

Removal of Methylene Blue Dye from Waste Water Using Agro – Waste as Low Cost Adsorbent

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ABSTRACT: The present study is to evaluate the adsorption potential of Citrus Limonum (Lemon) peel as a low cost adsorbent for the removal of methylene blue dye from aqueous solution. Agricultural waste products are quite commonly distributed as the result of agricultural practices. They are inexpensive and subject to biodegradable. Agricultural wastes are good sources for the adsorption of the dyes. Batch experimental studies were performed to evaluate the influence of various experimental parameters like adsorbent dose, effect of pH, effect of agitation time, initial dye concentration at different temperature, particle size of the adsorbents and different contact time. The sorption data were correlated with Langmuir and Freundlich isotherm models. The results of the present study confirmed that, lemon peel adsorbent can be effectively used as an inexpensive adsorbent for the removal of dyes from waste water or industrial effluents.

KEYWORDS: lemon peel, adsorption, methylene blue Langmuir and Freundlich isotherms.

I. INTRODUCTION

Colour is the most obvious indicator of water pollution. The discharge of coloured wastes into streams not only affects their aesthetic nature but also interferes with the transmission of sunlight into streams and therefore reduces photosynthetic action [1]. Dyes are used extensively in the textile, leather, food processing, cosmetics, paper and dyeing industries [2]. It is estimated that 2% of dyes produced annually are discharged as effluents from textile and associated industries [3]. Over 10^5 commercially available dyes exist and more than 7×10^5 tonnes of dye are produced annually [4]. However, approximately 7×10^5 tonnes / year of dyes are discharged into waste streams by the textile industry [5]. Most of these dyes are of synthetic origin and toxic in nature with suspected carcinogenic and genotoxic effect [6, 7]. In addition the dyes in water cause human health disorders, such as severe damage to the kidneys and central nervous system [2]. The presence of these dyes even at a very low concentration is highly observable and undesirable. Many health related problems such as allergy, dermatitis, skin irritation, cancer and mutations in humans are associated with dye pollution in water [8]. Therefore, dye removal has been a very important but challenging area of waste water treatment. The effluents containing dyes are highly coloured and cause serious water pollution. Dyes are broadly classified as anionic, cationic and non – ionic depending on the ionic charge on the dye molecules. Cationic dyes are more toxic than anionic dyes [9]. Therefore, the removal of dyes from effluents prior to mixing with natural water is very important method.

Many treatment processes have been applied for the removal of dye from waste water such as Fenton process, photo catalytic and electrochemical combined treatments, photo catalytic degradation using UV / TiO_2 , chemical coagulation / flocculation, ozonation, cloud point extraction, adsorption, ion exchange, reverse osmosis and ultra filtration method [10].

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Among treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent. Some of the advantages of adsorption process are possible regeneration, at low cost, availability of known process equipment, sludge – free operation and recovery of the sorbate [11]. Activated carbon is the most widely used adsorbent for dye removal because of its extended surface area, micro – pore structures, high adsorption capacity and high degree of surface reactivity. However, commercially available activated carbon is very expensive and has high regeneration cost while being exhausted. Furthermore, regeneration using solution produces a small additional effluent while regeneration by refractory technique results in a 10 – 15 % loss of adsorbent and its uptake capacity [12]. This has lead to search for cheaper substances. Researchers are always in a hunt for developing more suitable efficient and cheap and easily available types of adsorbents, particularly from the waste materials.

Agricultural waste materials have little or no economic value and often pose a disposal problem. The utilization of agricultural waste is of great significance [13]. In this work, the low cost adsorbent Sulphonated Citrus Limonum Charcoal (SCLC) has been tested for effectiveness in decolourisation of wastewater containing methylene blue (MB) hazardous dye. Effect of various parameters such as P^H , adsorbent dose, particle size, concentration, time and temperature has been investigated in the study.

II. EXPERIMENTAL METHODS

ADSORBENT MATERIAL

The Citrus Limonum waste (SCLC) (Fig.1) were collected from agricultural land area and carbonized with con. sulphuric acid in the weight ratio of 1:1 (W/V). Heating for 12 hrs in a furnace at 400°C for complete carbonization and activation. The resulting carbon was washed with distilled water until a constant pH of the slurry was reached. Then the carbon was dried for 4 hrs at 100°C in a hot air oven. The dried material was ground well to a fine powder (Fig.2) and sieved to 0.2mm by using a standard mesh. The activated carbon prepared was characterized by conventional chemical and physical methods.



