

PURIFICATION OF TEXTILE DYE WATER USING NATURALLY AVAILABLE MATERIALS AND ITS KINETIC STUDIES

Project submitted to the University of Kerala in partial fulfillment of the requirement for the award of the First Degree Program in Chemistry.

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CERTIFICATE

This is to be certify that the project entitles “Purification of Textile dye water” is an authentic record of the dissertation work carried out by Ajith T, Aparna A, Gayathri S B, Kavya S Kumar, Greeshma Jose under my guidance in partial fulfillment of the requirements for the first degree program in Chemistry under CBCSS of the University of Kerala and further that no part of this has been presented before for the award of any other degree.

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DECLARATION

We hereby declare that the dissertation entitled “ **Purification of Textile dye water using naturally available materials and its kinetic studies**” is an authentic record of the dissertation work carried out by us under the guidance of **Dr.Vivek.B** Assistant Professor, Department of Chemistry, Sree Narayana College,Kollam in partial fulfillment of the requirements for the award of the First Degree Programme in Chemistry ,University of Kerala and that no part this project has previously been present for the award of any other degree in any University.

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CHAPTER 1

INTRODUCTION

1.1. IMPORTANCE OF WASTE WATER TREATMENT

Saving water to save the planet and to make the future of mankind safe is what we need now. With the growth of mankind, society, science, technology our world is reaching to new high horizons but the cost which we are paying or will pay in near future is surely going to be too high. Among the consequences of this rapid growth is environmental disorder with a big pollution problem. Anthropogenic activities have caused a great harm to the quality of our lifeline, i.e. water. Because of fast depletion of the freshwater resources, there seems to be a crisis of the same. Water pollution is a global concern and, it is the high time that we realize the gravity of the situation. Removing pollutants from water is the crying need of the hour and developing a cost effective and environmentally safe method to achieve the same is a challenging task for chemical engineers. After all, it is the future of mankind, which is at stake

A dye is a coloured substance that has an affinity to the substrate to which it is being applied. Dyes appear to be coloured because they absorb some wavelengths of light more than others. Humans are estimated to use dyes for thousands of years and the earliest use of the colorant is believed to be by Neanderthal man about 1,80,000 years ago [1, 2]. The year 1856 witnessed a historic discovery of first synthetic dye, Mauvine, by Perkin [3, 4]. In due course of time, these synthetic dyes gained huge popularity and began to be synthesized on a large scale. In

fact, it has reached to a level of annually, over 7.0×10^5 and nearly 1000 different types of dyes are produced worldwide [5].

1.2. BACK GROUND OF PRESENT WORK

Now-a-days, a large amount of waste water having colour is generated by many industries like textile, leather, paper, printing, plastic and so on [6]. The presence of dye materials greatly influence the quality of water and the removal of this kind of pollutant is of prime importance. Owing to their complicated chemical structures, dyes are difficult to treat with municipal waste treatment operations [5]. Even a small quantity of dye does cause high visibility and undesirability. Moreover, the colour produced by dyes in water makes it aesthetically unpleasant [6]. They can have acute or chronic effects on exposed organisms, which depend on the concentration of the dye and the exposed time [5]. In addition to that, many dyes are considered to be toxic and even carcinogenic [6-8]. Few decades earlier the dye selection, applications and uses were not given much importance. With the growing health concerns, it was in the 80s that people started paying much attention to the dye wastes [2]. An indication to the magnitude of this problem can be inferred from the fact that two percent of dyes produced are directly discharged into aqueous effluents [9, 10]. With the increased stringent laws on industrial discharge, it has become very important to treat this wastewater. Because of their detriment and large scale distribution in the ecological environment, their separation and determination has become one of the important studies of environmental analysis. Of prime importance is the need for clear information on the safety related properties of the colorants and the measure to be taken for lowering exposure. If all these elements are seriously considered, then the technical use of colorants and the handling involved might be possible without much health danger.

