ADSORPTION STUDY FOR THE TREATMENT OF WASTEWATER USING CLOISITE 15A AS AN ADSORBENT

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BY

SHIVANI KALOTRA

ROLL NO. (601211006)

UNDER THE GUIDANCE OF

Dr. RAJEEV MEHTA
Head and Associate Professor
Department of Chemical Engineering
Thapar University, Patiala

Dr. V.K. SANGAL
Assistant Professor
Department of Chemical Engineering
Thapar university, Patiala

Department of Chemical Engineering
Thapar University
Patiala-147004, Punjab, India.
June 2014

CERTIFICATE

This is to certify that the dissertation entitled, "Adsorption Study for the Treatment of Wastewater using Cloisite 15A as an Adsorbent" is an authentic record of my own work carried out as requirements for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, under the supervision of Dr. Rajeev Mehta, Head and Associate Professor, Department of Chemical Engineering and Dr. V.K. Sangal, Assistant Professor, Department of Chemical Engineering.

Date:

Shivani Kalotra

(601211006)

It is certified that the above statement made by student is correct to the best of our knowledge and belief.

Dr. Rajeev Mehta

Head and Associate Professor

Chemical Engineering Department

Dr. V.K. Sangal

Assistant professor

Chemical Engineering Department

Countersigned by:

Dr. Rajeev Mehta

Head and Associate Professor

Thapar University, Patiala

Dr. S.K. Mohapatra

Dean, Academic Affairs

Thapar University, Patiala

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ABSTRACT

Textile industries consume large amount of water. It produces highly coloured wastewater. The quality of water is greatly influenced by the color. Textile wastewater needs proper treatment before discharged into the environment. Textile dyes are toxic, carcinogenic in nature and this causes a serious problem to living organisms. Adsorption study was conducted for the removal of Reactive Black 5 onto Cloisite 15A. Adsorption of RB5 was highly affected by contact time, pH, adsorbent dosage and initial dye concentration. The adsorbent dosage study was contacted by taking C_0 = 100 mg/l at natural pH and T = 303 K. The pH study was carried out in the initial pH range (pH_i) of 3 to 11 at 303K with optimum adsorbent dosage (0.35g/l). HCl or NaOH was used to adjust the pH of RB5 solution. To study the effect of time the equilibrium experiments were performed at various dye concentration (C_0 = 50 to 300 mg/l), m_{ad}= 0.35 g/l and at optimum $pH_{opts.}$ Pseudo first order and second order model were used to study the kinetic models. It was found that all the experimental data fitted well in the second order kinetic model. Three equilibrium isotherms were analyzed: Langmuir, Freundlich and Temkin isotherm. The isothermal experiments were performed at different C_0 values ranges from 50 to 300 mg/L with optimum adsorbent dosage and at optimum pH and the result shows that the process is endothermic in nature. Characterization was done by using XRD and TEM techniques.

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LIST OF SYMBOLS

q_m	**Adsorption Capacity**
N	**Heterogeneity factor**
T	**Temperature**
t	**Time**
K_1	**Pseudo first order rate constant**
K_2	**Pseudo second order rate constant**
q_t	**Amount of adsorbate adsorbed on the adsorbent at time t**
C_t	**Concentration of dye at time t**
C_0	**Initial dye concentration**
pH_{opt}	**Optimum pH**
pH_i	**Initial Ph**
m_{ad}	**Optimum adsorbent dosage**
q_e	**Amount of the adsorbate adsorbed on the adsorbent under equilibrium condition**
h	**Initial sorption rate**
V	**Volume of the solution**
C_e	**Equilibrium liquid phase concentration**
K_F	**Freundlich constant**
K_L	**Langmuir constant**
q_{exp}	**Experimental values**
q_{cal}	**Calculated values**
q_{max}	**Maximum adsorption capacity**
β	**Exponent**

MPSD	**Marquardt's percent standard**
n_p	**Number of parameters**
n_m	**Number of measurements.**
CHI^2	**Chi-square error**
λ_{max}	**Maximum wavelength**
λ_{min}	**Minimum wavelength**

CHAPTER – 1

INTRODUCTION

Rivers and lakes contamination with dyes causes serious damage to wild and human life. Currently there are more than ten thousand dyes commercially available **(Eren et al., 2006)** and the annual production of dyes is more than 7 x 10^5 tonnes across the world **(Ip et al., 2009).** It is expected that around 2 % of dyes produced yearly are discharged in effluent from manufacturing operations. The worldwide textile industry overall dye consumption is more than 107 kg $year^{-1}$. Although in the textile industry, it is expected that 10–15% of the dye is lost throughout the dyeing process and it has been released with the effluent **(Tan et al., 2010).** In various industries such as paper printing, textile, pharmaceutical, plating, leather, rubber and cosmetics dyes are commonly used **(Choi et al., 2008).** There are different types of dyes like cationic include basic dyes, anionic include acid, direct and reactive dyes, and non –ionic include dispersive dyes **(Eren at al., 2006**). The most common type of dyes is reactive dyes **(Choi et al., 2008).**

Textile industry is the topmost consumer of reactive dyes. Dye contamination causes a serious environmental problem. It is very important to eliminate dye from textile effluents before discarded into wastewater (**Zhang et al., 2014).** Real textile effluent is a combination of dyes, heavy metals, surfactants, total dissolved solids, salts, organic compounds, biological oxygen demand, chlorinated compounds and chemical oxygen demand **(Salleh et al., 2011).**

1.1 USES, PROPERTIES AND TOXICITY OF REACTIVE BLACK 5 DYE

Reactive dye is a class of dyes which make a covalent bond between the dye and the fiber. Reactive dyes developed between 1952 and 1955 by Rattee and Stephen. Reactive dyes are toxic to human and carcinogenic in nature.

Reactive black 5 is an anionic dye and anionic dyes depend on a –ve ion. The Molecular formula of RB5 is $C_{26}H_{21}N_5Na_4O_{19}S_6$. The molar mass of RB5 is 991.83g.mol^{-1}. It is soluble in water. It is available in solid form. **Figure 1** shows the chemical structure of reactive black 5 in non-hydrolyzed form.

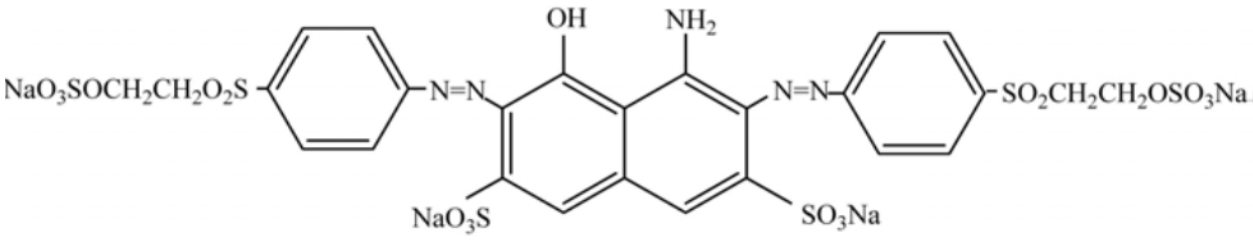


Figure 1.1: Structure of Reactive Black 5 (Eren et al., 2006)