Fig. 1 Citrus Limonum waste



Fig. 2 Activated carbon prepared from lemon waste

ADSORBATE MATERIAL

All the chemicals including methylene blue dye used were of high purity commercially available analytical grade (AR – sd fine - India). Stock solutions of 1000mg/L of dye were prepared using double distilled water. From this stock solutions, we used for adsorption studies.

BATCH EQUILIBRIUM METHOD

The adsorption experiments were carried out in a batch process at 30, 40, 50 and 60°C temperatures. The known weight of adsorbent material was added to 50 ml of the dye solution with initial concentration of 10mg/L to 50mg/L. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120rpm. The solution was then filtered at preset time intervals and the residual dye concentration was measured using UV-spectrometer [14].

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The amount of dye adsorbed per gram of adsorbent i.e q_e at a time t , has been calculated by using the following formula [15],

$$q_e = \left(\frac{C_0 - C_e}{W} \right) V \quad \text{-----(1)}$$

Where, q_e is the amount of dye adsorbed, C_0 and C_e (mg/L) are the liquid phase concentrations of dye at initial and equilibrium respectively.

The percentage of dye removed was calculated by the following formula [15],

$$\% \text{ of dye removed} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad \text{-----(2)}$$

EFFECT OF VARIABLE PARAMETERS

The various doses of the adsorbents are mixed with the dye solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

In order to determine the rate of adsorption, experiments were conducted with different initial concentration of dyes ranging from 10 to 50mg/L. All other factors were kept constant.

The effect of period of contact on the removal of the dye on adsorbent in a single cycle was determined by various time intervals and keeping particle size, initial concentration dosage, pH and concentration of other ions constant.

Adsorption experiments were carried out at pH 2,4,6,8 and 10. The acidic and alkaline pH of the medium was maintained by adding the required amount of dil.HCl and NaOH solutions. The parameters like particle size dye concentration,, dosage of adsorbent and concentration of other ions are kept constant while carrying out the experiments. The pH of the samples was determined using a portable pH meter (Systronics model).

The adsorption experiments were performed at four different temperatures viz 30, 40, 50 and 60°C in a thermostat attached with a shaker. The constancy of the temperature was maintained with an accuracy $\pm 0.5^\circ\text{C}$.

III. RESULT AND DISCUSSION

SPECTRAL CHARACTERIZATION - FT-IR SPECTRA

The FT-IR spectra of the free and MB loaded adsorbents were presented in Fig.3. It can be seen that these peaks moved away or moved out after the adsorption of MB onto the adsorbents

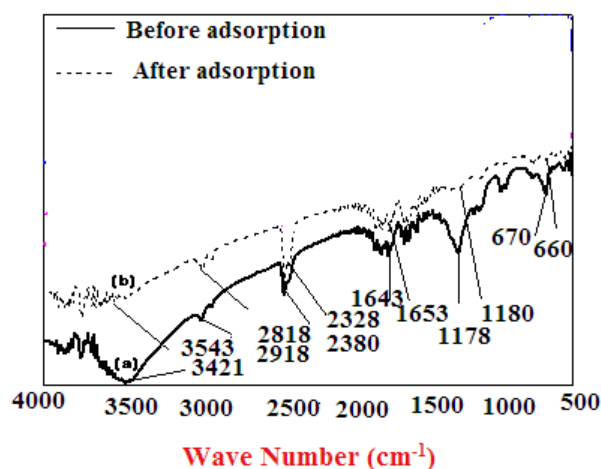


Fig.3 (a) and (b) FT-IR spectra of the free and MB loaded SCLC

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SEM

The SEM images of free and MB loaded SCLC (Fig.4 a & b) showed various surface characteristics. The surface of free adsorbents appeared to be bumpy in nature, at the same time as a few solids were observed on the surface after MB adsorption, possibly due to the formation of MB – adsorbents complex [16].