1.3. OBJECTIVES

Several physical, chemical and biological de-colorization methods such as coagulation/flocculation treatment, biodegradation processes, oxidation methods, membrane filtration and adsorption have been reported to be investigated for the removal of dyes from industrial effluents [11-13]. Among the studied methods, removal of dyes from adsorption is found to be the most competitive one because it does not need a high operating temperature and several colouring materials can be removed simultaneously [6]. The versatility of adsorption is due to its high efficiency, economic feasibility and simplicity of design [8]. As there are various parameters to effect adsorption process such as, charge density and structural stability of the adsorbent so, in the thrust of a comprehensive study, we have selected one basic dye (METYHYL ORANGE) and one acidic dye (METHYLENE BLUE) for this present study. Several adsorbents have been used for this purpose such as Zeolites (4A,5A and 13 X). One of the conventional and most studied adsorbent is Activated Carbon (AC). The reasons for this popularity are its high adsorption capacity, high surface area and microporous structure [5]. In fact, Activated Carbon adsorption has been listed by the US Environmental Protection Agency as one of the best available control technologies .

Our objective is to remove dyes from textile waste water using natural materials like Orange Peel, Straw,Coconut Husk. The main constituents of these materials are: 64-74% volatile matter and 12-16% fixed carbon and 15-20% ash (Armesto *et al.* 2002; Daifullah *et al.* 2003). The rice husk composition are: 32.24% cellulose, 21.34% hemicellulose, 21.44% lignin, 1.82% extractives, 8.11% water and 15.05% mineral.These are helps to adsorb the dyes using hydrophobic, electrostatic and other physical interactions.

CHAPTER 2

REVIEW OF LITERATURE

2.1. ADSORPTION PRINCIPLES

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or atomic film. In other words, adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface and this process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It is a surface phenomenon and a consequence of surface energy. The atoms on the surface of the adsorbent are not wholly surrounded by other atoms and thus, can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as follows:

(1)Physisorption: It is a type of adsorption in which the adsorbate adheres to the surface through vander Walls (weak intermolecular) interactions.

(2)Chemisorption: It is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond.

Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. As the pores are generally small, the internal surface area is greater than the external area. Separation occurs because differences in molecular weight, shape or polarity cause some molecules to be held more strongly on the surface than others. In many cases, the adsorbate is held strongly enough to allow complete removal of that component from the fluid.

2.2. DYES

Dyes are coloured substances which can adhere to the surface of materials and are used to give color to paper, food- stuffs, and various textiles such as cotton, wool, synthetic fibres, silk etc. For example, alizarin, indigo, congo red, etc. Chemically, a dye contains:

- i. Some group (such as azo, indigoid, triphenylmethyl, anthraquinone, etc.) which is responsible for the color of the dye.
- ii. Some groups (such as -NH_2 , $\text{-SO}_3\text{H}$, -COOH , etc) which makes the dye stick to the fabric by formation of some salt.

The dyed fabrics appear to be colored because a particular dye absorbs radiations of some specific wavelengths from the visible region of electromagnetic radiations which fall on the surface. The remaining radiations (complementary colors) of light are reflected. The color which we observe is due to the reflected light. For example, if a dye absorbs the light in the wavelength region corresponding to red, then it would appear green, which is the complementary color of red. Similarly, if a dye absorbs blue color, it would appear orange.



Figure 1: Photograph of dye coloured clothes.

2.3. TYPES OF DYES

Acid dyes:

These are azo dyes and are characterized by the presence of acidic groups. The presence of soluble and serves as the reactive points for fixing the dye to the fibre. They are chiefly used for dyeing wool, silk and nylon. For example, Orange I and Orange II. 2.

Basic dyes:

These dyes contain NH_2 or NR_2

. In acidic solutions, these form water soluble cations and use the anionic sites on the fabric to get used for dyeing wool, silk and nylon. For example, aniline yellow, butter yellow. 3.

Direct dyes:

These are also azo dyes and are used to dye fabrics directly by placing in aqueous solution of the dye. These dyes attach to the fabrics by means of hydrogen bonding. 4.

Disperse dyes:

These dyes are applied in the form of dispersion of minute particles of the dye in a soap solution in the presence of phenol or benzoic acid. These dyes are used to dye rayons, Dacron, nylon, polyesters etc. For example, celliton fast pink B and celliton fast blue B.

Mordant dyes:

These dyes uses a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. These are basically used for wool.

Sulfur dyes:

These types of dyes have intermediate structures. They form a relatively small group of dyes, but the low cost and good wash fastness properties make it very important from the economic point of view. Its main uses are for cotton and rayon.

