Adsorption of Thymol Blue dye from Aqueous solution using modified Chitosan

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ABSTRACT

The main objective of this research project is to perform some experimental procedures to study the ability of the novel adsorbent used in this project. The chemical modification of the adsorbent is the chemical oxidation of pure powder chitosan using some specific redox pairs which are potassium dichromate and sodium bisulphite. After preparing the modified chitosan, there are some parameters that must be discussed during the adsorption process. The first parameter is the time parameter, showing experimentally the optimum time for adsorption under certain conditions by collecting values of absorbance and concentration of thymol blue adsorbed after the process from the spectrophotometer showing that the optimum time is 120 minutes. While for the optimum pH experiment, it is shown that optimum pH is 4, 0.5% v/v is optimum concentration and 0.05 grams is the optimum dose for the adsorbent. Then after computing these conditions and values of absorbance, some mathematical calculations and classifications are done to show the reaction kinetics classification of the process. By performing some equations using mathematical rules it is provided that the reaction is not a first order reaction, showing by calculations and graphs that the reaction is a second order reaction.

Key words: *Dye removal, Spectrophotometer, pH, Wastewater treatment, Novel adsorbent.*

1. INTRODUCTION

In our world there are many types of pollutants which can affect the environment, where environmental pollutants are considered to be the greatest pollution problems that human beings are facing in this world [1-10]. There are three types of pollution which are considered the main types of pollution. These types are classified into three basic types which are; water, air and soil [11, 12]. Among these types of pollutants water pollution is caused by the usage of excess pesticides and fertilizers in agriculture, industrial discharge and waste water emitted in textile industries which contains a large amount of dyes that are the mostly pollutant for water [13-

16]. Dyes which are found in waste water effluent are always difficult to be separated from water streams as they are complex molecular structures that make dyes able to be stable in water toward light and resistant to biodegradation. Synthetic dyes were discovered in the 19th century, while the usage of natural dyes has been started from about 5000 years, but synthetic dyes took the lead in textile industries which has covered up the use of natural dye. Synthetic dyes are involved in many industries and can be produced largely in such industries like; leather, fabrics, food, cosmetics, electroplating and distillation [17-20].
These synthetic dyes can be classified into different classes such as; basic, acidic, direct, disperse, pigment and reactive dyes and also other classes which are not mentioned. This classification reflects the macroscopic behavior and prevailing functionalities. Studies proved that more than 700000 tons of dye are produced annually. Also, an estimation proved that about 10-15% of dyes are gone astray in wastewater mainly in the manufacturing and application processes. In this work, finding a solution for the treatment of wastewater contaminated mainly by dyes is our big issue, where a lot of surveys and searches proved that cationic and anionic dyes are involved largely in many industries such like paper , silk , wool and cosmetics industries [21-25], So many investigations have been done to find a good and a low cost solution to remove theses dye from wastewater effluents, where adsorption was found to be the most effective way to remove these dye from wastewater effluents due to its low cost and easy way of operation in addition to the effectiveness of removing dyes from wastewater effluents [26,27]. So, chitosan was chosen to be the novel adsorbent which can remove cationic and anionic dyes from these effluents but of course some modifications must be held on this adsorbent to give the highest effect of adsorption and adsorb as much as it can [28-30]. Oxidation of chitosan was the chosen modification for chitosan since studies proved that it was the most effective modification on chitosan through studying the parameter affecting the adsorption after oxidation takes place [31-36].

1. EXPERIMENTAL

1.1 Chitosan Oxidation

The oxidation process of chitosan is applied using some chemical reagents which help in proceeding the oxidation quickly. First of all, a small amount of pure powder chitosan is prepared to be dissolved in an acetic acid solution which is diluted under certain conditions like temperature and stirring rate, where the temperature must be adjusted on 40 ^{o}C and 700 rounds per minute for four hours long. After dissolving the chitosan powder two reagent are added by sufficient amounts to the solution in a three necked flask and kept also at temperature 40^{o} C for 4.5 hours long to be quenched after the oxidation process by sodium hydroxide solution and an ice bath to obtain the hydrogel chitosan before passing it through some processes like filtration, washing by distillate water and drying in an oven at temperature 40^{o} C till it has a constant weight.