1.2 PROPERTIES

1. Reactive dyes are soluble in water.
2. Natures of reactive dyes are anionic.
3. With the cellulosic fiber they make a strong covalent bond.
4. Dyeing process of reactive dyes is easy and it needs low temperature and less time for dyeing.
5. These are available in many colors and are noted because of their properties such as brightness and excellent fastness.
6. Absorb up to 90%

Table 1.1: Properties of RB5

PARAMETERS	REACTIVE BLACK 5
Synonym	Remazol Black B
Molecular formula	$C_{26}H_{21}N_5Na_4O_{19}S_6$
Melting point	$>300^0C$
Density	$530kg/m^3$ at 20^0C
Molecular weight	991.83
Composition	Dye content, 55%
Maximum wavelength (λmax)	597nm

Source: http://www.sigmaaldrich.com/catalog/product/sial/306452

1.3 METHODS FOR REMOVAL OF REACTIVE BLACK 5

Biological wastewater treatment and physicochemical wastewater treatment methods are not very effective to remove reactive dyes. Biological treatment is very expensive and due to low biodegradability of dyes, biological treatment is not efficient for the complete

elimination of dyes from wastewater **(Eren et al., 2006).**Solvent extraction, ion-exchange, adsorption, chemical precipitation, membrane filtrations, flocculation and ozonation are the methods which are generally used to treat dyes containing wastewater. Among these techniques, adsorption technology has been found to be an effective method to remove dye using different adsorbents such as activated carbon **(Choi et al., 2008).** Adsorption can be used for wastewater treatment because due to its ability to remove of dye contaminations, ease of operation, an inexpensive and simple in design **(Ip et al., 200**9). Biological, coagulation and flocculation are conventional treatments; these are no longer able to attain high quality treated water **(Ip et al., 2009).** Due to the high solubility of dyes in water, it is very difficult to eliminate reactive dyes by chemical coagulation **(Aguiar et al., 2013).** Coagulation, flocculation and biodegradation have some disadvantages like handling problem, disposal problems, high sludge production, slow process, maintenance and nutrition requirements and essential to create an optimal favorable environment **(Crini, 2006).**

Adsorption is the most common choice to remove dye. It is the process for separation of mixtures on a laboratory and industrial scale. Adsorption is a surface phenomenon **(Noll, 1992; Dabrowski et al., 2001).** Dyes adsorption depends on the surface chemistry of the adsorbent and on the properties of the dye **(Noroozi et al., 2007; Salleh et al., 2011).** Adsorption has suitable for both processes i.e. continuous and batch processes. Therefore, adsorption becomes a preferred technique for recovery and removal of dyes from wastewater **(Bhattacharyya et al., 2008).**

Today there are different types of adsorbents are available which are used for removing color from wastewater. To remove dye from wastewater activated carbon is widely used. Adsorption by activated carbon has been found to be an efficient adsorbent because it has extremely large surface area and also has high adsorption capacity **(Choi et al., 2008; Eren et al., 2006).**

However activated carbon is expensive and has some restrictions like cost of the activated carbon, regeneration problems and after regeneration the loss of adsorption efficiency **(Salleh et al., 2011; Srivastava et al., 2007).** Activated carbon can be attainable in granular and powdered form.

1.4 BENEFITS OF POLYMERIC ADSORBENTS AS COMPARE TO CONVENTIONAL ADSORBENTS

Cost is essentially an important parameter for comparing the adsorbent materials **(Bailey et al., 1999).** A low cost adsorbent is that which requires small processing and abundant in nature. Polymeric adsorbent is low-cost adsorbents. They are abundant in nature, inexpensive, require little processing and are effective materials for the adsorption of dyes **(Crini, 2006).** Clay is a naturally occurring adsorbent. Clay present market price is 20 times cheaper than that of activated carbon **(Babel and Kurniawan, 2003).**

1.5 UNMODIFIED AND ORGANICALLY MODIFIED NANOCLAY AS AN ADSORBENT

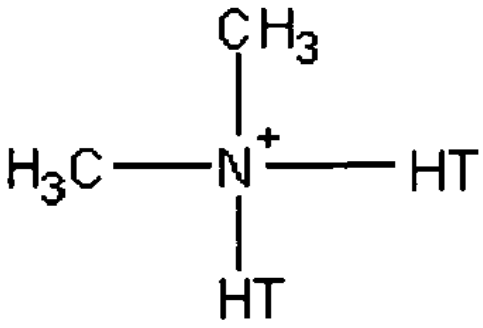
Nanoclay can be used for wastewater treatment as adsorbent due to their large specific surface area, nanometer scale size, layered structure, chemical and mechanical stabilities, high cation exchange capacity and a variety of surface and structural properties**(Liu and Zhang, 2007;Bhattacharyya, 2008).**

As a clay, montmorillonite has been one of the most considered nanofillers due to its abundance**(Jin et al., 2013;Essington, 2003; Gunister et al., 2007**) and large aspect ratio from 50 to 1000 **(Azeredo, 2009; Corre et al., 2010).** Aspect ratio means ratio of length to thickness. To improve properties of nanocomposites the large aspect ratio of montmorillonite (MMT) is a very essential factor **(Jin et al., 2013).** MMT is a member of the smectites family. The natural clays type smectites have been widely used, but due to their hydrophilic and thixotropic properties they present some difficulty. Moreover, clays can be modified by the intercalation of organic cations into their interlayer surface.

After the modification, the –ve charges of the clay surfaces are neutralized and the clays become organophilic. Therefore due to the organic layer organoclays are attractive for use as selective sorbents **(Elemen et al., 2012).**

As compared to natural clays, a modified material from clays has a higher porosity and a higher surface area**.** These materials also have a lower hydrophilicity and a higher acidity than of the former natural clays **(Aguiar et al., 2013).** Modified clay has a great potential for the removal of textile dye through adsorption **(Elemen et al., 2012). Table 1.2 and 1.3** represent the properties of Cloisite 15A and Characteristics of various organoclays fillers.

Structure of Cloisite 15A



Anion: Chloride

Figure 1.2: structure of Cloisite 15A

Here HT is hydrogenated Tallow (65 % C18, 30 % C16 and 5 % C14)

(1) 2M2HT: dehydrogenated tallow, quaternary ammonium.

Source: http://www.neunano.com/index.php

Table 1.2: PROPERTIES OF CLOISITE 15A

PROPERTIES	CLOSITE 15A
Organic Modifier (1)	2M2HT
Modifier concentration	125meq/100g clay
% moisture	<2%
% weight loss on ignition	43%
Color	Off white
Specific gravity	1.4-1.8
Physical state	Solid
Form	Powder
Loose bulk density, lbs/ft^3	10.79
Packed bulk density, lbs/ft^3	18.64
Density, g/cc	1.66

Source: http://www.neunano.com/index.php

Table 1.3: Characteristics of various organoclay fillers (Kracalík1 et al., 2007)

Organoclay	**Organic modifier(1)**	**Modifier concentration [mequiv/100 g clay]**	**Moisture [%]**	**Weight loss on ignition [%]**
Cloisite 6A	**2M2HT**	**140**	**<2**	**45**
Cloisite 10A	**2MBHT**	**125**	**<2**	**39**
Cloisite 15A	**2M2HT**	**125**	**<2**	**43**
Cloisite 20A	**2M2HT**	**95**	**<2**	**38**
Cloisite 25A	**2MHTL8**	**95**	**<2**	**34**
Cloisite 30B	**MT2EtOH**	**90**	**<2**	**30**
Cloisite 93A	**M2HT**	**90**	**<2**	**37.5**

Where (1): quaternary ammonium chlorides

Dialkyldimethyl: (2M2HT)

Alkyl (benzyl) dimethyl: (2MBHT)

Alkyl (2-ethylhexyl) dimethyl: (2MHTL8)

Alkylbis(2-hydroxyethyl)methyl: (MT2EtOH)

Methyl: (M2HT)

Alkyls are a mixture of 65 % C18, 30 % C16 and 5 % C14, derived from hydrogenated tallow.