Solvent dyes:

These type of dyes are generally non-polar or little polar and thus, are water insoluble. They are used for plastics, gasoline, lubricants, oils etc.

Vat dyes:

This type of dye is water insoluble and incapable of dyeing fibers directly. But, reduction in alkaline liquor produce the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fiber. These are used mainly for cotton, wool and nylon.

2.4. REVIEW OF RECENT STUDIES

In 2016, adsorption of acid dyes on SBA-3 ordered mesoporous silica, ethylenediamine functionalized aminopropyl functionalized and pentaethylene hexamine functionalized materials was studied. The MATERIAL was found to have the highest adsorption capacity for all acid dyes. Batch studies were performed to study the effect of various experimental parameters such as chemical modification, contact time, initial concentration, adsorbent dose, agitation speed, solution pH and reaction temperature on the adsorption process. The Freundlich model was found to be fit with the equilibrium isotherm data. In 2015, chemically modified sugarcane bagasse as a potentially low-cost biosorbent for the removal of methyl red was studied. The kinetics of methyl red adsorption followed the pseudo first order kinetic expression and Langmuir isotherms model fit well. From the study, it was inferred that sugarcane bagasse has a good potential to be used for small scale industries, which produces dyes as their effluent, after it was being pretreated with phosphoric acid.

In 2016, the study was done on the ability of activated carbon in the removal of two anionic dyes (Direct Blue 78 and Direct Red 31) from coloured wastewater in single and binary systems. The effects of adsorbent dosage and initial dye concentration were studied at 25°C. The kinetics was found to conform to pseudo second order kinetic model. The equilibrium data fitted well with Langmuir adsorption isotherm. Results indicated that Activated Carbon is an effective adsorbent in this case.

CHAPTER 3

MATERIALS AND METHODS

This chapter describes the materials and methods adopted for the removal of textile dyes from waste water. The chemicals used for the estimation were purchased from Merck and were of AR Grade

3.1 Materials

Chemicals Required

- i) Methyl orange
- ii) Methylene Blue
- iii) orange peel
- iv) Straw
- v) Rice Husk

3.2 Method adopted for the preparation of dye water

Dye water was prepared by dissolving 10mg of dye methyl orange and methylene blue in 100ml water. The concentration of the dye was determined by colorimeter.

3.3 Method adopted for the adsorption of dye

100 ml of the working solution was put in each different conical flask. Then, different adsorbent dose was added in each flask. All the flasks were kept inside the shaker at 100 rpm and 25°C. For each time intervals, the flasks were withdrawn from the shaker and the dye solutions were separated from adsorbents by using centrifuge at 4000 rpm for 10 minutes at regular intervals. The absorbance of all the solutions was then measured.

3.3.1. Principles of Colorimetric estimation

Variation of the colour of a solution with change in concentration forms the basis of colorimetric analysis. Colorimetry is concerned with determination of the concentration of a substance by measurement of the relative absorption of light with respect to a known concentration of the substance.

3.3.2. Theory

When light falls upon a homogeneous medium, a portion of the light is reflected (I_r), a portion is absorbed (I_a) by the medium and the remainder is transmitted (I_t). The intensity of the incident light, $I_o = I_t + I_r + I_a$. For air - glass interface about 4% of incident light is reflected and hence I_r is eliminated by the use of a comparison cell. Then, $I_o = I_a + I_t$.

3.3.3. Laws of Colorimetry

I. Lambert's Law

The intensity of transmitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically.

$$I_t = I_o 10^{-Kt}$$

Where I_t is the intensity of transmitted light, I_o is the intensity of incident light, K is a constant usually termed the extinction coefficient and t is the thickness. From the above equation it follows that,

The ratio I_t / I_o is termed as the transmittance, T and the quantity $\log I_o / I_t$ is termed as *the absorbance or optical density* and is usually designated as A or D , K is referred to as *the absorption coefficient*.