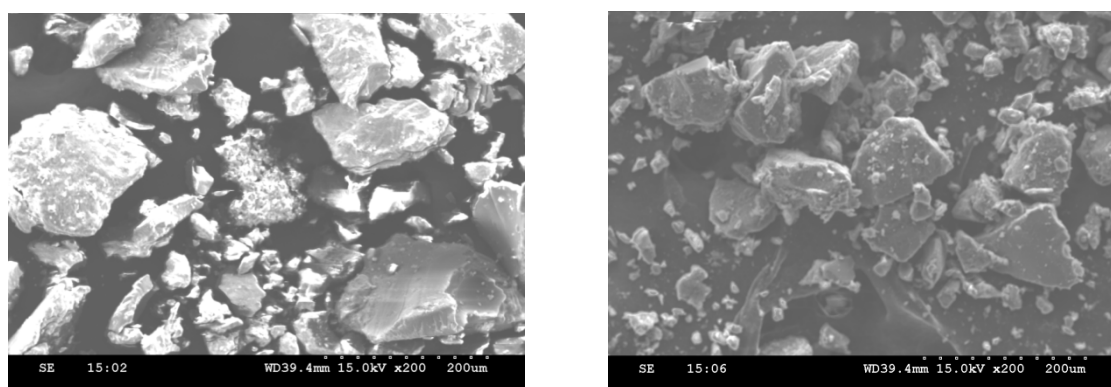


Fig.4 (a) and (b) SEM images of free and MB loaded SCLC

TGA & DTA

The TGA (Fig.5a & b) & DTA (Fig.6a & b) analysis of the free adsorbents and MB loaded adsorbents are showed a move in temperature dominant peaks related with the loaded dye. This change in the temperature shows that the MB binding process taking place at the surface of adsorbents [17].

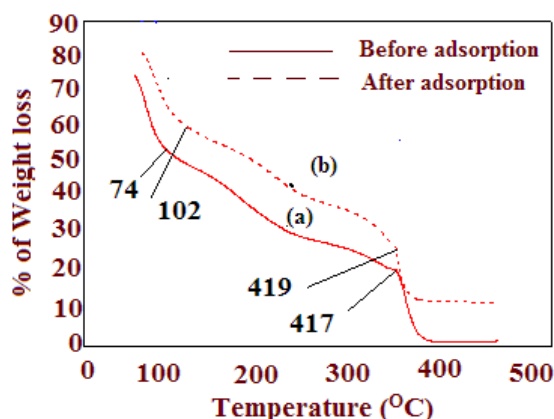


Fig.5 (a) & (b) TGA analysis of free and MB loaded SCLC

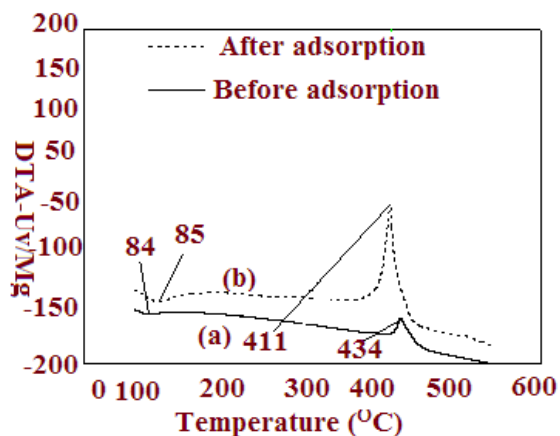


Fig.6 (a) & (b) DTA analysis

EFFECTS OF RESIN DOSAGE

Fig.7 gives an idea about the correlation between adsorbent dosage and adsorption capacity. The maximum adsorption capacity was observed for the resin dosage of 0.060g/L. It is clear that the adsorption capacity of MB increased with increasing adsorbent amount from 0.010 to 0.060g/L. It can be due to the increase in adsorbent site available for the adsorption of MB. Followed by there is a slender turn down with an increase in adsorbent amount from 0.060 to 0.080g/L. This movement can be accredited due to the decreasing efficient surface area. Hence, 0.060g/L was desired as the optimum dose and was used in further experiments [18].

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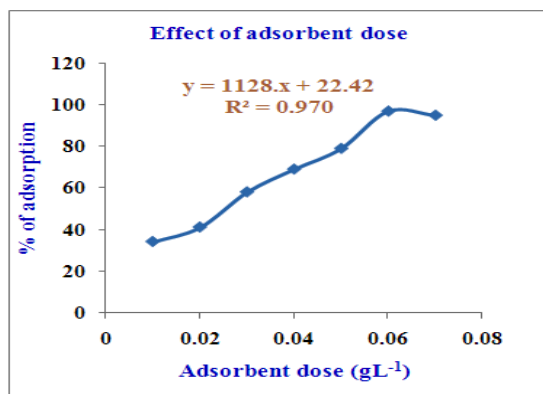


