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# DYE REMOVAL USING FROM WASTE MATERIAL AS A LOW COST ADSORBENT

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## ABSTRACT

Adsorbent prepared from granite powder (building waste material) was used to remove the methylene blue from an aqueous solution. The batch adsorption study was carried out by varying the parameters such as pH, Adsorbent dose, initial concentration of dye and contact time to obtained kinetic data. At optimum experimental condition maximum 84.62 % removal of dye was achieved. Equilibrium data were best represented by both Langmuir and Freundlich isotherms .The adsorption kinetic data are adequately fitted to the pseudo second order kinetic model. On the basis of experimental results sulphuric acid treated granite powder was found to be an excellent adsorbent for the methylene blue removal from wastewater.

## KEY WORD

SATGP (Sulphuric Acid treated Granite Powder), Methylene blue dye, Batch study, Adsorption isotherm.

## INTRODUCTION

Dyes are widely used in various industries, such as textile, paper , plastic , cosmetics as leather for coloring their final product. Dyes are highly coloured polymers and low biodegradable in nature. Dyes being one of the important recalcitrant persist for long distances in flowing water, retards photosynthetic activity, inhibit the growth of active biota by blocking out the sunlight and utilizing dissolved oxygen and also decrease the recreation value of stream.

Synthetic dyes have been extensively excreted in waste water from different industries particularly from textile, paper, rubber, leather, cosmetic, food and drug industries which used dye to colour their products. It is reported that over 100000 commercially available

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dyes exist and global annual production of synthetic dyes is more tham $7x10^5$ (1).

Dyes are widely used in the convectional biological treatment process is not very effective in treated by either physical or chemical processes. However, many of these technologies are expensive, especially when their used for treatment for large water streams. Consequently adsorption methods using low cost adsorbents have the most potential for application in industrial wastewater treatment (2).

Coloured effluent from dyes consuming industries give undesirable perspective to the water streams where as some dyes and their metabolites pose toxic. Carcinogenic, mutagenic and teratogenic effects.

Methylene blue (M.B) is the most common among all other dyes of its category. It is generally used in dyeing textile specially cotton and silk and in some medical treatments. Though MB is not strongly hazardous it can cause some harmful effects. It can cause eye injury for both human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting profuse sweating, diarrhea, gastritis, mental confusion and methemoglobinemia (3,4). Acute exposure to MB can cause increased heart rate, vomiting, jaundice and tissue necrosis in humans (5). Thus, the removal of MB from industrial effluents has become one of the major environmental concerns.

The most commonly used adsorbent for this purpose has been activated carbon (6) but due to the relatively high operating costs, such as regeneration of the used adsorbents has limited application on a larger scale recently numerous approaches have been studied for the development of cheaper and effective adsorbents (7).

Many non-conventional low-cost adsorbents including natural materials, biosorbents and waste materials from industry and agriculture have been proposed by several workers. These materials could be used as adsorbents for the removal of dyes from solution. Some of the reported adsorbents include clay materials (bentonite, kaolinite ), Zeolites, siliceous material (silica beads , alunite, perlite), agricultural wastes ( bagasse pith, maiz cob, rice husk, coconut shell) (8-10), industrial waste products (waste carbonslurries, metal hydroxide sludge) biosorbents (chitosan, peat, biomass) 11-13. The present study is aimed towards the development of an industrially viable, cost effective we use low cost adsorbent for the removal of methylene blue dye.

## MATERIALS AND METHODS:

### Adsorbent Preparation

The waste granite stone powders were collected from construction sites/suppliers of building material, or local stone cutting shop. The building waste granite stone were grinded into powder and were boiled in distilled to remove any dust from it and filter the residue of granite (untreated) and it was treated with formaldehyde and finally with very dilute solution of sulphuric acid and left to dry at room temperature for 24h. the dried material (sample) then kept in an oven for 24h at $180^0$ for activation step were blended to produce granular activated adsorbent and washed with distill water to remove excess acid. The pH of it becomes constant and the filtrations during washing were carried by vaccum filtered through whatsmann filter paper. The product obtained was wet-screed and dried in oven at $80^0$c overnight.