1.6 OBJECTIVES

1. To study the characterization of the Cloisite 15A.
2. To study the effect of initial pH, contact time, adsorbent dose, initial concentration and temperature on the removal of Reactive Black 5 from the aqueous solution.
3. To perform the equilibrium adsorption and the kinetics of adsorption of Reactive Black 5 onto Cloisite 15A nanoclay and to analyze the experimental data using various kinetic and isotherm models.

CHAPTER – 2

LITERATURE REVIEW

GENERAL: In this chapter, a number of adsorption studies of Reactive Dye on varieties of adsorbent, available in open literature, have been reviewed.

Eren et al. (2006) investigated the adsorption of Reactive black 5 onto powdered activated carbon and fly ash depending on pH, contact time, adsorbent dosage and initial dye concentration by employing batch adsorption technique. The adsorption of RB5 onto powdered activated carbon and fly ash were determined at room temperature ($T=20^0C$). The result indicated that the adsorption capacity of PAC was higher than the adsorption capacity of fly ash but the fly ash was an effective adsorbent for the removal of Reactive Black 5. PAC is an expensive material but fly ash is a low cost adsorbent and the regeneration for fly ash is not necessary. The adsorption process fitted in well with both the isotherm (Freundlich isotherm and Langmuir isotherm). The monolayer capacity of fly ash and PAC were found to be 7.936 mg/g and 58.823 mg/g. The adsorption of RB5 onto PAC and fly ash was better described by pseudo second order model.

Sonawane et al. (2008) investigated the adsorption of basic methylene blue dye onto originally modified nanoclay (bentonite). In this study two different types of originally modified nanoclays (adsorbents) were synthesized by using tetrabutyl ammonium chloride, N-cetyl-N, N, N-trimethyl ammonium bromide. In this paper, adsorption of basic methylene blue dye was carried out by two methods shirring and sonication and the result revealed that TBAC nanoclay sonication > TBAC nanoclay stirring > CTAB nanoclay sonication > CTAB nanoclay shirring > natural bentonite sonication > natural bentonite stirring. It was seen that adsorption is highly dependent on clay structure. For TBAC modified nanoclay (tetrabutyl ammonium chloride), the XRD spectra showed amorphous nature, whereas CTAB modified nanoclay (N-cetyl-N, N, N-trimethyl ammonium bromide) indicated crystalline nature. TEM images observed tactoid

structure. For TBAC modified nanoclay the calculated values of Langmuir constant b and Langmuir adsorption isotherm Q_e were 0.2468 and 0.3485 mg/mg.

Choi et al. (2008) investigated adsorption characteristics of Reactive Black 5 (RB5) using surfactant-modified activated carbon. The characteristics were studied by kinetic and equilibrium isotherm model in terms of adsorption capacity, affinity and sorption rate constant. Three different Activated carbon (ACs) i.e. AC in CPC (cetylpyridinium chloride) solution, precoated AC by CPC and pure AC were studied. Three kinetic models were applied pseudo first-order, pseudo-second-order and intra-particle diffusion. Regardless of presence of CPC, the sorption kinetics followed pseudo-second-order kinetic model with the highest correlation coefficient compared to the other models. By fittings adsorption experimental data to three well-known isotherm models such as Freundlich, Langmuir and double scheme of Langmuir models, the equilibrium adsorption capacities were determined. It is found that a double scheme of Langmuir model was more suitable to describe experimental data than the conventional Freundlich and Langmuir model. Surface modification could enhance the sorption capacity and rate of RB5 on AC but overall performance of the modified AC is highly dependent on pore size distribution and surface area of AC.

Bhattacharyya et al. (2008) studied the removal of Co (II), Ni (II) and Fe (III) from aqueous solution with kaolinite and montmorillonite as adsorbents. The adsorption study was performed by observing the effect of various parameters i.e. amount of adsorbents, temperature, time, pH and concentration of metal ions. The equilibrium time for Fe (III) was 300 min, 240 min for Co (II) and 180 min for Ni (II) respectively. The pseudo second order kinetic model was predominant for the adsorption of all three metal ions. From all three metal ions, the adsorption capacity of kaolinite is much lesser than of montmorillonite. The Langmuir monolayer capacity (q_m) was 10.4 to 11.2 mg/g for kaolinite and 28.4 to 28.9 mg/g for montmorillonite. The adsorption isotherms were well represented by Langmuir and Freundlich equations. It was found that both the adsorbents are suitable for the treatment of Co (II), Ni (II) and Fe (III).

Elemen et al. (2012) investigated the potential of the organoclays for the removal of Reactive Red 141. The clay was synthesized by using cationic surfactant (HDTMA). By batch technique the dye adsorption was studied and it was observed that approximately more than 80% of the dye color was removed by using (hexadecyltrimethylammoniumbromide) HDTMA - bentonite. Adsorption studies were contacted by varying parameters such as initial dye concentration (20-200 mg L^{-1}), adsorbent dosage (0.05-0.1 g L^{-1}), temperature (30-40^{0}C) and contact time (0-1440 min) and result revealed that it was highly dependent on these conditions. The XRD and FTIR techniques were used to examine the surface modification of bentonite. The adsorption of dye was well defined by pseudo-second order. The equilibrium data correlated well with Langmuir model. For the all adsorbent dosages and temperatures, R_L values were found to be between 0 and 1 and it showed that organoclay was favorable for the adsorption of RR 141. It was seen that adsorption of dye increases with increasing the adsorbent amount regardless of initial concentration of dye. An artificial neural network model (ANN) was developed to predict the adsorption performance of organo-bentonite in the treatment of RR 141 solutions. As a result the mean square error and determination coefficient (R^2) values were found to be 0.027364 and 0.978 respectively.

Aguiar et al. (2013) studied the adsorption of Reactive Black 5 an anionic dye and Methylene Blue a cationic dye using aluminum pillared clays (AL-PILC), natural clays and activated carbon as an adsorbent depending on various parameters such as initial dye concentration, Initial pH, contact time and effect of addition of NaCl by employing batch adsorption. The clay charged surface is strongly influenced by NaCl. X-ray diffraction was used to determine the structural properties of pillared and natural clays and the textural properties of these materials were attained by N2 adsorption-desorption isotherm at 77 K. The effect of pH for the removal of RB5 and MB onto natural and pillared clay was investigated in the range of pH 2-12 and the result shows that the maximum adsorbed amounts were attained at pH 2 to RB5 and pH 12 to MB. It was found that with increase in the initial pH for RB5 the adsorption capacity decrease and increase with

decrease initial pH for MB. The adsorption equilibrium data fitted well into both the Langmuir and Langmuir-Freundlich isotherms models. It was found that pillaring process only enhanced the adsorption of the RB5. The salt concentration can either impaired or increased adsorption of dye depending on the system studied. In the adsorbate or adsorbent the salt influenced more strongly. The result revealed that a special morphology formed during the process of pillaring greatly increased adsorption of the MB cationic dye in the range of high salt concentrations.

