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Removal Of Methylene Blue Dye From Aqueous Solutions By Neem Leaf And Orange Peel Powder

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Abstract : The objective of this work is the study of adsorption of dye solution methylene blue using low cost adsorbent like neem leaf and orange peel powder. Liquid phase adsorption experiments were conducted. Batch adsorption studies are carried out by observing the effect of experimental parameters, namely amount of adsorbents, dye concentration and contact time. Optimum conditions for dye removal are studied like contact time required, amount of adsorbent and dye concentration. Spectrophotometric technique was used for the measurement of concentration of dye before and after adsorption. The removal data were fitted on Langmuir adsorption equations. The equilibrium time was found to be 18 min for 2.5×10^{-5} mg/L dye concentration respectively. A maximum removal of 90-95% was obtained for an adsorbent dose of 0.3 gm. at 2.5×10^{-5} mg/L dye concentration The results generated by this work can be used for determination of optimum conditions for adsorption of dye in aqueous solutions. Dyes are present in mixture form in various Industrial effluents like Textile Industries, Sewage water, Water treatment plants. This work could have use in Design of adsorption columns for dye removal.
Key words: Adsorption; Methylene blue; Low cost natural adsorbent; Langmuir isotherm; Dye removal.

Introduction

Dyes are highly colored polymers and low biodegradable in nature. Dye being one of the important recalcitrant, persist for long distances in flowing water, retards photosynthetic activity, inhibit the growth of aquatic biota by blocking out the sunlight and utilizing dissolved oxygen and also decrease the recreation value of stream.
Numerous studies have been conducted to assess the harm impacts of colorants on the ecosystem. It was found that dyes may cause problems in water in several ways:
(i) dyes can have acute and/or chronic effects on exposed organisms with this depending on the dye concentration and on the exposure time;(ii) dyes are inherently highly visible, minor release of effluent may cause abnormal coloration of surface waters which captures the attention of both the public and the authorities; (iii) the ability of dyes to absorb/reflect sunlight entering the water, this has drastic effects on the growth of bacteria and upsets their biological activity; (iv) dyes have many different and complicated molecular structures and therefore, are difficult to treat and interfere with municipal waste treatment operations; (v) dyes in wastewater undergo chemical and biological changes, consume dissolved oxygen from the stream and destroy aquatic life; (vi) dyes have a tendency to

sequester metal ions producing micro toxicity to fish and other organisms.[2]

Methods for treating textile dye wastewaters consist of various chemical, physical and biological processes. These include: adsorption, nanofiltration, colloidal gas aphrons, ultrasonic decomposition, electro coagulation, coagulation and precipitation, advanced chemical oxidation, electrochemical oxidation, photo-oxidation, predispersed solvent extraction, ozonation, supported liquid membrane and liquid-liquid extraction.[6]

The most commonly used adsorbent for this purpose has been activated carbon[7] but, due to the relatively high operating costs, such as regeneration of the used adsorbent had limited application on a larger scale. Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents.[4]

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, maize cob, rice husk, coconut shell)[21-23], industrial waste products (waste carbon slurries, metal hydroxide sludge), biosorbents (chitosan, peat, biomass)[13-15] and others (starch, cyclodextrin, cotton).[16-19] In the present study, we report the use of neem leaf and orange peel powder as an adsorbent for the removal of methylene blue dye.

Materials and methods

a. Preparation of stock solution of Methylene blue dye

Methylene blue dye is widely used in textile, paper and carpet industries. It is a basic cationic dye. Methylene blue dye [C.I. =52015B, chemical formula=$C_{16}H_{18}ClN_3S$; molecular weight= 373.91g; melting point =100–110 °C and λ_{max}=660 nm (reported) and 662 nm (experimentally obtained) was manufactured by Merck India. An accurately 0.0373 gm. weighed quantity of the dye was dissolved in 100 ml distilled water to prepare stock solution. The solution is blue in colour. Experimental solutions of the desired concentration were obtained by dilutions of stock solution in 100 ml of distilled water.

b. Preparation of the adsorbent

Orange peel is discarded in the orange-juice and soft-drink industries all over the world. It has been used as an adsorbent for the removal of dyes from wastewater[14]. Waste orange peel was obtained from a fruit stall, cut into small pieces, dried in sunlight for 4 days and powdered. The powdered orange peel was sieved and used as an adsorbent.