$$\log \frac{I_o}{I_t} = Kt$$

II. Beer's Law

According to Lambert's law light absorption and light transmission depend on the thickness of the absorbing layer only. In quantitative analysis solutions are used. Beer studied the relationship between concentration of the coloured solution and light transmission. *Beer's law states that the intensity of transmitted light decreases exponentially as the concentration (c) of the absorbing solution increases arithmetically. This may be written in the form*

$$I_t = I_0 10^{KC} \text{ or } \log \frac{I_0}{I_t} = KC$$

$\log \frac{I_0}{I_t}$ is the absorbance A and K is the absorption coefficient

III. Beer – Lambert Law

By combining Beer's law and Lambert's law

$$I_t = I_0 10^{-\epsilon ct} \text{ and } \log \frac{I_0}{I_t} = \epsilon Ct$$

Where $\log I_0/I_t$ is the absorbance (A) or optical density (D), c is the concentration, t is the thickness of medium and ϵ is a constant whose value depends upon the method of expression of concentration and of thickness. If c is expressed in mol dm⁻³ and t in cm, and ϵ is called *molar extinction or molar absorption coefficient or molar absorptivity*. Thus, the absorbance A, transmittance T and molar absorption coefficient ϵ are related as, $A = \epsilon ct = -\log T$. According to the above equation, the absorbance (or optical density) of a solution in a container (a cell) of a fixed path length is directly proportional to the concentration. Thus a graph between absorbance and concentration should be linear and a solution giving such a behavior is said to obey Beer Lambert law.

Application of Beer's law

Consider two solutions of a coloured substance with concentrations c_1 and c_2 . These are placed in an instrument in which the thickness of the layers can be altered and which allows a comparison of the transmitted light. When two layers have the same colour intensity,

$$\log \frac{I_0}{I_{t1}} = \epsilon C t_1 / \log \frac{I_0}{I_{t2}} = \epsilon C t_2$$

Here t_1 and t_2 are the lengths of the columns of solutions with concentrations c_1 and c_2 respectively. When the solutions are optically balanced, $c_1 t_1 = c_2 t_2$. So if we know the concentration of one, that of unknown can be calculated by the equation,

$$C_2 = \frac{c_1 t_1}{t_2}$$

3.3.4. Conditions for a satisfactory colorimetric analysis

- i. The colour intensity should increase linearly with the concentration of the substance to be determined.
- ii. The colour produced should be sufficiently stable to permit an accurate reading to be taken.
- iii. The solution must be free from precipitate. Turbidity scatters and absorbs light.
- iv. It is desirable that the colour reaction be highly sensitive. Further, the reaction product should absorb strongly in the visible region.
- v. The colorimetric procedure must give reproducible results under specific experimental conditions.

3.3.5. Advantages of colorimetric analysis

- i. At low concentrations colorimetric method gives more accurate results than volumetric or gravimetric procedures.
- ii. For certain biological substances colorimetric method may be applied under conditions where no satisfactory gravimetric or volumetric procedures exist.

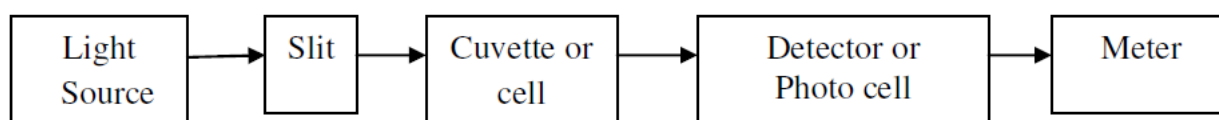
iii. Colorimetric method is simpler to carry out.

3.3.6. Colorimeter

The instrument used for measuring absorption of light in the visible region of the spectrum is known as *colorimeter*. There are two types of colorimeters which are commonly used. They are : (1) **Duboscq colorimeter** and (ii) Photoelectric colorimeter. For colorimetric estimation photoelectric colorimeters are very convenient. The visual colorimetry suffers from the human errors such as persistence of vision, fatigue and the need for maintaining colour standards over long periods. On the other hand, electronic devices for measuring the colour intensity are gifted with several advantages such as speed, sensitivity and accuracy.

Photoelectric colorimeter – Instrumentation

A photoelectric colorimeter consists essentially of a light source, a cup / cell / cuvette for holding the solution, a photoelectric cell to capture the radiation transmitted by the solution and a measuring device to indicate the response of a photocell. A schematic diagram as follows:



Using a photoelectric colorimeter intensity of light absorption can be measured in two ways – as absorbance or as percent transmittance. Absorbance A is defined as $A = \log I_0/I_t$ where I_0 is the intensity of incident radiation and I_t is the intensity of transmitted radiation. The quantity $I_t/I_0 \times 100$ is known as percent transmittance and is designated as % T . The two scales are graduated in opposite directions.