Mohammed Saeed. (2013) studied the adsorption of Reactive Black 5 by using two surfaces CaO and ZaO. The effects of various parameters were studied such as initial concentration of dye, pH, contact time and adsorbent weight. The result showed that the removal efficiency was increased by increases in the initial dye concentration where 50 mg/L was the best dye concentration and dye removal was decreased by increasing the adsorbent weight where 0.1gm was the best weight. Maximum amount of RB5 dye was removed within 70min and reached equilibrium. It is also observed that high removal of dye was attained at pH = 5. The adsorbed amount onto Zno surface (3.645mg/g) was less than that of Cao surface (8.665mg/g). The order of reaction for ZaO surface was pseudo-second order and the order of reaction for CaO was pseudo- first order.

Rasouli et al. (2014) studied the activation and modification of MMT–K10 by using sulfuric acid for activation and cetylrimethylammonium bromide (CTAB) for modification. Optimization was done to determine the maximum decolonization efficiency of activated modified MMT- K10 and it was attained at the optimum condition of activation (contact time = 2.2 h, concentration = 3.6mol/L, T = 50^0C).The amount of R^2 and adjusted R^2 was 0.968 and 0.940 (R^2 = 0.968, Adj R^2 = 0.940). FTIR spectra (Fourier transform infrared spectrum), XRD spectra, TEM and SEM images analyses provide the successful modification on the activated MMT-K10. The result shows that activated – modified MMT-K10 was a very good adsorbent for the adsorption of Reactive Navy Blue SP-BR dye.

Zhang et al. (2014) studied the removal of crystal violet by clay/PNIPAm nanocomposites (CPN) hydrogels were prepared by using lithium magnesium silicate hydrate (LMSH) to eliminate CV (crystal violet) from aqueous solution. SEM (Scanning electronic microscopy) and DSC (differential scanning calorimetry) analysed the morphology and thermal responsibility of resulting hydrogels. Kinetic study was held under different parameters (pH, contact time, initial dye concentration) and the adsorption capacity of clay was evaluated by using UV/Vis spectroscopy. The pore sizes range from 30 to 50 µm, which is favorable for CV adsorption. The Q_t values of CPN20 = 4.71 mg/g, CPN10 = 4.23 mg/g, CPN05 = 2.74 mg/g and CPN15 = 4.32 mg/g at temperature 25^0C and time = 12 h. At 37^0C the Qt values for CPN05 and CPN30 was 1.2 mg/g and 1.8 mg/g. When the pH values increases from 3 to 8.9, the Q_t values increases 1 to 1.5 times. When the CV concentration was added from 10 to 30 mg/L, the Q_t values of CPN hydrogel increases 2 to 4 times.

CHAPTER – 3

ADSORPTION THEORY

3.1 ADSORPTION

Adsorption is a chemical process that occurs when a liquid or most usually a gas (adsorbate) accumulates on the surface of a solid (adsorbent), forming a molecular or atomic film. Adsorption is a temperature dependent process. Adsorption depend on the various factors like nature of adsorbent and adsorbate, activation of adsorbent, the surface area of adsorbent and experimental conditions like temperature, pressure etc. Adsorbent is the substance on whose surface the adsorption occurs.Adsorbent is a porous substance and it has the capability to adsorb or absorb other substances onto its surface using intermolecular forces. Depending on the nature of attractive forces, there are two types of adsorption chemical adsorption (chemisorption) and physical adsorption (physisorption). There is a strong chemical bond in chemisorption. **Table 3.1** shows the difference between Physisorption and Chemisorption.

3.1.1 Physisorption: In physisorption the forces involved are Vander Waals forces. The nature of Physisorption is exothermic. Therefore according to Le-Chatelaine's principle, with an increase in temperature it decreases. This means at a lower temperature the physisorption occurs more readily. It is a reversible process. The activation energy and enthalpy values are very low (20– 40 kJ mol-1). In this adsorption the force of attraction are very weak between the adsorbent and adsorbate, therefore by decreasing the pressure or by heating, physical adsorption can be easily reversed.

3.1.2 Chemisorption: Chemisorption involving a chemical bonding between the adsorbate and the adsorbent. Chemisorption is also known as Langmuir adsorption. It takes place at higher temperature. For chemisorption the enthalpy values are higher (80-240 kJ mol-1). It is irreversible and also an exothermic process. This adsorption is not usually affected by small changes in pressure. Chemisorption is less common than

physisorption. It is highly specific. In chemisorption adsorption cannot be easily reversed because the force of attraction is very strong. Chemisorption occurs generally at much higher temperatures than the critical temperature.

Table 3.1: Difference between Physisorption and Chemisorption

PROPERTY	PHYSISORPTION	CHEMISORPTION
Heat of adsorption	**Heat of adsorption ranging from 10 to 40 kJ/mole.**	**Heat of adsorption higher than 200 kJ/mole.**
Temperature	**It is usually takes place at low temperature and decrease with increasing temperature.**	**It takes place at relatively high temperature.**
Pressure	**High pressure is favorable and decrease of pressure causes desorption.**	**High pressure is favorable but decrease of pressure does not causes desorption.**
Activation energy	**No appreciable activation energy is required.**	**Appreciable activation energy may be involved in the process.**
Rate of adsorption	**It is reversible, non-activated and rapid.**	**It is irreversible, activated and may be slow.**

Source:http://jscienceclass.blogspot.in/2012/06/physisorption-and-chemisorptionhttp://entrancechemistry.blogspot.in/2012/11/physisorption-and-chemisorption

3.2 PROCESS OF ADSORPTION

The rate of adsorption is determined by the rate of transfer of the adsorbate from the bulk to the adsorption sites. The transport of adsorbate components from the solution into the pores of the adsorbent particles can be controlled either by one or more of the following steps, pore diffusion surface diffusion, film or external diffusion and adsorption on the pore surface. During the adsorption process, it is necessary to calculate the slowest step involved among these steps to identify the controlling step **(Srivastava, 2009).**

The intraparticle diffusion controls the adsorption process with large particle sizes of adsorbent, high concentration of adsorbate, good mixing and low affinity of adsorbate for adsorbent. On the other hand external diffusion control the adsorption process with dilute concentration of adsorbate, small particle sizes of adsorbent, poor mixing and higher affinity of adsorbate for adsorbent. Adsorption occurs in three stages, if the adsorbate concentration increases **(Aravindhan et al., 2007).**

First, over the surface of the solid a single layer of molecules is formed. This monolayer may be chemisorbed and is associated with a change in free energy that is a characteristic of the forces that hold it. While second and third layer is formed by physical adsorption. By the size of the pores the number of layers is decided. Finally, for adsorption from the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate, when its partial pressure reaches a critical value relative to the size of the pore. The parameters that affect the adsorption process are initial pH, contact time (t), adsorbent dose (m_{ad}), and temperature (T).