The adsorbent once prepared were used throughout the experimental work. The particle size of the adsorbent was of the same mesh (micron)

**DYE SOLUTION PREPRATION**

Methylene blue dye is widely used in textile, paper and carpet industries. It is a basic cationic dye used for the present work is given in table1. An accurately weighed quantity of the dye is dissolved in double distilled water to prepared stock solution (1000ppm) solution used in the experiment for the desired concentration was determined by using absorbance values measured before and after the treatment at 650nm with shimadzu UV visible spectrometer (Model: UV mini 1240). Experiments were carried out at initial pH value is 6.5 and was controlled by addition of sodium hydroxide or hydrocholoric acid, adsorbents given in Table 2

**Table 1: properties of methylene blue**

| | |
|---|---|
| Chemical formula | C14H18N3SCl |
| Molecular weight | 319.85 g/mol |
| Melting point | 100-$110^0$c |
| Type of dye | Basic blue |
| Boiling point | Decmopses |
| Tmax | 665nm |

**Batch adsorption experiment**

Batch experimentation were carried out at room temperature to the study the effects of important parameters such as effect of pH, contact time, initial concentration and amount of adsorbent.

In each adsorption experiment, 100ml of dye solution of known concentration and pH was added to 1gm of adsorbent in 250ml round bottom flask.

This was done at room temperature ($27+_{-}\ _1{}^{0c}$) and the mixture were stirred on a rotator orbital shaker at 160rpm. The initial pH of the mixtures was varied between 2-7 this was controlled by addition of dilute HCI or NaoH Solutions.

Kinetic of adsorption was determined by analysing adsorptive uptake of the dye form the aqueous solution therefore samples were withdrawn from the shaker every 15-30 minutes and adsorbent was separated from the solution by centrifugation at 4500 rpm for 5 minutes. In order to determine the residual concentration the absorbance value of the supernatant solution was measured before and after the treatment at 617nm with shimadzu spectrophotometer.

The experiment was done by varying the amount of adsorbents (1gm to 5gm $100ml^{-1}$) and pH (2-7) at different time interval.

## RESULTS AND DISCUSSION

### EFFECT OF pH

The interaction between dye molecule and adsorbent is basically a combined result of charges on dye molecule and the surface of the adsorbent (14). **Figure 1.** shows that pH of the solution has significantly affect adsorption of MB on SATGP (sulphuric acid treated granite powder) achieved its optimum adsorption capcity for methylene blue at pH=7. It is evident that uptake of the dye is the increased consistently with pH. The adsorption of the methylene blue on the adsorbent surface is influenced by the surface charge on the adsorbent and the initial pH of the solution (15). As the pH of the solution increases, the number of the negatively charged site increased strong electrostatic attraction exists between the positively charged cationic dye molecules. As a result a negatively charged surface on the adsorbent favours the adsorption of the dye (16). Several investigations have reported that MB 76 % adsorption usually increased (17-19).

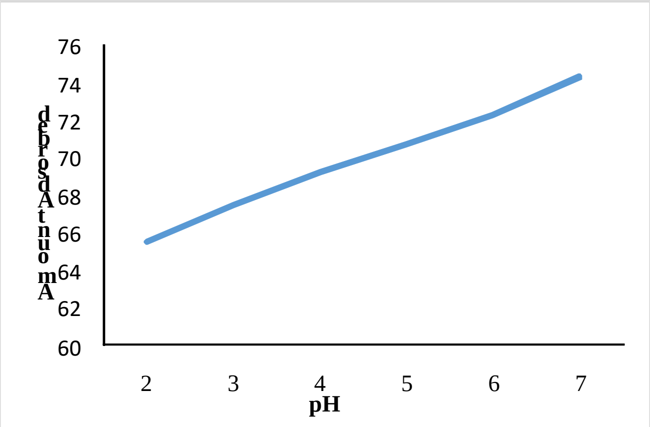


**Fig 1:** Effect of pH on percentage removal of methylene blue (250mg/L) at room temp.

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## EFFECT OF ADSORBENT DOSE

Adsorbent dose is representing important parameter due to its effect on the capacity of an adsorbent at given initial concentration of adsorbate. Effect of adsorbent dose on removal of MB was monitored by varying adsorbent dose (1,2,3,4 and 5gm/100ml) in the solution while keeping the initial dye concentration (250mg/L) temperature(27 +/- $1^0$c) and pH (7.0) constant.