After switching on the instrument pure solvent is placed in a cell and the cell is inserted

into the groove for it. By turning the concerned knob, intensity of light is so adjusted that percent transmittance is 100 (absorbance = zero). The cell containing solvent is then replaced by a cell containing solution and the reading noted. For example, if light absorption by a solution of potassium permanganate in water is studied, water alone is used first and the solution next. It is important that the concentration of the solution is such that absorption is measurable on the scale. A number of solutions of known concentrations are prepared and their absorbance measured. A plot of concentration Vs absorbance will give a straight line with positive slope and passing through the origin. The absorbance of the unknown solution is also observed, and thus from the graph the concentration of the unknown solution can be found. Knowing the concentration, the amount of the substance in the given solution can be calculated.

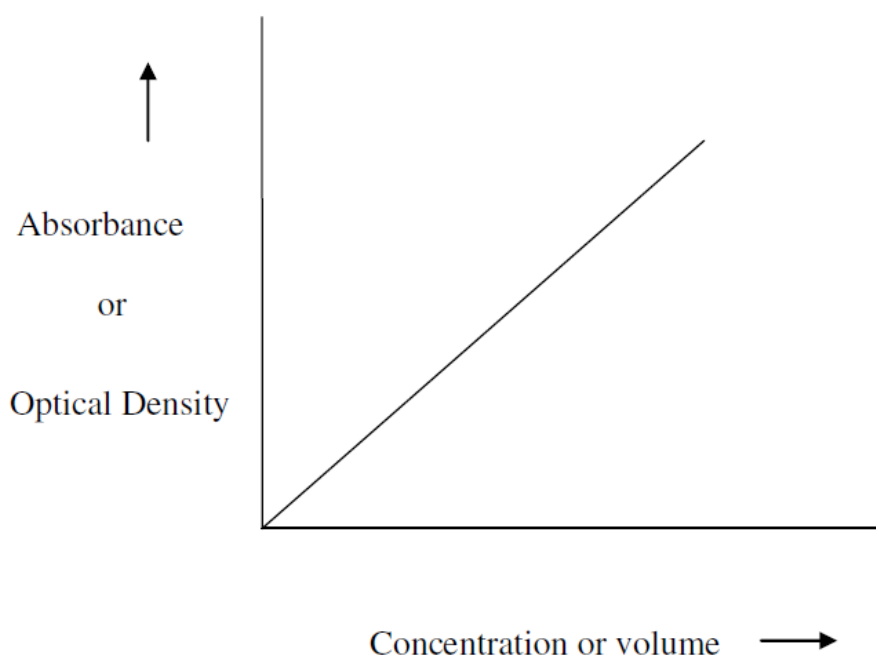


Figure 2: Optical density versus concentration graph.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter describes the results of the removal of methyl orange and methylene blue from water using orange peel, Straw, and Rice Husk. This chapter also gives the detailed kinetic studies of the adsorption.

The purified adsorbent material (10 mg) were stirred with 100 ml water containing heavy organic dyes (10 ppm) for 1.5 hours. At definite time intervals, 5 ml of the sample was taken out and concentration of the metal ions was monitored by colorimeter. The adsorption capacity, q_e , was found out by the following equation,