3.3 ADSORPTION KINETICS

There are various kinetic models that describe the adsorption process. The pseudo-first-order kinetic model and the pseudo-second-order kinetic model are the most commonly used models **(Elemen et al., 2012).**

3.3.1 Pseudo-first-order kinetic model

The equation for pseudo-first-order kinetic model is given by

$$\mathbf{dq_t/dt = k_1 (q_e - q_t)}$$

After integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ and $t = 0$ to $t = t$, the integrated form of equation becomes:

$$\mathbf{\log (q_e - q_t) = \log q_e - (k_1 / 2.303)\, t}$$

Where, q_e and q_t (mg/g) are the amount of dye adsorbed on the adsorbent at equilibrium and at time t, k_1 (1/min) is the rate constant of first-order adsorption **(Eren et al., 2006).**

3.3.2 Pseudo-second-order kinetic model

The rate equation for pseudo-second-order model is expressed as:

$$\mathbf{dq_t / dt = k_2 (q_e - q_t)^2}$$

Where, k_2 is the second-order adsorption rate constant (g/mg min). By taking boundary conditions $q_t = 0$ to $q_t = q_t$ and $t = 0$ to**t = t,** the linearized form of equation becomes:

$$\mathbf{t/q_t = 1 / k_2 q_e^2 + (1 / q_e)\, t}$$

The theoretical adsorbed dye q_e (mg/g) can be calculated from pseudo-second-order. **(Elemen et al., 2012)**

$$\mathbf{h = k_2 q_e^2}$$

h is the initial sorption rate (mg/g min)

3.4 ADSORPTION ISOTHERM

Isotherm equations for the adsorption process are given in **Table 3.1**. The Langmuir and Freundlich equations are commonly used to describe adsorption isotherms. The

equilibrium isotherms define how the adsorbent interacts with the adsorbate **(Ip et.al., 2009).** It is essential to examine to obtain an ideal isotherm model indicating the adsorbate adsorption system onto adsorbent **(Elemen et al., 2012).** Therefore equilibrium adsorption equations are required for the design of an adsorption system **(Sharma et al., 2010).** Langmuir, Temkin and Freundlich are three commonly used isotherm models were employed to describe the adsorption of adsorbate.

3.4.1 Langmuir isotherm model

In the Langmuir adsorption model, adsorption of adsorbate takes places at specific homogeneous sites within the adsorbent and valid for monolayer adsorption onto adsorbents **(Reza et al., 2012).**

3.4.1.1 Assumption of Langmuir isotherm (Oremusová et al., 2007)

1. All adsorption occurs through the same mechanism.
2. The surface of the adsorbent is uniform that is all the adsorption sites are equal.
3. Adsorbed molecules do not interact.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The expression of the Langmuir isotherm model is given by the Eq. **(Elemen et al., 2012)**

$$q_e = q_{max} K_L C_e / 1 + K_L C_e$$

Where K_L (L/mg) is the Langmuir adsorption constant, q_{max} (mg/g) is the maximum adsorption capacity. C_e (mg/L) and qe (mg/g) are the equilibrium dye concentration and amount of dye adsorbed respectively. The linear form of above equation is written by:

$$C_e/q_e = 1/q_{max}K_L + C_e/q_{max}$$

3.4.2 Freundlich isothern model

The Freundlich model equation describes heterogeneous systems. In the Freundlich model, the adsorption of adsorbate occurs on a heterogeneous surface by multilayer sorption and the adsorption capacity can increase with an increase in adsorbate concentration **(Reza et al., 2012).** The empirical Freundlich equation describes heterogeneous systems is given as:

$$q_e = K_F C_e^{1/n}$$

Where, K_F (mg/g)(L/mg)$^{1/n}$ is the Freundlich constant and 1/n is the heterogeneity factor **(Elemen et al., 2012)**

By taking logarithm, a linear form of the Freundlich isotherm model can be written by

$$\log q_e = \log K_F + 1/n \log C_e$$

3.4.3 Temkin isotherm model

The Temkin isotherm has been commonly applied in the form:

$$qe = (R_T/b_T) \ln(K_T C_e)$$

The linear form of Temkin equation can be written as:

$$q_e = (R_T/b_T) \ln K_T + (R_T/b_T) \ln C_e$$

Where B = R_T/b_T, b (J/mol)is the Temkin constant related to heat of sorption, K_T(L/g) is the Temkin isotherm constant, R is the gas constant (8.314J/ molK), and T (K) is the absolute temperature **(Zheng et al., 2009).**

Table 3.2: isotherm equations for the adsorption process

Isotherm	Equation	References
Langmuir Isotherm	$q_e = q_{max} K_L C_e / 1 + K_L C_e$	**(Elemen et al., 2012)**
Freundlich Isothern	$q_e = K_F C_e^{1/n}$	**(Elemen et al., 2012)**
Temkin Isotherm	$q_e = \frac{R_T}{b_T} \ln A_T + \frac{R_T}{b_T} \ln C_e$	**(Zheng et al., 2012)**

CHAPTER-4

MATERIAL AND METHODS

4.1 GENERAL: This chapter involves the preparation of adsorbent and experimental procedure.

4.2 ADSORBATE

Reactive Black 5dye was purchased from sigma Aldrich chemical company. The Reactive Black 5 purity was 90%.RB5 was used as a wastewater. A stock solution of 1g/l of reactive black 5 dye was prepared in double distilled water and used for further studies by diluting as per experimental requirement.

4.3 PREPARATION OF ADSORBENT

In this study cloisite 15A was used as an adsorbent. Cloisite 15A is a natural organically modified montmorillonite nanoclay with a quaternary ammonium salt. Organically modified montmorillonite nanoclay was prepared by dispersing adsorbent (Cloisite 15A) in 50ml of double distilled water by using ultrasonic probe for 10 min. After using ultrasonic probe this mixture was homogenize using homogenizer for 4min at 10,000 rpm. Homogenizer is mainly used for uniformly distributing solid particles in the liquid. Ultrasonic probe are generally used where high amplitude waves are required.

4.3.1 ULTRASONIC PROBE

Ultrasonic probe is commonly used for dispersing nanoparticles in liquids. This is ideal for nanoparticle dispersion, creating emulsions and homogenization. Ultrasonic probe is a LCD screen with a touch screen control and all the operating parameters are clearly displays. The probe should be injected without touching the container walls. Cooling bath is essential during the dispersion of particles. Probes should be placed around 1cm

away from the bottom of the container i.e. contact between the probe and the container walls should be avoided.

Figure 4.1: ultrasonic probe

4.3.2 HOMOGENIZER

Homogenizer is a high-performance dispersing instrument with digital speed display. The speed range of homogenizer is from 3000 to 25000 rpm. It has a digital speed display, electronic speed control and electronic overload protection. The minimum volume range is 0.001 L and maximum volume range is 2 L. It is a batch process and power input is 700W.The maximum viscosity of homogenizer is 5000 mPas.