Fig.7. Effect of resin dosage

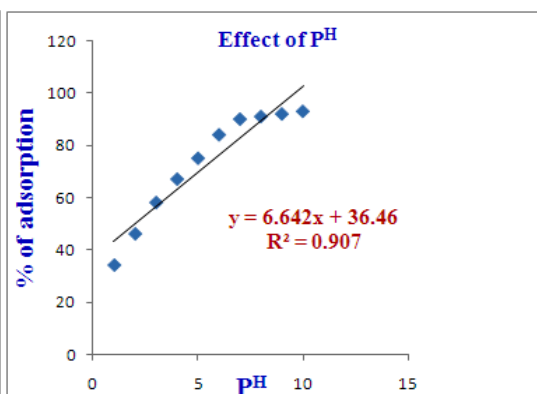


Fig.8. Effect of P^H

EFFECT OF P^H

pH as a very important factor was found to have participated significant role in adsorption of MB dyes from the synthetic dye wastewater. The maximum adsorption of MB dyes (90%) onto SCLC was achieved at pH 8 (Fig.8). At pH 8, the adsorbent surface is negatively charged that provides more electrostatic attraction between SCLC 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 [19].

ADSORPTION ISOTHERM STUDY

The found equilibrium data from the adsorption of MB onto the SCLC fitted to the linear equation of Langmuir and Freundlich isotherm models. The linear equation for Langmuir, Freundlich and Redlich Peterson isotherm models are given below,

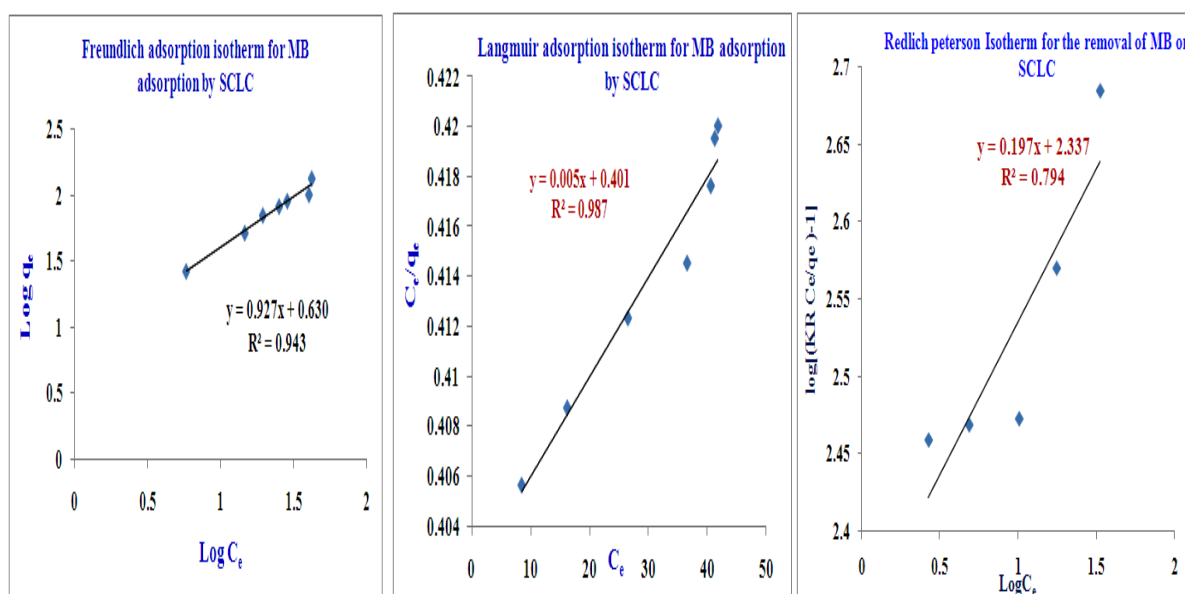


Fig.9.(a), (b) & (c) Freundlich, Langmuir & Redlich Peterson plots for the MB removal

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Adsorption isotherm parameters

Dye	Langmuir			Freundlich			Redlich Peterson				
	Q_0 (mg/g)	b (g/l)	$R_L = 1/(1+Q_0b)$	R^2	N	K_F	R^2	K_R	αR	β	R^2
MB	194.25	0.0124	0.1853	0.987	1.0787	8.4527	0.943	2.493	2.337	0.197	0.794

IV. CONCLUSION

The removal of MB dye onto the SCLC was investigated under various conditions. The adsorption process was studied under parameters like pH, contact time, initial dye concentrations and adsorbent doses. The maximum dye removal occurred at pH 6 within 60 minutes time intervals. The experimental data fitted well with Langmuir isotherm data than the other isotherm data, which indicates the monolayer adsorption. The Langmuir constant (R_L) and Freundlich constant (n) both are favoured the adsorption system. SCLC could be employed as a best suitable low cost adsorbent for the efficient removal of MB dye molecules.

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