$$\text{Absorbance yield} = \frac{(C_o - C_e)V}{m} \quad (1)$$

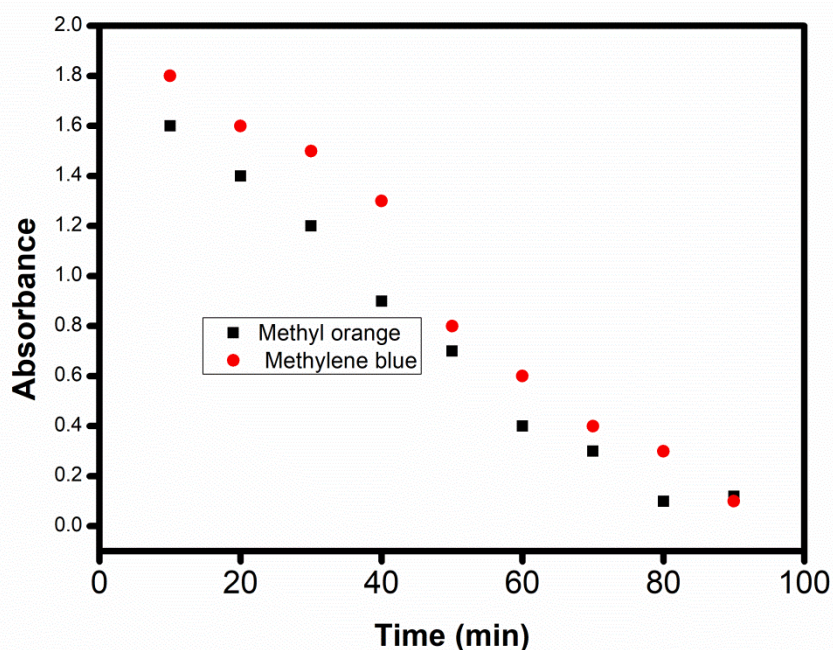


Figure 3: Absorbance versus time graph of methyl orange and methylene blue using rice husk.

In figure 3 the absorbance of MO and MB decreases with increase in time. The results indicate that more than 90 % of MB and MO were removed from water by 100 min. The photographic images of dye solution, before and after adsorption, are given in Figure 4. The significant decrease in the absorbance can be seen from the figure 3.

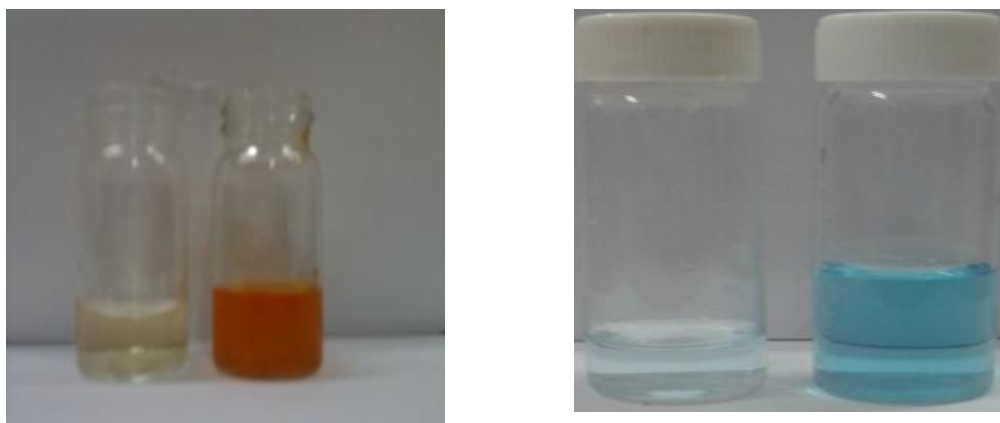


Figure 4: Photograph of dye solution before and after the adsorption.

Adsorption of dyes from water was done using rice husk, orange peel and straw. We found out that these natural material were an excellent adsorbent for dyes from water. MO and MB were chosen as adsorbate, the initial concentration of all this were kept at 10 ppm. 10 mg of adsorbent and was introduced in to the polluted water and stirred for 1 h ,at definite time interval 2-3ml of sample was withdraw and quantitative measurement was done using colorimeter. The adsorption yield was found out using the following equation

$$q = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

where C_e is the equilibrium concentration, q_e corresponds to adsorption amount at equilibrium, C_0 is the initial concentration of metal ions or organic dyes, V and m are the volume of solution and mass of the hydrogel, respectively.

Figure 5 shows adsorption yield versus time plot of different MO and MB using Rice husk, orange peel and straw. These three adsorbents could remove 80-98% dyes from water within 1h. The adsorption yield was more in the case of rice husk compared to other two.