Figure 4.2: Homogenizer

4.4 ANALYTICAL METHODS

Figure 4.3 and 4.4 shows the calibration curve for color removal and dye removal of RB5.The amount of RB5 adsorbed was evaluated using a UV/VIS spectrophotometer (Perkin Elmer, Schimadzu, Japan). A well-known concentration solution (10, 20, 30, 40, 50 ppm) was taken to find out the absorbance of the solution. The maximum wavelength (λ_{max}) equivalent to maximum absorbance was determined by UV/VIS spectrophotometer. The maximum wavelength (λ_{max}) for the color removal and minimum wavelength (λ_{min}) for the dye removal was found to be 597 nm and 312nm.A

Calibration curve of the RB5 was plotted between the different absorbance and the concentration of RB5 solution.

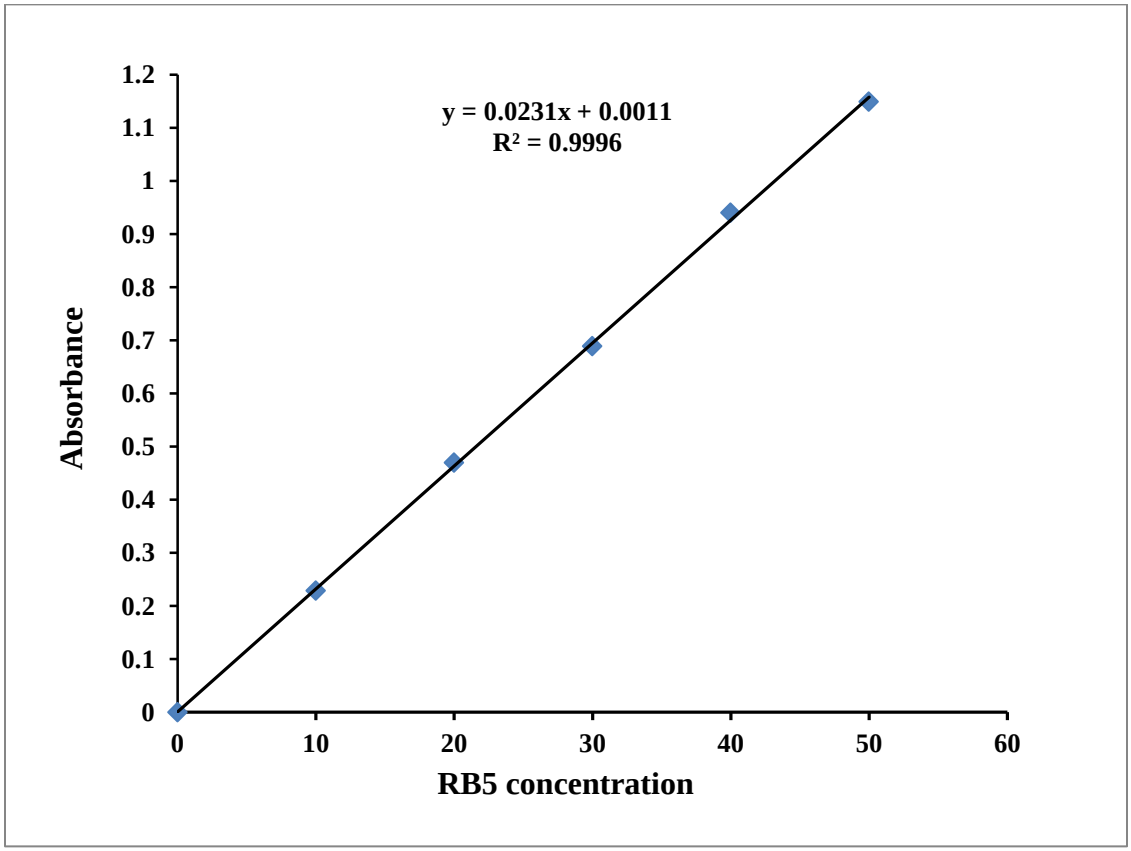


Figure 4.3: Calibration curve for RB5 at wavelength 597

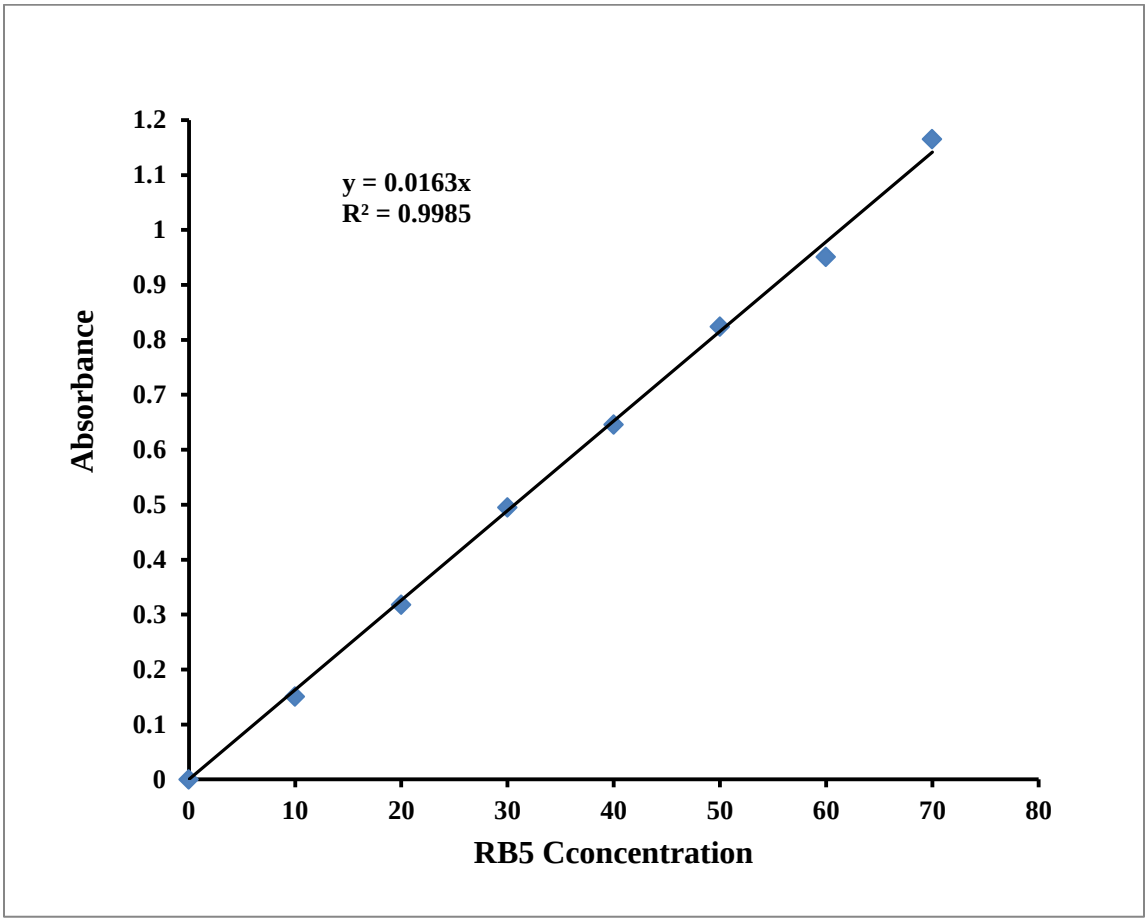


Figure 4.4: Calibration curve for RB5 at wavelength 312

4.5 EXPERIMENTAL PROCEDURE

The functions of adsorbent dosage, temperature (20 to 40^0C), contact time (0 to 35 min) and initial dye concentration (50 to 300mg/L) on the RB5adsorptionwereanalysed.A known amount of adsorbent was placed in a 250ml stoppered conical flasks containing 100ml of dye solution (known pH) for each experiment. All adsorption experiments were performed through a batch method on a shaking incubator with a constant speed at 150 rpm and a constant temperature for 35min to attain the equilibrium. After 35min the adsorbate and the adsorbent was separated from the Reactive Black 5 solution by filtration and the absorbance was analysed using a UV/VIS spectrophotometer. The concentration was determined from calibration curve.

