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Removal of Methylene Blue from Waste Water Using Activated Carbon Prepared by Impregnating it with KOH and $Cacl_2$

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Abstract: *In this work ,removal of methylene blue from waste water through adsorption was studied using activated carbon prepared from agricultural waste by impregnating it with KOH and $Cacl_2$. On adsorption capacity the influence of pH was noted. An overview about adsorption was given. Comparison and investigation on kinetics of adsorption (two parametric models) was done referring to various other research papers. Various isotherm models were studied among which Langmuir isotherm was found to be the most suitable for this study as it works for monolayer adsorption. Chemically activated carbon was found to be more effective than physically activated carbon because of its better pore structure. Experimental set up was made using a magnetic stirrer in which contact was made between MB dye and adsorbent in different batches to determine the maximum capacity, batch experiments were carried varying ,initial dye concentration, adsorbent dosage, PH, agitation speed, contact time and temperature. Increase in temperature increased the rate of adsorption.*

Keywords: Methylene blue [MB], waste water, dye, adsorption, removal, activated carbon

I. INTRODUCTION

Water pollution is the utmost issue faced nowadays. The waste water released from textile, printing, plastics, pharmaceuticals, food, rubber manufacturing, cottons, cosmetic products and other industries are detrimental to the environment because of the pollutants such as dyes present in it [1]. High concentration of these dyes in water is not good for humans as well as life under water. Total quantity of 7×10^5 tons of dyestuff is manufactured yearly, and it is estimated that about 200,000 tons is discharged from these industries into water bodies [2] [3]. dyes present in waste water creates an imbalance in aquatic life as it reduces the oxygen content and also makes sunlight penetration difficult in water which thus decrease photosynthetic processes of water bodies, they damage the physical and chemical characteristics of water [4]. Study of removal of methylene blue [MB] dye from waste water is a major research nowadays. Methylene blue[MB] is not regarded as extremely toxic but however it affects human body in numerous ways like increased heart rate, vomiting, shock, jaundice, tissue necrosis, cyanosis, Heinz body formation, skin diseases, digestive disorder, risk of cancer and methemoglobinemia-like syndrome if consumed or if it comes in contact with skin [5] [6].

Among the various other removal processes like physical and chemical removal, adsorption that is a physical type of process was preferred for MB removal. Many researchers chose adsorption because of its efficiency, easy to understand process, easy operation, high sensitivity to hazardous substances, and mainly because it is economical [7]. In other removal processes there may be a chance of producing a byproduct which is not intended when treating waste water. As an adsorbent for removal activated carbon shows the maximum efficiency and therefore it is favored for adsorption of methylene blue. Activated carbon is mostly used because of the following reasons: high internal surface area, micro porosity, contaminant removal efficiency, chemical nature, environmental friendliness [8]. Adsorption capacity improves by increasing the surface area but shows little improvement by increasing the pore size [9].

Activated carbons are produced by a two stage process of carbonization followed by activation which can be done both physically as well as chemically. Over the period of few years attempts were made to find an economical raw material for the production of activated carbons such as wheat shells [10], rice husk [11], saw dust [12], peel of Cucumis sativus fruit

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[13], Ananas comosus Activated carbon [14], bagasse fly ash [15], mango seed kernel powder [16], walnut shell, almond shell, hazelnut shell, apricot stones [17], coconut shells, groundnut shell, bamboo dust [18], deolied soya [19], pistachio shells [20], banana pith, maize cob, silk cotton hull, coconut tree sawdust [21], date pits [22]. Adsorption efficiency of methylene blue depends upon the following factors:- initial dye concentration, adsorbent dosage, PH, agitation speed, contact time, particle size, temperature therefore batch experiments were carried out to determine the same. In this study various isotherm models and kinetics of adsorption was applied to determine the adsorption and removal capacity of methylene blue.

II. ADSORPTION

The term adsorption was first given in 1881 by Heinrich Kayser who was a German physicist. Adsorption is often represented as a surface phenomenon where particles adhere and settle on the top layer of material. Adsorption is the attachment of atoms, ions or molecules of a gas, liquid or dissolved solid particle to a surface. This process is not similar from absorption, in which an absorbate is dissolved in the *absorbent*. Adsorption process requires contact of solids with either gases or liquids in which the mass transfer operation is on the way to solids. Desorption is known as the reverse of this process. The adsorbed substance is known as adsorbate and the medium used for adsorption is called adsorbent. Surface energy is responsible for adsorption. Adsorption is present in many natural, physical, biological and chemical systems and is widely used in industrial applications such as for treating waste water, froth floatation process, separation of inert gases, gas mask used in coal mines, control of humidity, production of high vacuum, color removal from solutions. Two components are required for the adsorption process, which are -

1. Adsorbate**:** A substance that has settled on the surface of another substance. For example, H_2, N_2, and O_2 gases.
2. Adsorbent**:** On the surface of a substance Adsorbate adsorbs. For example, charcoal, and alumina.