1.2 Time Optimization

After obtaining an amount of oxidized chitosan, firstly the effect of time is studied. As mentioned above that there are some depending parameters that affect the adsorption capacity. In this paper, reaching to the optimum conditions is the desired work to know the optimum conditions of oxidized chitosan to get the best adsorption

capacity. Thymol blue is used as the dye desired to be removed. So, a certain concentration of thymol blue is prepared which is 0.5% v/v. After adjusting the pH of the six beakers, the weighted six samples of chitosan are poured in six conical flasks with the solution in each one after adjustment. Before placing the conical flasks in the shaker to begin the adsorption process, the flasks are labelled, where each one is labelled referring to the lengths of time that each flask will take in the shaker starting from 5 minutes reaching to 2 hours {5, 10, 30, 60, 90, 120} minutes with stirring rate 250 rounds per minute.
Six samples are placed in the shaker to begin the adsorption process and when it is time to each sample to be removed, filtration takes place. After finishing the hours shaking, these six samples are taken to spectrophotometer to measure the adsorption capacity through knowing the concentration of dye before and after shaking.

1.3 pH Optimization

The optimum time experiment showed the optimum time needed for the modified chitosan to adsorb as much as it can. In the previous experiment all conditions were constant except the variation of time intervals, where pH and concentration of thymol blue were 4 and 0.5% respectively and mass of adsorbent is constant too which is 0.05 grams. In this experiment the same conditions are prepared but with a wide change in values of pH of each beaker to conduct the optimum pH that the adsorbent can evaluate highest adsorption capacity. The six beakers filled with thymol blue solution are then taken to adjust the pH. Six beakers are divided into two parts equally, providing three acidic beakers and three basic beakers. Three acidic beakers are adjusted using hydrochloric acid obtaining three different values of pH which are {2, 4, 6}, knowing that the pH of thymol blue solution without any adjustments is 6 so, no drops of HCl are needed to obtain pH of 6. On the other hand, basic beakers are adjusted using sodium hydroxide drops, obtaining different values of pH which are {8, 10, and 12}. After adjusting the pH, these beakers are taken to be poured in six conical flasks labelled with its pH value to proceed the adsorption process by adding the six weighed samples of modified chitosan to thymol blue solution. The adsorption will take two hours shaking with stirring rate 250 rounds per minute, knowing from the previous experiment the optimum time for adsorption.

1.4 Concentration Optimization

In this experiment the optimum concentration of thymol blue is observed by preparing 6 different samples of thymol blue each with its concentration. The original sample of thymol blue which is 0.5% v/v is taken to be diluted obtaining other five concentrations, to show the adsorption capacity of oxidized chitosan with different concentrations of thymol blue. These different concentrations are prepared the same way that 0.5% v/v thymol blue is prepared but using the 0.5% v/v thymol blue and distilled water. As by some calculations it was found that each sample needs a certain amount from distilled water and certain amount from diluted thymol blue, where these concentrations having values of {0.4, 0.3, 0.2, 0.1, 0.05}.
Before mixing the oxidized chitosan with the different concentrations a pH adjustment is required, where the optimum pH for chitosan adsorption is 4. These samples are adjusted using 0.1 M hydrochloric acid. After adjustment, sample in each beaker is poured to its conical flask labelled by its concentration then mixing

the weighed oxidized chitosan to start adsorption on the shaker leaving the reaction for two hours with stirring rate 250 rounds per minute.

1.5 Dose of Oxidized Chitosan Optimization

In such an experiment different masses of oxidized chitosan are used with constant time, pH and concentration, to show the optimum mass/dose of oxidized chitosan needed to give the best adsorption capacity with these parameters. Five different samples of oxidized chitosan are prepared having different masses where these values are {0.05, 0.04, 0.03, 0.02, 0.01} grams. As done before in the previous experiments, five beakers are prepared each containing 25 ml of 0.5% v/v thymol blue. These beakers are taken to the pH meter for adjustment, hydrochloric acid of 0.1 M is used for adjusting these samples reaching them to pH of 4. Then each sample is poured to the conical flask having its mass labeled mixing the weighed samples of oxidized chitosan with thymol blue, where each mass is filled in its flask. These flasks are taken to the shaker to proceed the adsorption reaction keeping the process for two hours shaking with stirring rate 250 rounds per minute.