The percentage removal of RB5 was calculated using the following relationship:

Percent RB5 removal = $(C_0\text{-}C_e)\ 100/C_0$

Where, Co (mg/L) is initial RB5 concentration and Ce (mg/L) is the equilibrium RB5 concentration.

4.6 Kinetics of Adsorption: Pseudo-first order and pseudo-second-order kinetic parameters of Reactive Black 5 were calculated at various C_0 values (50-250 mg/L) at optimum adsorbent dosage (m_{ad}-opt), optimum pH (pH_{opt}) and optimum contact time. The amount of adsorbate adsorbed, q_t (mg/g), at any time t was calculated as:

$$\mathbf{q_t = (C_0 - C_t)\ V/m_{ad}}$$

Where, C_t is the Reactive black 5concentration (mg/L) at time t, V is the volume of the solution (liter).

An error function, Marquardt's percent standard deviation (MPSD) (Marquardt, 1963) was used to find out the most suitable kinetic model to represent the experimental data. This error functions is given as:

$$\text{MPSD} = 100\sqrt{\left(\frac{1}{nm-np}\right)\sum_{i=1}^{n}\frac{(qt,i,exp - qt,i,cal)^2}{(qt,i,exp)^2}}$$

In this equation, the subscript 'exp' and 'cal' represent the experimental and calculated values, n_p is the number of parameters in the model and n_m is the number of measurements.

4.7 Study of Isotherm: For the design of adsorption systems the equilibrium adsorption equations are required. Thus, for the equilibrium isotherm, it is very important to establish the most suitable correlation. Adsorption isotherm experiments were performed at three different temperature 293, 303 and 313 K with C_0 values of 50, 100, 150, 200, 250 and 300 mg/L at optimum pH ($pH_{(opt)}$) and optimum amount of adsorbent (m_{ad}-opt).

Langmuir, Freundlich and Temkin are three commonly used isotherm models were employed to describe the adsorption of RB5.

After 30 min the adsorbent separated from the RB5 dye solution and analysed for equilibrium RB5 concentration (Ce). The equilibrium adsorption uptake, q_e (mg/g), were calculated using the following relationship

$$\mathbf{q_e = (C_0 - C_e) V / w}$$

To find out the best fit isotherm model the Chi-square error analysis function was used and it is written as:

$$CHI^2 = \sum_{\mathbf{k=0}}^{\mathbf{n}} \frac{(\mathbf{qe,i,exp} - \mathbf{qe,i,cal})^2}{\mathbf{qe,i,exp}}$$

CHAPTER - 5

RESULTS AND DISCUSSION

5.1 GENERAL

Adsorptive treatment of RB5 in batches onto nanoclay is reported in this chapter. Results obtained during the adsorption of Reactive Black 5 and their interpretations have been discussed in detail. Symbols: initial pH (pH_i), contact time (t), adsorbent dose (m_{ad}), and temperature (T), optimum pH (pH_{opt}),optimum adsorbent dosage (m_{ad}-opt).

5.2 CHARACTERIZATION OF CLOISITE 15A NANOCLAY

The structures of Cloisite 15A were investigated by using XRD and TEM technique.

5.2.1 XRD (X-ray diffraction)

The XRD pattern of dispersed Cloisite 15A nanoclay is shown in **figure5.13**. The XRD was performed on an X'pert pro PANalyatical in the 2Ɵ range of 2^0 to 50^0. The Cloisite 15A have three peaks at 2Ɵ = 3.6^0, 21.9^0 and 36.07^0.

The interlayer spacing for the organically modified nanoclay (Cloisite 15A) is 2.446 nm, 4.04 nm and 2.48 nm respectively. The results revealed that the intercalation is occurred. The intercalation of polymer in between clay layers will increase the interlayer spacing resulting in an increase in d_{001} value. The degree of intercalation is determines by the interaction between the polymer and the organic modifier **(Zhu et al., 2006).**

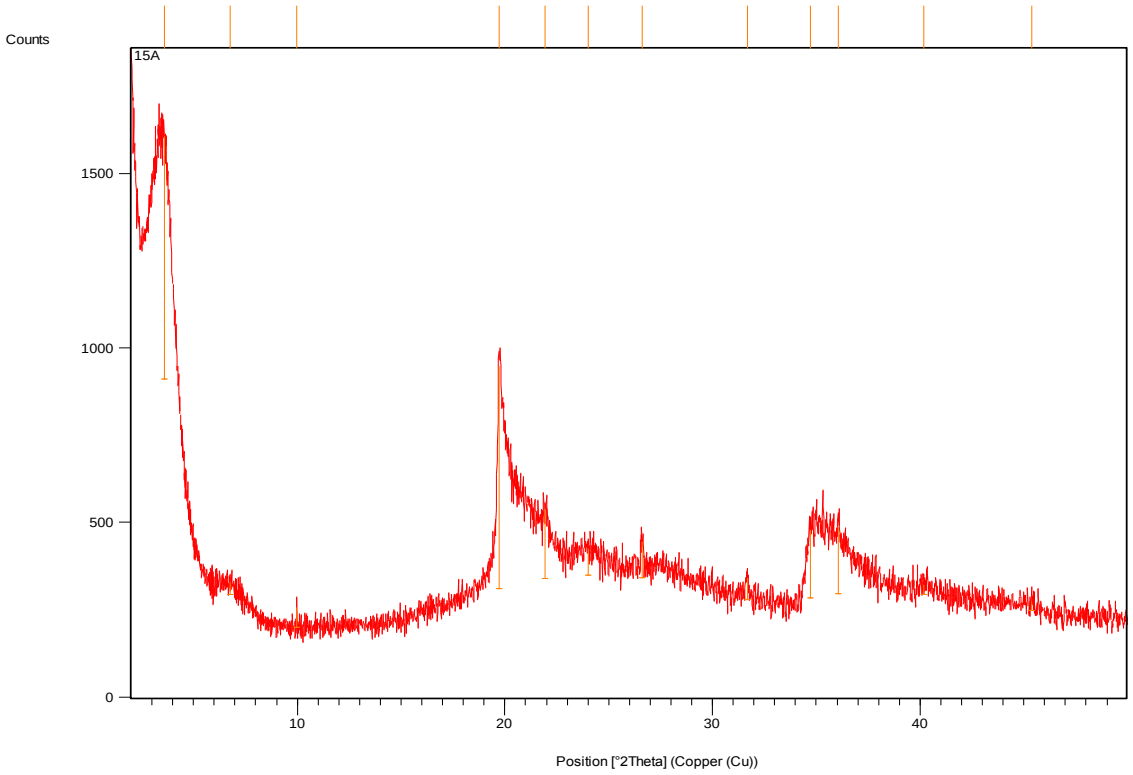


Figure 5.1: XRD pattern of cloisite 15A nanoclay

5.2.2 TEM (transmission electron microscopy)

Figure 5.2: shows the TEM (transmission electron microscopy) morphology of 0.35g of dispersed nanoclay (Cloisite 15A). The morphology shows that the nanoclay intercalation is present and observed a tactoid structure. The interlayer spaces of dispersed Cloisite 15A is 4.02 nm. TEM is a direct method to detect the intercalation. TEM images were analyzed to achieve in-depth knowledge of the structure of the nanoclay.