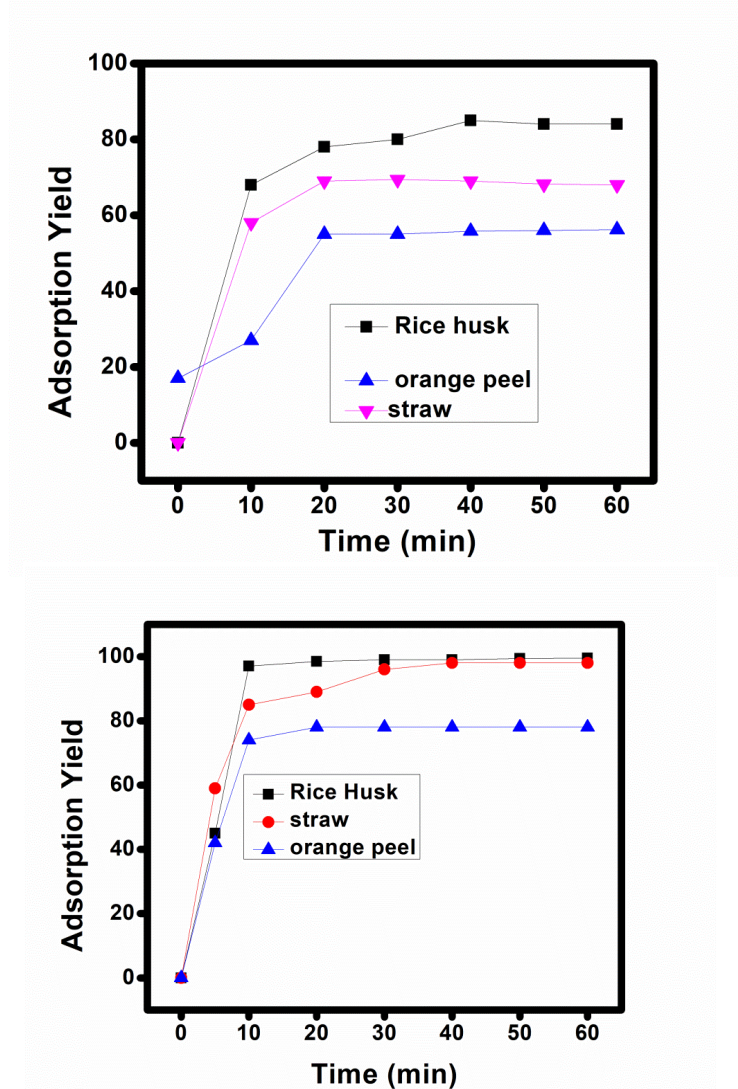


Figure 5: Adsorption yield versus time plot of MO and MB using rice husk, orange peel and straw

Kinetic studies were carried out to understand the detailed chemistry behind the metal ion adsorption, which followed the pseudo second order kinetic equation given below.

$$\frac{t}{q_t} = \frac{1}{k_a q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_t is the amount of metal ion adsorbed per unit mass at time t , q_e is the amount of metal ion adsorbed at equilibrium, and k_a is the rate constant of the pseudo second order reaction.

The plot of t/q_t vs t is shown in Figure6 indicates that the fit is reasonable.

