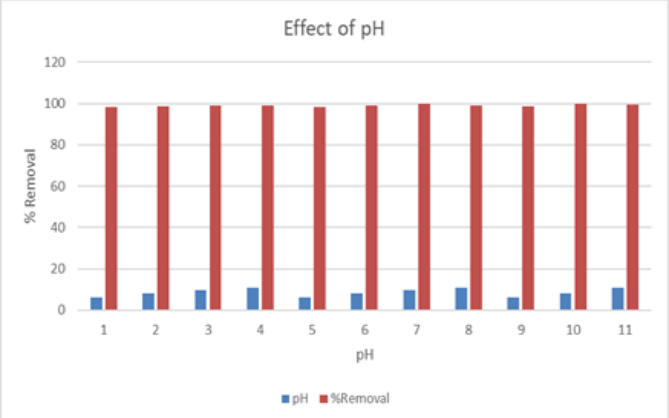

Fig. 4: Effect of pH and % Removal of MB

4.2 EFFECT OF CONTACT TIME

The removal efficiency also depends on the contact time. when the contact time increases % removal also increases so, varying the contact time from 30min till

120min. It is higher due to more active sites and then it is proceeds at low rate, so 60min is considered as optimum contact time for the dye removal.

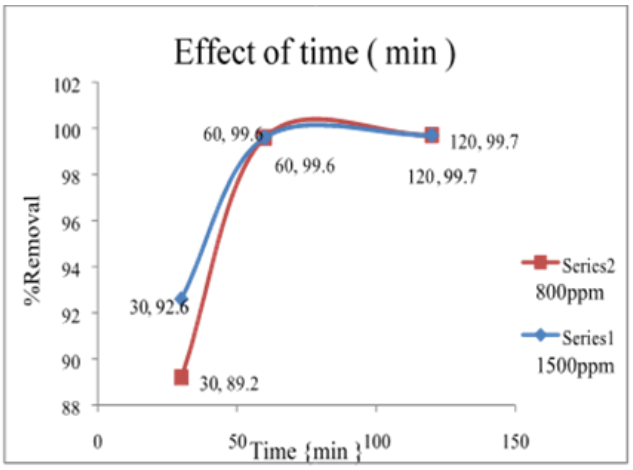

Fig. 5: Effect of Contact time on the Adsorption of MB to groundnut carbon

4.3 EFFECT OF ADSORBENT

The effect of AC dosage is a prime factor. The results say that increases in the conc of the dye the AC dosage also need to increases. Dosage of the adsorbent increases removal efficiency also increases as per above results for 100ppm 0.3g is very sufficient, for 800ppm 1.0g, for 1500ppm 2.0 g shows the higher removal efficiency When more amount of AC was added to solution which contain dye, the movement of dye ions to the active adsorption sites will be reduced, hence decrease the effectiveness in adsorption. As the adsorbent dosage increases % removal also increases, but equilibrium Qe (mg\g) decreases. The adsorption capacity of the Groundnut carbon is the accumulation of the MB dye on the AC mass & was identified on the basis of the principle called mass balance.

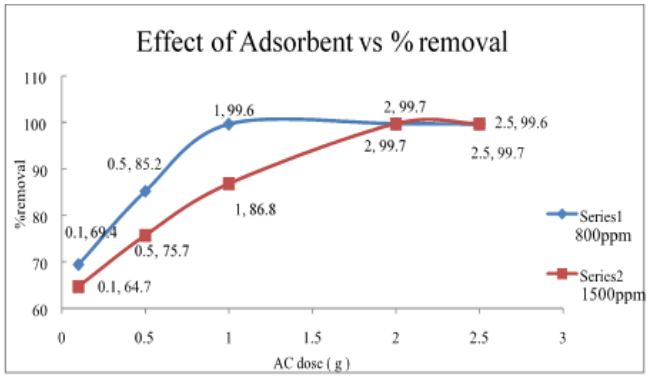

Fig. 6: Effect of AC as Adsorbent mass on adsorption

4.4 EFFECT OF ADSORBATE

At the lower concentration dye removal is efficient, when the concentration of dye increases removal % decreases so dosage of AC must be required to increased according to rise in conc to obtain higher removal efficiency. Lesser the removal % leads to increase in Qe.