The two types of adsorption are mainly known as physical adsorption or physi-sorption and chemi-sorption (activated adsorption). Physical adsorption occurs from the intermolecular forces of attraction between a solid and the substance adsorbed. It is a readily reversible operation. Chemi-sorption happens from chemical interaction, it is generally stronger than physic-sorption process. Chemi-sorption is an irreversible process. It is mostly used in catalysis. Adsorbent should be such that it shouldn't get carried away by flowing stream and should not create a high pressure drop. If the temperature is increased at a constant pressure it decreases the amount of solute adsorbed. Pressure is also an important factor in adsorption rate, lowering of pressure reduces the amount of adsorption. Adsorption experiments can be carried out using fluidized beds, steady state moving bed, contact filtration equipments (mixing tank). Various isotherm models are used to describe the adsorption process some of which are Langmuir, Freundlich Theory, temkins, BET theory etc.

2.1 Characteristics of Physical Adsorption

1. This type of adsorption process is generated by physical forces.
2. It is a weak phenomenon compared to chemi-sorption.
3. This type of adsorption is given as a multi-layered process.
4. Physical adsorption is not particular and takes place all over the adsorbent.
5. Surface area, temperature, pressure, nature of adsorbate affects this process.
6. Energy for activation is comparatively low.

2.2 Characteristics of Chemical Adsorption

1. This type of adsorption process is generated by chemical forces.
2. It is a strong process compared to the physical one.
3. It is mostly a single-layered phenomenon.
4. It is highly particular and takes place at the reaction centers on the adsorbent.
5. Surface area, temperature, nature of adsorbate affects this process.
6. Energy of activation is comparatively very high. [23] [24]

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III. Materials And Methodology

3.1. Adsorbate

Methylene blue (C.I. name: basic blue 9 with its class: Thiazine and C.I. number: 52015) is a cationic dye with molecular formula $C_{16}H_{18}N_3SCl$ and molecular weight of 319.9 g/mol and it was purchased from Mumbai, India. The dye content of methylene blue was 95% that was purchased from a chemical trader. 665 nm is the maximum wavelength of adsorption of this dye [25]. Methylene blue structure is shown in fig 1.

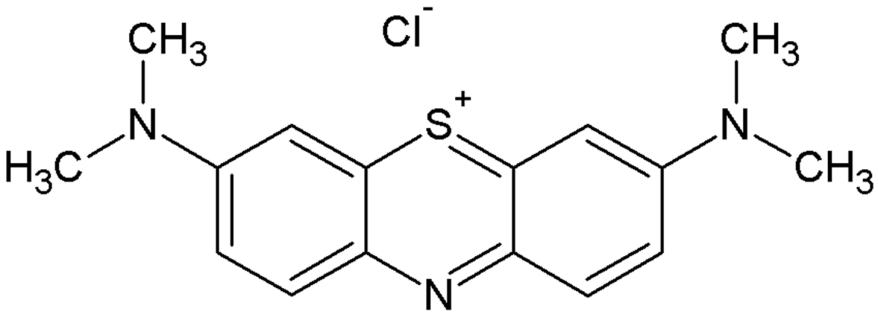

Figure 1: Structure of methylene blue

A market survey was conducted to find the availability of the raw material and its costing, after this survey a raw material was selected and finalized to be used as a raw material for preparation of activated carbon. This raw material was collected from vile parle (Mumbai, India) vegetable market from one vendor at a rate of 50rs per kg.

3.2. Preparation of Activated Carbon.

A. CARBONIZATION

The collected raw material was washed thoroughly with distilled water to remove all the impurities present on its surface, then performed the work of crushing, cutting, sieving, and grinding operations to remove the excess water content in it and then finally kept for drying in sunlight for 4 days straight. After sunlight drying, dried raw material was again dried in a dryer at 70°C for 2 hrs to make it crisp and to remove moisture content if any present in it then it was sieved to a smaller particle size and stored for batch activation. Dried raw material was now again washed with distilled water for 4 times to remove dirt and other impurities from the material, this was carried out using a filter paper on which the raw material was collected and the washed water was thrown away. It was again dried in a dryer before carbonization. 30g raw material was initially taken for carbonization it was then carbonized in a furnace at a temperature of 450°C for 20 minutes.

Figure 2. Raw material after drying

Figure 3. Charcoal after activation

B. ACTIVATION

Chemical activation was done by impregnating the raw material with KOH and$Cacl_2$, for the first batch KOH was used as an activating agent and then later the second activating agent was used. For activation chemical to charcoal ratio 1:1 was

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prepared and was kept for settling for 30 mins, later this solution was heated in a furnace at 400°C set point for 15 minutes. After that it was kept in a dryer for 1 hour at 115°C and finally it was crushed into powder. 0.1 M HCL solution was made in distilled water and it was used to wash activated carbon to remove activating chemical present in it then it was washed with hot DW water to remove HCL. And powdered activated carbon was finally stored in a sip lock for further use [26].