2.RESULTS AND DISCUSSION

2.1 Standard Curve

As shown in the standard curve table, that at different concentrations of thymol blue, different values of absorbance in (nm) are given by the spectrophotometer, as the concentration of thymol blue increase the values of absorbance increase giving the shown values in table 2. So, the least concentration which is 0.1% v/v has the least absorbance value which is 0.011 nm, while the largest concentration which is 0.5% v/v gives an absorbance value of 0.0588 nm.

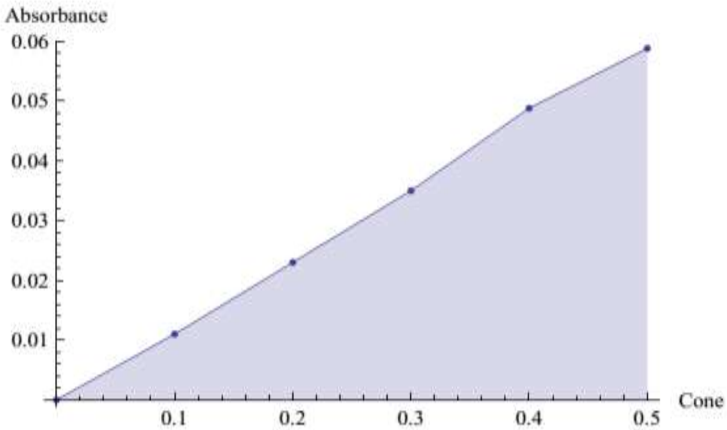

Figure 1: The relation between thymol blue concentration and absorbance

This figure shows the relation between the concentration of thymol blue and the absorbance value given from the spectrophotometer, fitting the line on the best fit of dots to give a straight line, where concentration of thymol blue is on x-axis and absorbance on y-axis. Also, R^2 is calculated showing a promising result having a value of 0.9985. This relation was plotted to make it easy for each experiment to get the concentration of thymol blue after adsorption to know how much thymol blue are adsorbed on the surface of oxidized chitosan, knowing the optimum condition in each experiment, where the least value of thymol blue concentration after adsorption gives the optimum condition of the experiment whatever any experiment.

2.2 Optimum Time

Figure 2 shows the relation between the concentration of thymol blue after adsorption and time for adsorption, whereas mentioned above that concentration of thymol blue decreases with time, the more time it spends in shaking the more concentration it loses.

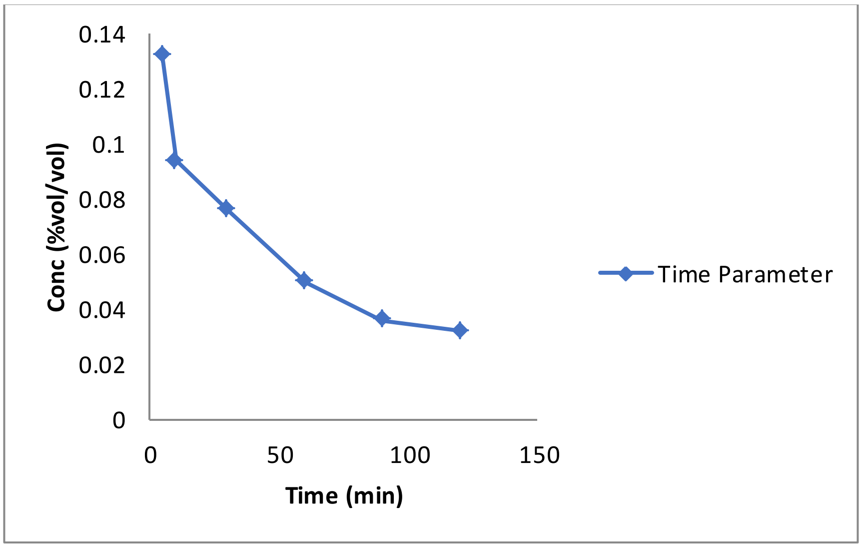

Figure 2: The relation between thymol blue concentration and time of adsorption

Figure 3 shows the relation between % of removal and time is opposite to that of figure (2). Where, percent of removal increases with time as shown in graph, where % of removal is
93.6 after two hours of shaking.