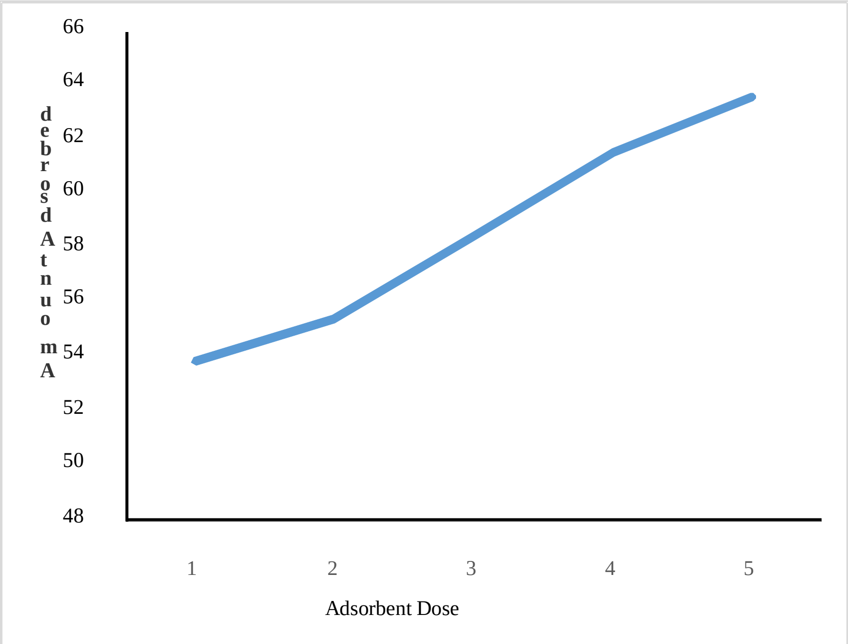


**Figure 2**. The effect of adsorbent of dosage.

The adsorption of dye increased with the adsorbent dosage and reach on the equilibrium value after 4.5gm of adsorbent dose (as shown in **fig. 2**) as one was accepted, the percentage of dye removal was increased with increasing amount of SATM, however the ratio of the dye adsorbed to SATMP (mg/g) decreased with increasing amount of adsorbent SATMP similar results were reported by patil *et al*. (20). Many factors can attribute to this adsorbent concentration effects. The most important factors is that adsorption site remains unsaturated during the adsorption reaction. This decrease in adsorption capacity with increase in adsorbent dose is mainly attributed non saturation of the adsorption sites during the adsorption process (21- 22). The ratio of the dye adsorbed to SATGP further increases after 1.0 there is no significant change in adsorption thus 5.0gm SATGP adsorbent dose was chosen for study other parameters. Figure **2**. Effect of adsorbent dose on removal of methylene blue for concentration 250mg/L agitation time 60 min at pH 7

**Effect of initial dye concentration**

In the present study, it has been observed that for SATGP, the percentage of dye removal was high. It is presented in fig 4. The experiments were carried out at fixed adsorbent dose (0-9gm/100ml) at constant temperature.

The variation in the concentration of the dye solution (0.5 to 5.0 /$10^{-5}$M). These concentration ranges follows the Lambert's Beer's law (23) generally adsorption consists of diffusion of the dye molecule from the bulk solution to the surface of the adsorbent mostly the adsorbed dye content gradually increases constantly upto certain time limit and finally attains the equilibrium indicating a saturated adsorption (24,25) . It was significant different with percentage removal that decreased from 84.10% to 71.32% as initial concentration increased. At lower dye concentration, the available adsorption site are relatively high and the consequently the dye species can find easily the accessible adsorption sites (26), However, at higher concentrations the available site of adsorption become fewer and consequently the dye ions take more time in order to reach the last available sites (27) furthermore the adsorption dynamic profile shows that equilibrium has been reach in 90 minutes.

**Isotherm Modeling**

The adsorption isotherm represents the relationship between the amount adsorbed by a unit weight of solid adsorbent and the amount of adsorbate remained in the solution in the equilibrium time (28) Langmuir and Freundlich isotherms were used to describe the equilibrium adsorption. Langmuir isotherms (29) refers to homogeneous mololayer adsorption whereas as the linear form of the Freundlich isotherm a heterogeneous adsorption capacity and adsorption intensity with non uniform distribution of heat of adsorption (33). The equation of these models are given as

**Langmuir isotherm**

$C_e / q_e = 1/q_{max}k_L + (1/q_{max})\, c_e.$

Where $q_e$- is the amount of adsorbate in the adsorbent at equilibrium (mg/g).

$C_e$- is the equilibrium concentration (mg/L) and

$Q_{max}$ and $k_L$ are the Langmuir isotherm constants related to free energy. The above equation can be linearized to get the maximum capacity, $q_{max}$ by plotting a graph of $c_e/q_e v_s c_e.$

**Freundlich isotherm**

$Q_e = k_f\, c_e^{1/2}$

On rearranging this equation we get

$\text{Log}\ q_e = \log k_f + 1/n \log c_e$

Where $k_f$ and 1/n are freundlich isotherm constants related to adsorption capacity and adsorption intensity respectively. A plot of log x/m $v_s$ log c yields a straight line with a slop of 1/n and intercept log $k_f$

The Langmuir and Freundlich adsorption isotherms of methylene blue on SATMP are shown in fig **2, 3.** Table **2** gives the values of parameters and correlation coefficient of the Langmuir and Freundlich equations. The experimental results indicated that the adsorption isotherm of methylene blue adsorption of SATMP followed both Langmuir and Freundlich models. Uddin *et al* (31) also reported the same observation for methylene blue figure **2**.