The neem belongs to the meliaceae family and is native to Indian sub-continent. Its seeds and leaves have been in use since ancient times to treat a number of human ailments and also as a household pesticide. The trees are also known as an air purifier. The medicinal and germicidal properties of the neem tree have been put to use in a variety of applications. The mature neem leaves used in the present investigation were collected from the trees in near by area. They are washed thrice with water to remove dust and water soluble impurities and are dried until the leaves become crisp. The dried leaves were powdered. The parameters which affect wastewater treatment, such as dye concentration and adsorbent dosage were investigated in batch-mode adsorption studies.

c. Estimation of optimum amount of adsorbent

In order to find out the optimum amount of adsorbent at which maximum adsorption takes place, 1.7×10^{-5} mg/L of methylene blue dye solution was taken in a series of flasks with different quantity of adsorbents; 0.1, 0.2, 0.3, 0.4 and 0.5 gm. of neem leaf and orange peel powder. The solution of dye was kept on a shaking magnetic stirrer for 15-20 min at 120 rpm for shaking. Dye concentration to be estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λ_{max}, using a spectrophotometer (systronics spectrophotometer 166). The samples to be withdrawn from the magnetic stirrer at predetermined time intervals and the dye solution should be separated from the adsorbent by the help of a Centrifuge. The absorbance of solution is then measured.

d. Estimation of optimum concentration of dye solution

For the determination of optimum concentration of dyes, solutions of different concentrations of dye were prepared. From 1.7×10^{-5} mg/L to 3.5×10^{-5} mg/L of dye solution was placed in respective flasks with optimum amount of adsorbents for 15-20 min. The samples to be withdrawn from the magnetic stirrer at predetermined time intervals and the dye solution should be separated from the adsorbent by the help of a Centrifuge. The absorbance of solution is then measured. Dye concentration to be estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λ_{max}, using a spectrophotometer (systronics spectrophotometer 166).

Results

Rate of adsorption of Methylene blue on the surface follows the classical Langmuir–Hinshelwood expression and that the sorption of the dye to the surface follows most often Langmuir sorption isotherm. In Langmuir–Hinshelwood treatment of heterogeneous surface reactions, the adsorption rate is described by pseudo first order kinetics which is rationalized in terms of the modified model to accommodate reactions occurring at a solid-liquid interface as-

$$r = \frac{-dC}{dt} \qquad \frac{k_r KC}{(1+KC)}$$

Where r is the rate of disappearance of the dye and C is the dye concentration in irradiation time t. K represents the equilibrium constant for adsorption of the dye and k_r represents the limiting rate of the reaction at maximum coverage under the experimental conditions.

The adsorption of Methylene blue dye follows pseudo first order kinetics. The detection was realized at 662 nm. The results for typical run are given in Fig. The absorbance of dye decreases with an increase in time.