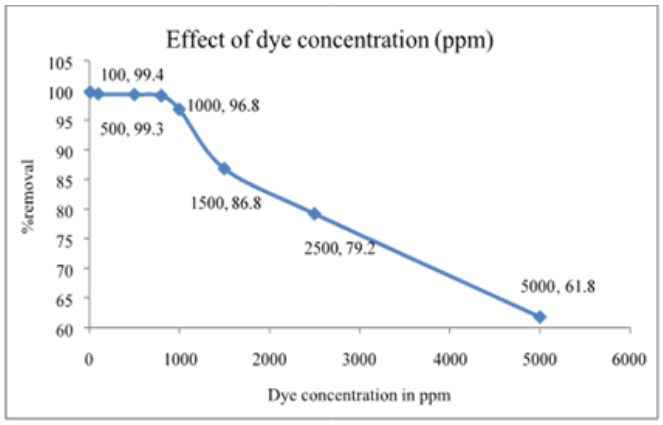

Fig. 7: Effect on Initial dye concentration

4.5 ADSORPTION ISOTHERMS

According to the above figures the adsorption best fit for Freundlich isotherm where R2 =0.992, n value must be between 0-1 here it was 0.555 hence the isotherm model of freundlich holds well.

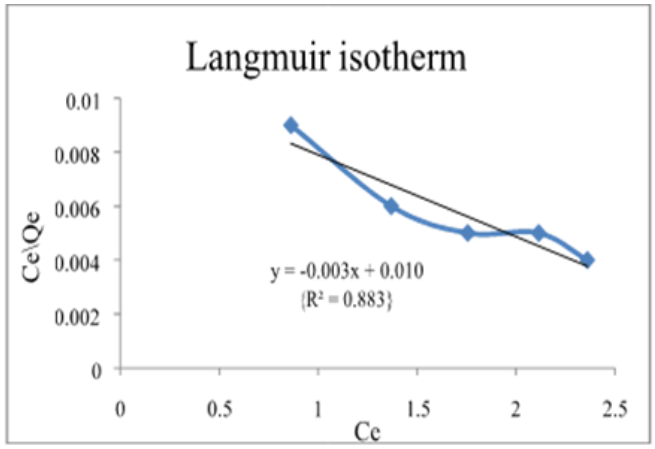

Fig. 8: Plot for Langmuir Ce / Qe vs Ce.

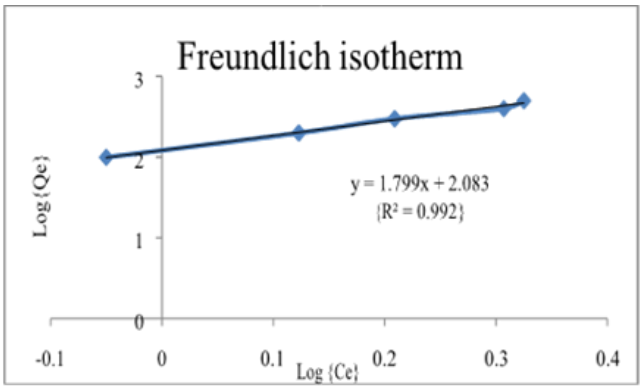

Fig. 9: Plot for Freundlich Log Qe vs Log Ce.

5. CONCLUSIONS

According to batch studies it was concluded that adsorption depend on contact time, adsorbate concentration, pH & also adsorbent AC dose. Main observation in this study was increase in the % removal leads to decrease in the Qe (dye adsorbed on AC) & vise–versa. sulphuric acid treated Activated Groundnut shell carbon results shows 95-99% of adsorption. When adsorbate conc. increases, accordingly adsorbent AC want to be increased. (100ppm=0.3g, 800ppm=1.0g, 1500ppm=2.0g). CT of 60 min and pH of 8 was considered as optimum. Adsorption followed by Freundlich isotherm where R2= 0.992.

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