**Table 2.** The values of parameters and correlation coefficient of the Langmuir and Freundlich equations

| **Langmuir** | | | **Freundlich** | | |
|---|---|---|---|---|---|
| $q_{max}$ | $K_L$ | $r^2$ | $K_F$ | 1/n | $r^2$ |
| 0.58 | 0.14 | 0.9710 | 6.975 | 0.5964 | 0.9820 |

**Adsorption kinetics**

The kinetic adsorption data were processed to study the dynamics of the adsorption process in expression of the order of rate constant. Kinetic date were analysed with the pseudo first order and pseudo second order kinetic models (32). Equation for pseudo first order model is

$$\text{Ln}(q_e - q_t) = \ln q_e - k_1 t$$

Where $q_e$ is the adsorption capacity at equilibrium (mg/g), $q_t$ is the amount of adsorbate adsorbed at time t (mg/g) and $K_1$ is the pseudo first order rate constant ($min^{-1}$). The pseudo first order equation of Lagergren model, traditionally used for describing sorption kinetics, is generally expressed by equation ( kanchana *et al* 1992, Szeto et al 2004 ) where k (mg/g.min) is the lagergren rate constant of the first order sorption, evaluated from the slope of the plot $\ln(Q_e-Q_t)$ versus t

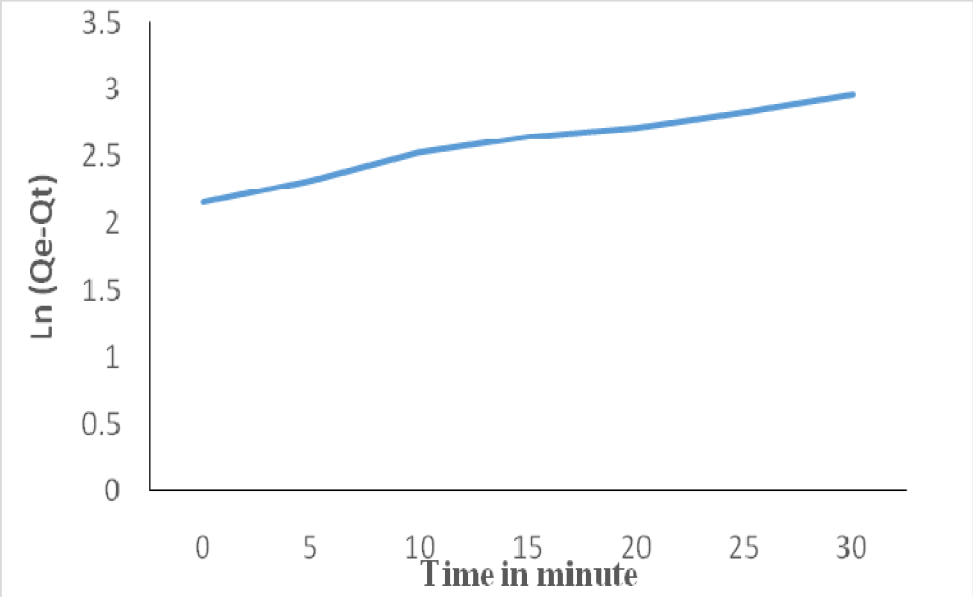


**Fig 3**: Pseudo first order kinetics models to methylene blue adsorption on SATMP.

## CONCLUSION

In the present study, building waste material, granite powder was treated with sulphuric acid. This sulphuric acid treated granite powder was selected as local, cheaper and readily available adsorbent for the removal of methylene blue from the aqueous solutions. SATGP as low cost adsorbent may be appropriate for the treatment of dye effluent released from small scale industries. The adsorption isotherms are considered and they well described the adsorption process indicating favourable adsorption of methylene blue onto treated granite powder. Removal of methylene blue is highly pH dependent the best results being obtained at pH 7. The adsorption capacity was found to increase significantly with increase in the adsorbate, pH and adsorbent dose therefore; the present study shows that the sulphuric acid treated granite powder can be effectively used as adsorbent for the colour removal from waste water.

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