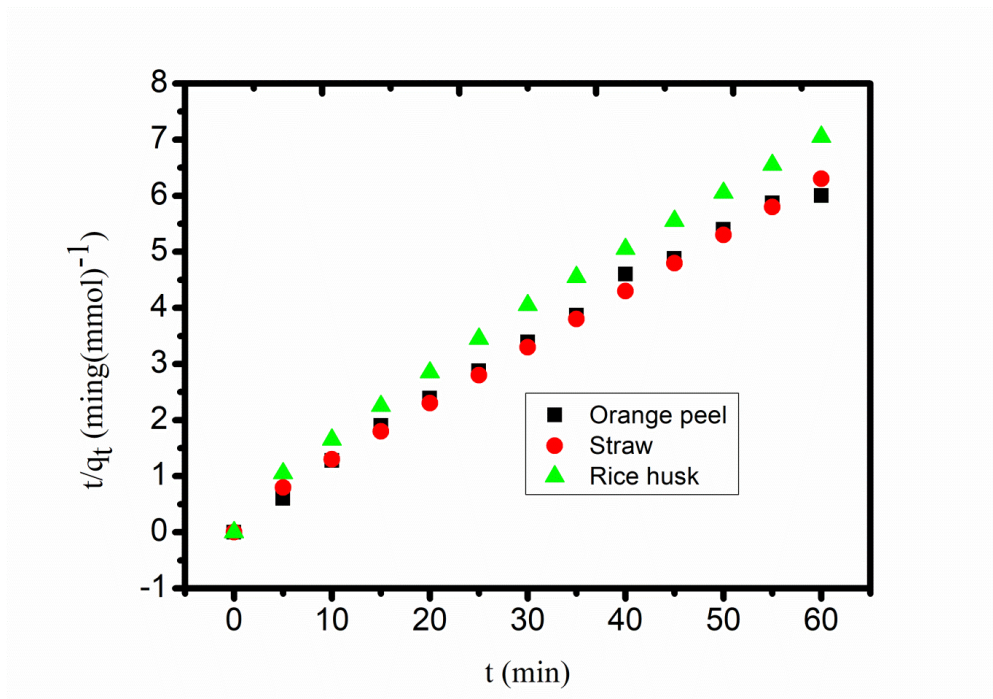


Figure 6: pseudo second order plot of adsorption using rice husk.

CHAPTER 5

CONCLUSION

In the present study adsorbent rice husk, straw and orange peel was used for removal of colour from waste effluent of textile industry. The materials were obtained and treated for the removal of colour at different doses. These materials also evaluated for the removal of colour at different time. The materials are capable of removing colour from waste water, their colour removal capacity for rice husk is 98%, straw is 95% and orange peel is 68 % respectively. The equilibrium time was found 55min for all the adsorbent. The experimental adsorption data fitted with pseudo second order kinetics. The experimental result shows that the materials have good potential to remove colour from effluent and good potential as an alternate low cost adsorbent.

REFERENCES

1. C. Namasivayam & N. Kanchana “Removal of Congo red from aqueous solution by waste banana pith” *pertanika j. sci. & techno!*. 1(1):33-42(1993) ISSN: 0128-7680
2. M Sarioglu,U.Atay “Removal of methylene blue by using biosolid” *global nest Journal*,vol 8, no 2, pp 113-120,2006
3. G. Annadurai et al “.Use of cellulose-based wastes for adsorption of dyes from aqueous solutions” *journal of hazardous materials* b92 (2002) 263–274 [
4. M C,Somasekhara Reddy “ Removal of direct dye from aqueous solutions with an adsorbent made from tamarind fruit shell, an agricultural solid waste” *journal of scientific & industrial research* vol.65, may(2006), pp 443-446
5. Shahbudeen.P.S.Syed “Study of the removal of malachite green from aqueous solution by using solid agriculture waste” *research journal of chemical sciences*, vol.1(1) April(2011)
6. R.Sivaraj et.al “Orange peel as an adsorbent in the removal of acid violet 17 from aqueous solutions” *technical note, waste management-* 21(2001), 105-110
7. Velmurugan. P, Rathina Kumar. V, Dhinakaran. g“Dye removal from aqueous solution using low cost adsorbent” *international journal of environmental sciences* volume 1 no.7,pg 1492- 1503 (2011)
8. M Jayaranjan, R Arunachalam and G.Annadurai “Use of low cost nano –porous materials of pameo fruit peel wastes in removal of textile.dye” *research journal of environmental sciences* 55: 434-443,(2011), issn 1819-3412,(2011)

9. Theivarasu, Mylsamy. S., Sivakumar n. "cocoa shell as adsorbent for the removal of methylene blue from aqueous solution: kinetic and equilibrium study" *universal journal of environmental research and technology*, vol-i, 70-78. (2011).
10. Tabrez a khan et.al " Removal of some basic dyes from artificial textile wastewater by adsorption on Akash kinari coal" *journal of scientific and industrial research*, vol 63, april (2004), pp(355-364).
11. Yavuz ö., Aydin h. "Removal of direct dyes from aqueous solution using various Adsorbents" *polish journal of environmental studies* vol. 15, no. 1 (2006), 155-161
12. Namasivayam c., Muniasamy n., Gayatri k., Rani m. and Ranganathan k. "Removal of dyes from aqueous solution by cellulosic waste orange peel", (1996) *Bio resource technology*, pg(37-43)
13. Papita Saha, (2010). "Assessment on the removal of methylene blue dye using tamarind fruit shell as bio sorbent." *Springer science+business media b.v.*, 213, pg(287–299). [14] Praveen Sharma et.al "COD reduction and colour removal of simulated textile mill wastewater by mixed bacterial consortium" *Rasayan .j. chem.* vol 3, no.4(2010), 731-735, issn-0974-1496.