3.3. Experimental Setup

UV-visible spectrophotometer (Shimadzu Model UV 1750) was used to analyze the initial MB concentration at a wavelength of 664 nm. PH of the methylene blue prepared solution was measured using a PH meter. 100 mL of MB solution of desired concentration (0.03, 0.06, 0.09, 0.12, 0.15, and 0.2 kg/m^3) was taken in a 500 mL conical flask. Different initial concentrations of the adsorbent was taken to measure the most effective removal of MB at varying temperatures (304, 312, and 326 K) at different agitation speed for every batch . This experiment was conducted using a magnetic stirrer in which the adsorbate and the adsorbent were added. After then it was allowed to settle and then filtered using a filter paper, and the clean water was obtained. This water was again analyzed using UV – visible spectrophotometer to know the amount of MB adsorbed, so that its removal efficiency can be improved by changing certain parameters [27].

In this experimentation Langmuir adsorption isotherm was found to be the best fit isotherm because it says about monolayer adsorption [28]. We can get the amount of methylene blue removed using equation (1).

$$q_e = \frac{(C_0 - C_e)\,V}{m}, \qquad \ldots\ldots \quad (1)$$

Where C_0 and C_e are the initial concentration and equilibrium liquid-phase concentrations of MB in aqueous solution (mg/L) respectively, V the volume of the solution (L), and m is the mass of the activated carbon used (g).

The removal efficiency of the methylene blue dye was calculated using the following equation (2).

$$\%R_E = \frac{(C_0 - C_e)\,100}{C_0}, \qquad \ldots\ldots\ldots(2)$$

Equation for Langmuir adsorption isotherm for linear form is given as:-

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e, \qquad \ldots\ldots\ldots(3)$$

Where maximum adsorption capacity is Q_m, and K_L is the constant of Langmuir [29].

IV. Effect Of Parameters on Adsorption

4.1 Effect of Contact Time and Initial MB Concentration

The contact time between the MB and Activated carbon and also the concentration of dye affects the process of adsorption. The percent removal efficiency and adsorption capacity of dye increased when contact time was increased and reached equilibrium after 55 min. Increase in contact time after 55 min cannot enhance the adsorption of MB dye [30]. At first the % removal of MB is very fast due to the adsorption of more molecules of MB on the unsaturated external surface of activated carbon. After 55 min the surface pores of activated carbon are covered and it becomes tough for dyes molecule to enter into the inner part of adsorbent. The starting rapid % removal of MB may be due to presence of more number of sites for binding for adsorption of methylene blue molecules and the removal of dye was seen to be slower in last stages that may be due to saturation of these binding sites with MB molecules [31]. The time required to reach equilibrium for the adsorption of different dye concentration is not dependent on their initial concentration. The time to reach equilibrium was seen to be same for all the initial dye concentration as per results. It was seen that with increase of the concentration of MB from 3 to 10 mg/L the adsorption rate and thus adsorption capacity as well as % removal increase. With increase of initial concentration of methylene blue the capacity of adsorption increased because of powerful driving force and transfers of more MB molecules from aqueous to solid phase gets increased [32].

4.2 Effect of Agitation Speed

The effect of stirring speed and adsorption of dye was investigated, the experiments were performed using different stirring speed from 90 to 500 using concentration of dye 10 mg/L, contact time was 55 min, and the temperature was 298 K. With increasing of the agitation speed the adsorption or % removal of MB from aqueous solution was seen to be increased. This increase of adsorption was seen to be the most at 290 rpm and after this there is not much considerable increase in the adsorption of MB. The increase in adsorption of dye may be because of the decrease in the diameter of diffuse layer around the surface of activated carbon with increasing the stirring speed [33].

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4.3 Effect of Adsorbent Dose

With the increase of activated carbon amount the % adsorption capacity of dye is increased. Adsorbent dosage greatly affects the adsorption of MB. The effect of activated carbon amount on MB adsorption was studied in the range from 15 mg to 90 mg. with increase of activated carbon amount the % adsorption was increased because of the more number of active sites and more surface area. By increasing the surface area more and more open adsorption pores are available for dye adsorption [34]. Further more amount of dosage of adsorbent had no effect on dye removal after 90 mg because it reached equilibrium. This was even reported by other researchers as well [35].

4.4 Effect of Temperature

Temperature condition plays an important role in the adsorption process of MB dye. It was investigated what is the effect of temperature on % adsorption capacity of dye. It was seen that with increase in temperature the faster adsorption happened and after a certain temperature it reached equilibrium and had no effect on adsorption efficiency later.

4.5 Effect of pH

PH value of a solution affects the efficiency of removal of a dye. In this study it was investigated and concluded that when the pH of the solution was increased till pH value 6 it increased the adsorption efficiency but when it was increased further it decreased the % adsorption of MB.

V. CONCLUSION

In this study activated carbon prepared by impregnating charcoal with activating agents such as KOH and ⟦Cacl⟧_2 was investigated for methylene blue removal from waste water. Activated carbon prepared by this method was found to be efficient for removal of MB. It was also seen that adsorption process is a successful method for removal of dyes from waste water. Langmuir isotherm model satisfactorily matched with the experimental results. And thus, methylene blue was removed from waste water successfully.

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