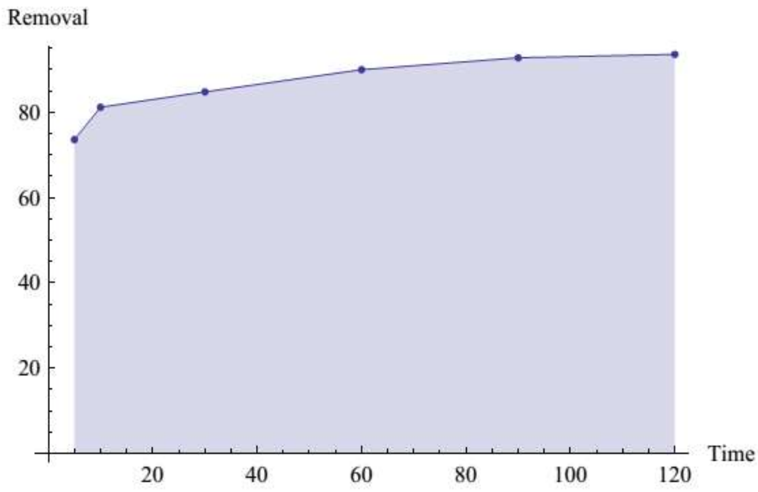

Figure 3: The relation between thymol blue removal percentage and time of adsorption

3.3 pH Parameter

Figure 4 shows the unstable conditions of samples having pH greater than 4, whereas the pH increases from 2 to 4, percent of removal increases showing the best value of removal, but as the increase to be more than 4 the curve start to drop showing unstable curves and unstable percentage of removal till reaching the most basic medium which is 12 having the lowest percent of removal.

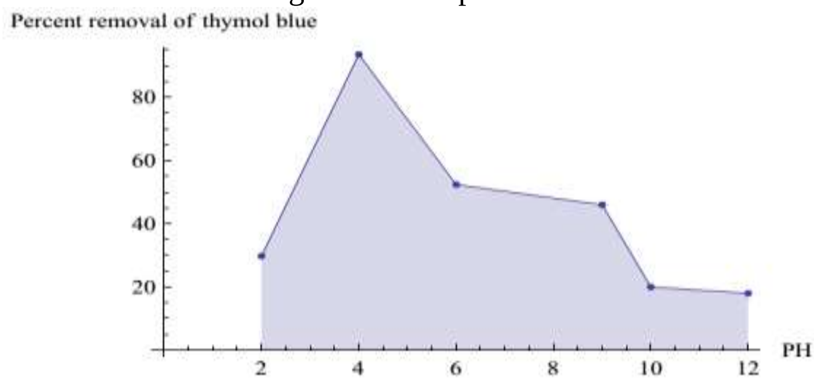

Figure 4: The relation between thymol blue removal percentage and pH

3.4 Optimum Initial Concentration

Increase the concentration of thymol blue after adsorption decrease instantly with noticed values which is clear from the points plotted that the least value of final concentration is at the highest amount of modified chitosan used. Where in figure (5) the opposite occur that the percent of removal increase with the amount of modified chitosan used as the final concentration decrease.

The 0.05% v/v sample shows a large value of removal, where the final concentration of thymol blue left in the solution is 0.0002% v/v which means that this sample has lost about 0.498% v/v during adsorption so, by substituting initial and final concentrations in the equation of % of removal. Percent of removal was 99.6 %

which is very high compared to the other concentrations. Also, to calculate thymol blue adsorbed in mg/g, Thymol blue adsorbed in (ppm) is multiplied by a fraction of volume of solution and mass of adsorbent (Vol. of thymol blue / Mass of chitosan).