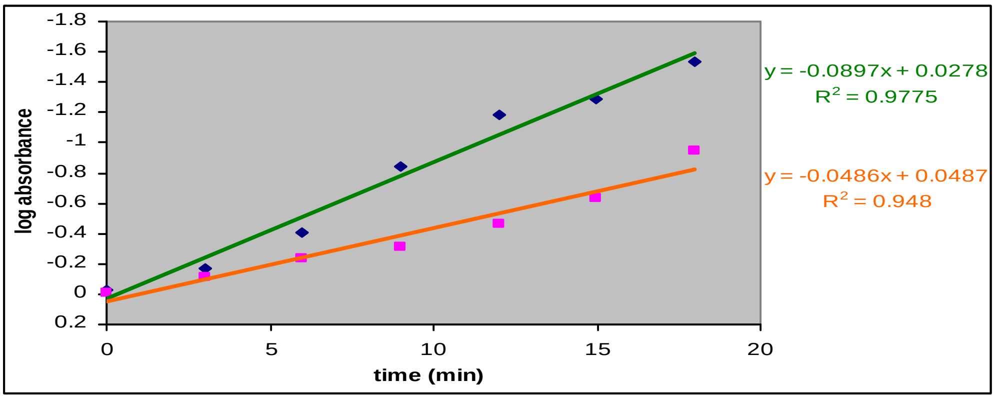

Fig 1: time Vs absorbance at 0.3 gm amount of adsorbent

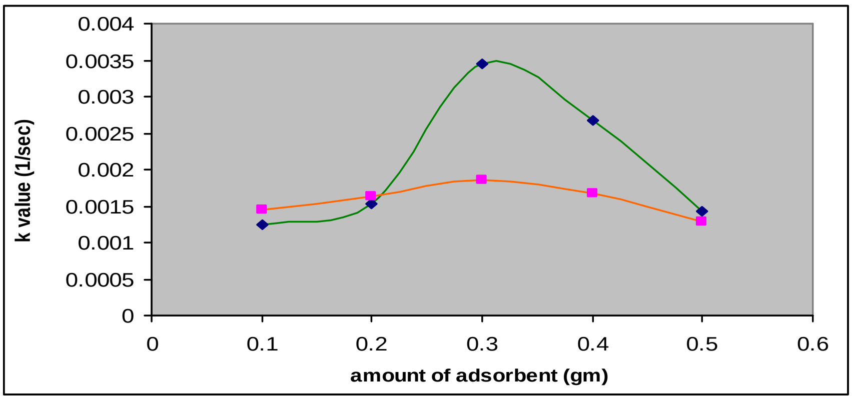

Fig 2: amount of adsorbents Vs k value

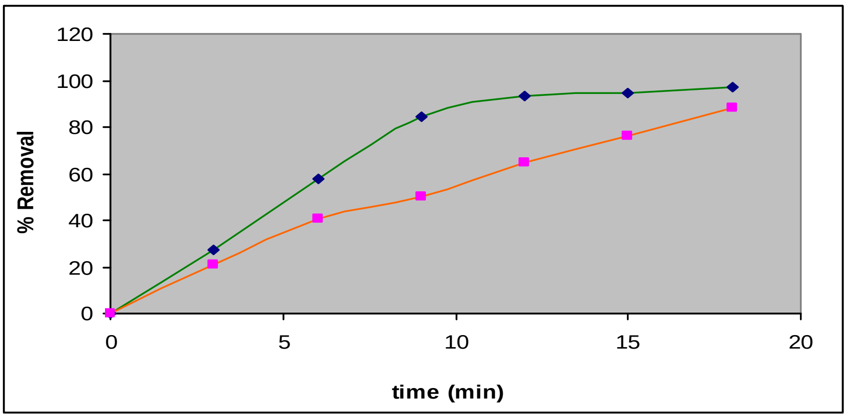

Fig 3: % Removal of dye at the optimum amount of adsorbent (0.3 gm.)