Table 1: Optimum initial concentration

Initial Conc. (%vol/vol)	Initial Conc. (ppm)	Final Concentration (%vol/vol)	Percent of removal	Thymol Blue adsorbed (%vol/vol)	Thymol Blue adsorbed (ppm)	Mass of adsorbent (x) (gm)	Thymol Blue adsorbed (mg/g)
0.05	50	0.0002	99.6	0.0498	498	0.05	249
0.1	100	0.003	97	0.097	970	0.05	485
0.2	200	0.009	95.5	0.191	1910	0.05	955
0.3	300	0.017	94.333	0.283	2830	0.05	1415
0.4	400	0.024	94	0.376	3760	0.05	1880
0.5	500	0.032	93.6	0.468	4680	0.05	2340

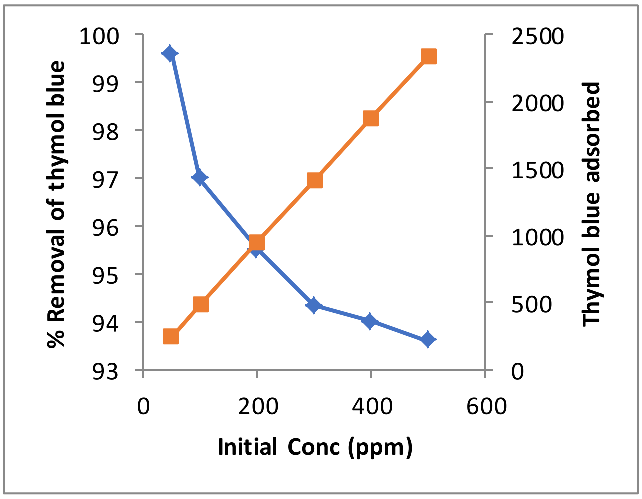

Figure 5: The removal efficiency of thymol blue

3.5 Optimum Dose of Chitosan

Though different amounts of modified chitosan are used with these conditions to observe exactly what is the amount needed of modified chitosan for this specific adsorption process by obtaining absorbance value from spectrophotometer. These values are then taken to the standard curve to get the concentration of thymol blue after adsorption in order to calculate the percentage of removal.
Figure 6 shows the relation between the dose of chitosan used in the experiment and the final concentration of thymol blue after adsorption, whereas the dose of modified chitosan

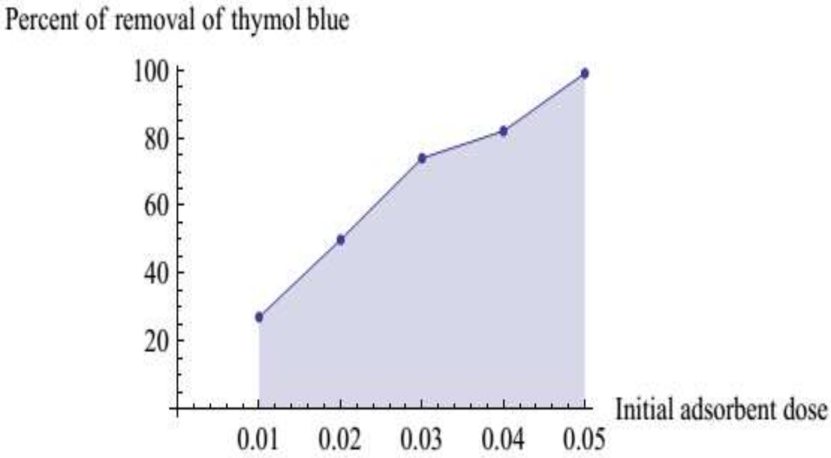

Figure 6: The relation between dose of chitosan used and percentage of removal of thymol blue after adsorption

3.6 Kinetic Study

The reaction kinetics of these experiments specially the modified chitosan are discussed, where it was needed to know whether modified chitosan is a pseudo first order or pseudo second order by applying some equations and plotting two graphs obtaining the R^2.

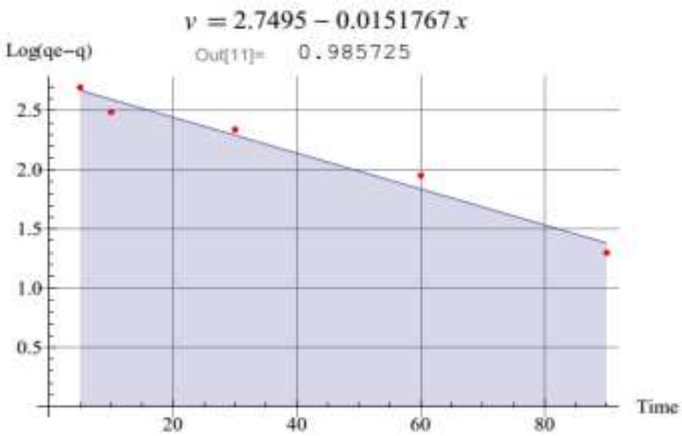

Figure 7: The kinetic model proposed as first order kinetics dye 0.5%

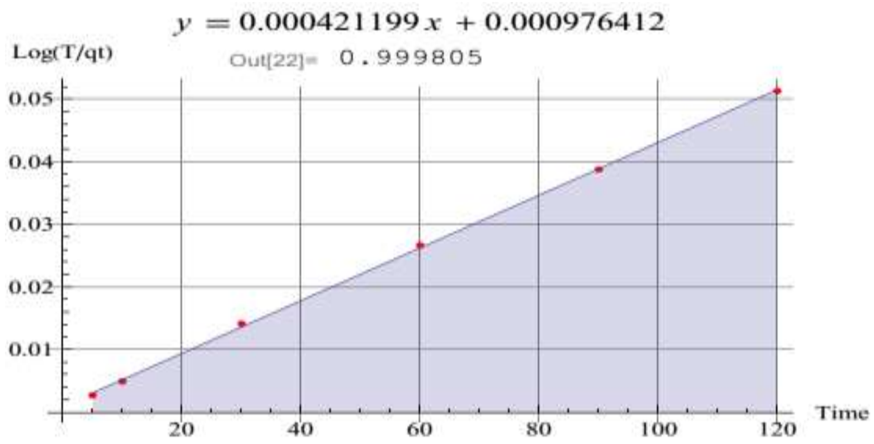

Figure 8: The kinetic model proposed as second order kinetics dye 0.5%

3. CONCLUSION

After preparing the oxidized chitosan, the first experiment which is optimum time took place to obtain the optimum time of adsorption which means to see the interval of time that achieved the best adsorption capacity by decreasing the concentration of thymol blue solution and the least concentration after adsorption process was the best time interval. After lifting each sample when it is time to be removed from the shaker, the samples are then taken to the spectrophotometer to measure the absorbance capacity by measuring the value of concentration of thymol blue after adsorption and a comparison was done between thymol blue before and after adsorption to see the difference in concentration for each sample to observe that the sample that took two hours (120 min) achieved the best adsorption capacity with absorbance value 0.0035 nm and concentration of thymol blue 0.032 % v/v .So the percent of removal of oxidized chitosan is 93.6 %. While the optimum pH of the solution was obtained to be 4 after proceeding the optimum time experiment. The spectrophotometer showed that the sample having pH of 4 achieved the best absorbance value as that of time experiment which is 0.0035 nm and final concentration of 0.032 with removal percentage 93.6 %. Then by concluding the optimum values of time and pH, It was observed that the sample having the concentration 0.05% v/v had the best values of absorbance where the concentration of thymol after adsorption was 0.0002 %v/v showing a big difference between the initial and final concentration of thymol blue with percentage of removal 99.6%. The last experiment was the optimum dose of modified chitosan, where after the three previous experiments it was concluded that the optimum values of thymol blue solution was determined. After the process the five samples were taken to the spectrophotometer to conclude that the sample having 0.05 grams oxidized chitosan show a promising adsorption value where the percentage of adsorption was 99% which means that the remaining thymol blue in solution is negligible by final concentration 0.0005 %v/v and 0.014 nm absorbance value.

Lastly the mathematical relations and equations using different techniques was applied to show whether the reaction is a first or a second order reaction, also knowing the classification of the reaction.

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