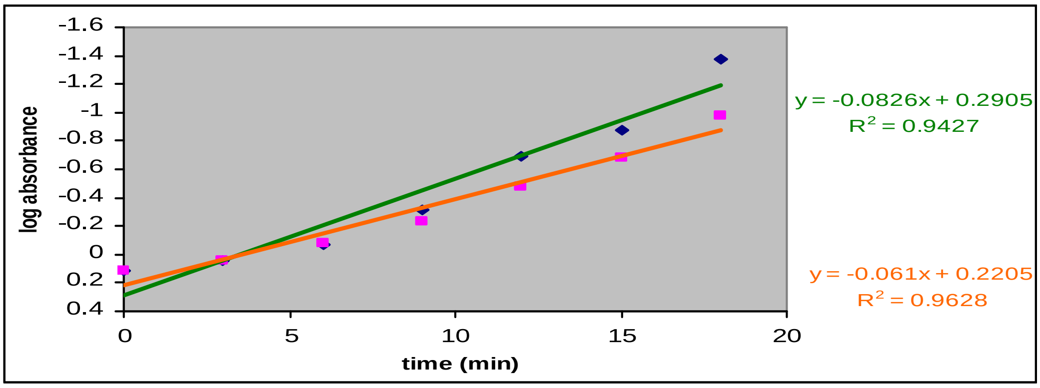

Fig 4: time Vs absorbance at 2.5×10^{-5} mg/L dye concentration

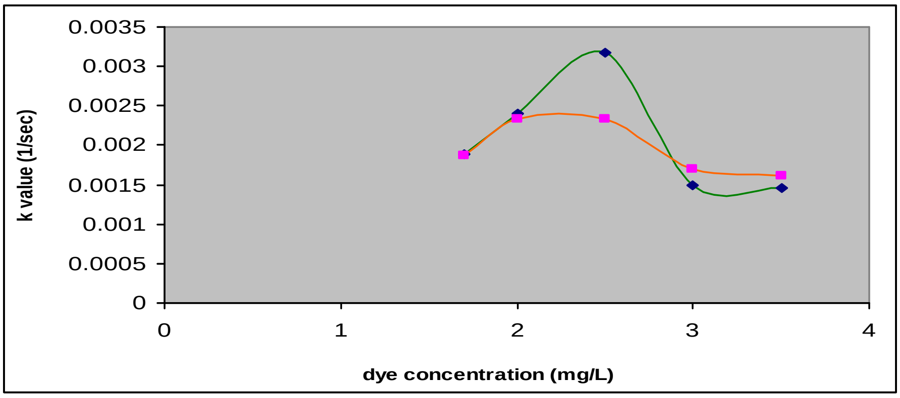

Fig 5: Dye concentrations Vs k value

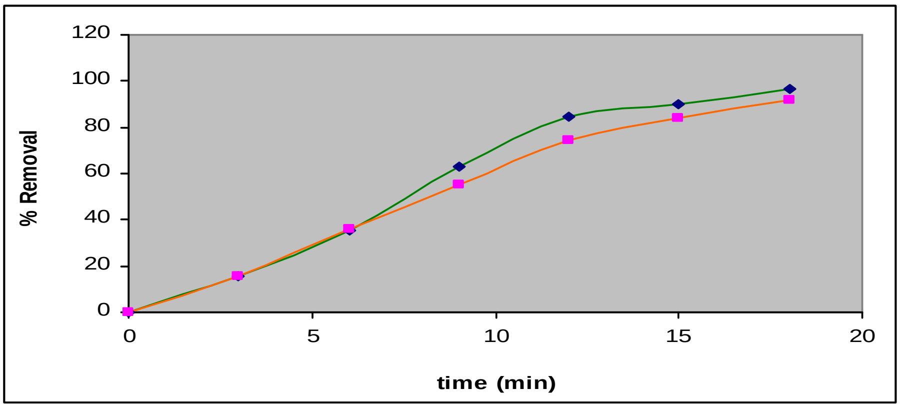

Fig 6: % Removal of dye at the optimum amount of dye concentration (2.5×10^{-5} mg/L)

Orange peel powder

Neem leaf powder

Discussion

The Fig. 1 represents the plot of Langmuir sorption isotherm at 0.3 gm. of adsorbent which follows pseudo first order kinetics. Fig. 2 represents the plot of k values at different amounts of adsorbent. According to Fig. 2 optimum adsorbent dose for the dye is 0.3 gm. And the maximum and minimum adsorption values were obtained at amount of 0.3 gm and 0.5 gm. It is obvious as with increasing amount the active sites for adsorption of dye increases which results in an increase in removal efficiency. The decrease in adsorption capacity with an increase in the adsorbent concentration could be ascribed to the fact that some of the adsorption sites remained unsaturated during the process and agglomeration of adsorbent as a result all the surface area is not available for adsorption process. In the Fig. 3 the plot of percentage removal of dye at 0.3 gm. of adsorbent with respect to time is shown and between 15-20 min. got 95% removal of dye.

The Fig. 4 represents the plot of Langmuir sorption isotherm at 2.5×10^{-5} mg/L dye concentration which follows pseudo first order kinetics. The effect of dye concentration on adsorption was carried out under the optimized conditions of amount of adsorbent 0.3 gm. and the results are plotted in Fig. 5. For adsorbate, the adsorption increased with increase in concentration of dye, and then it drops and again increases. The maximum and minimum adsorption values were obtained at concentrations of 2.5×10^{-5} mg/L and 1×10^{-5} mg/L, respectively. Fig. 6 the plot of percentage removal of dye at 2.5×10^{-5} mg/L dye concentration with respect to time is shown and between 15-20 min. got 95% removal of dye.

From the present studies we can conclude that Neem leaf powder is better low-cost, natural adsorbent as compared to orange peel powder low cost natural adsorbent for the removal of Methylene blue dye.

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