To understand the structural and surface morphology, TEM images were analyzed. TEM image for the Cloisite 15A was observed at magnification 441000×.

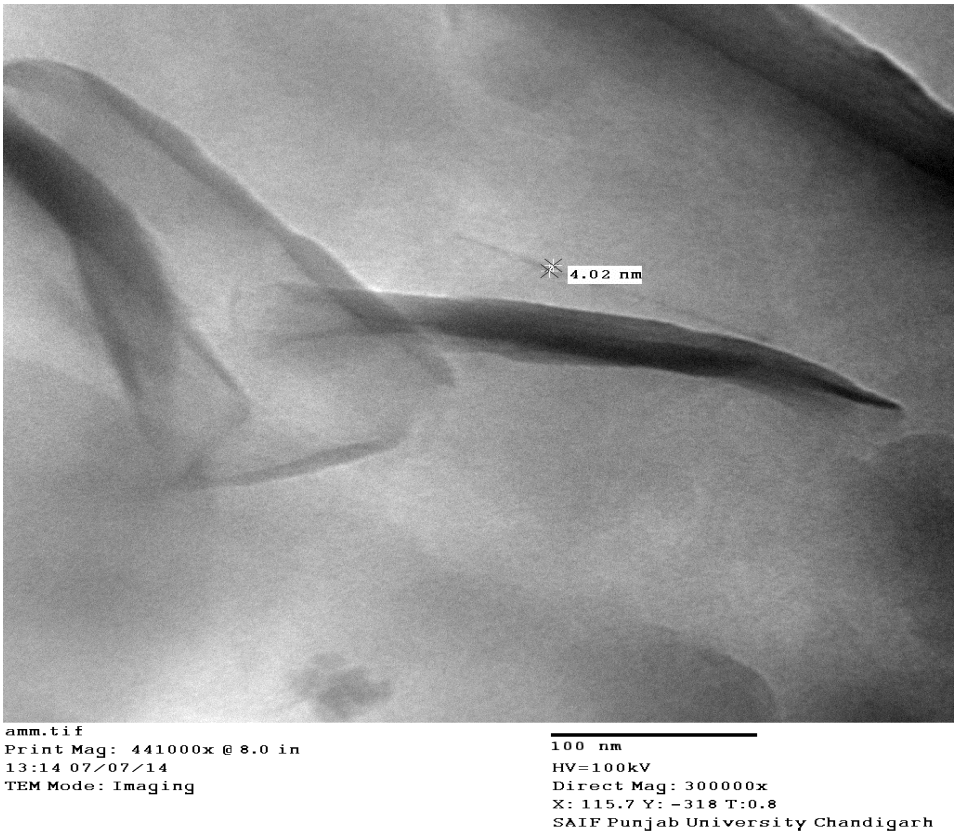


Figure5.2: TEM image of cloisite 15A nanoclay

5.3 EFEECT OF ADSORBENT DOSAGE (m_{ad})

Figure 5.3 and 5.4 shows the effect of adsorbent dosage on the removal of Reactive Black 5 from aqueous solution by organically modified nanoclay (Cloisite 15A).The effect of adsorbent dosage on the adsorption of RB5 was studied by taking C_0 = 100mg/l, pH = 5.6 and T = 303 K. It was seen that the removal efficiency increases by increasing adsorbent dosage. The percentage of RB5 removed was almost constant after 0.35 g/l amount of adsorbent. Therefore m_{ad} = 0.35g/l was chosen as optimum dosage for further study.

The effects of adsorbent dosage study identify the capability of a RB5 to be adsorbed with a minimum dosage. From the calibration curve, it was observed that the adsorbent dosage has more effect on the color removal as compare to dye removal with a very marginal difference.

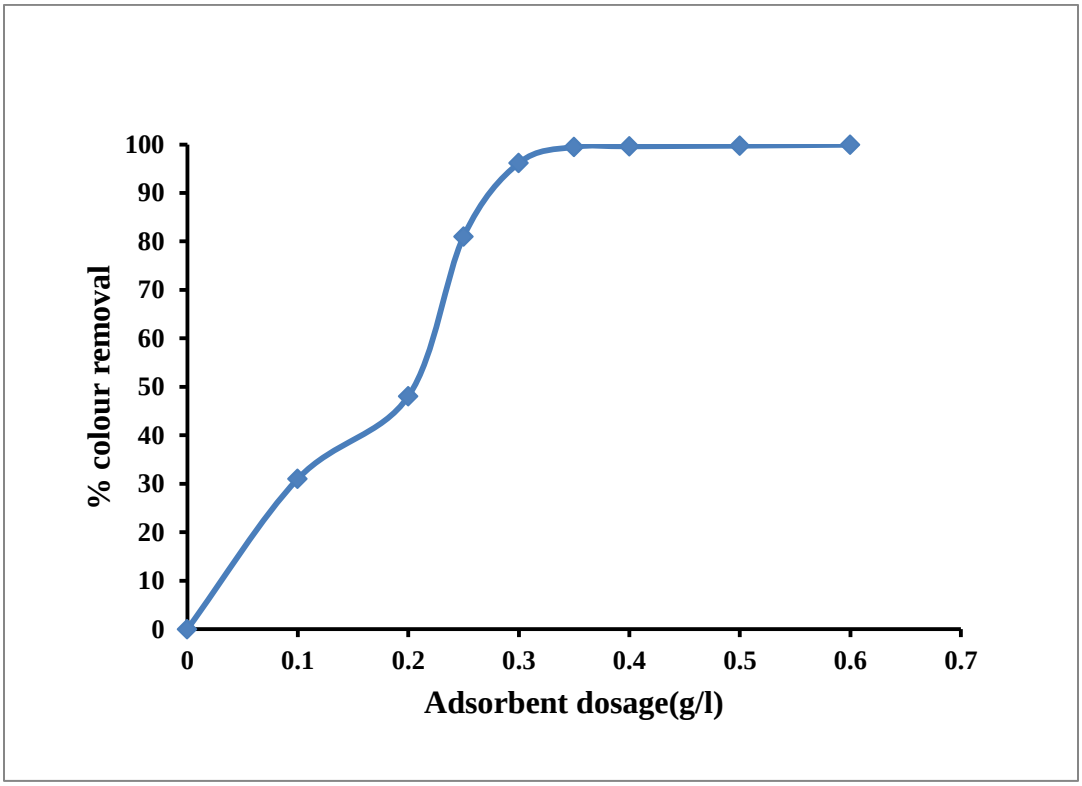


Figure 5.3: Effect of adsorbent dosage on the color removal by originally modified nanoclay (Cloisite 15A) as an adsorbent (T = 303 K, C_0 = 100mg/l, t = 50min, pH = 5.6)

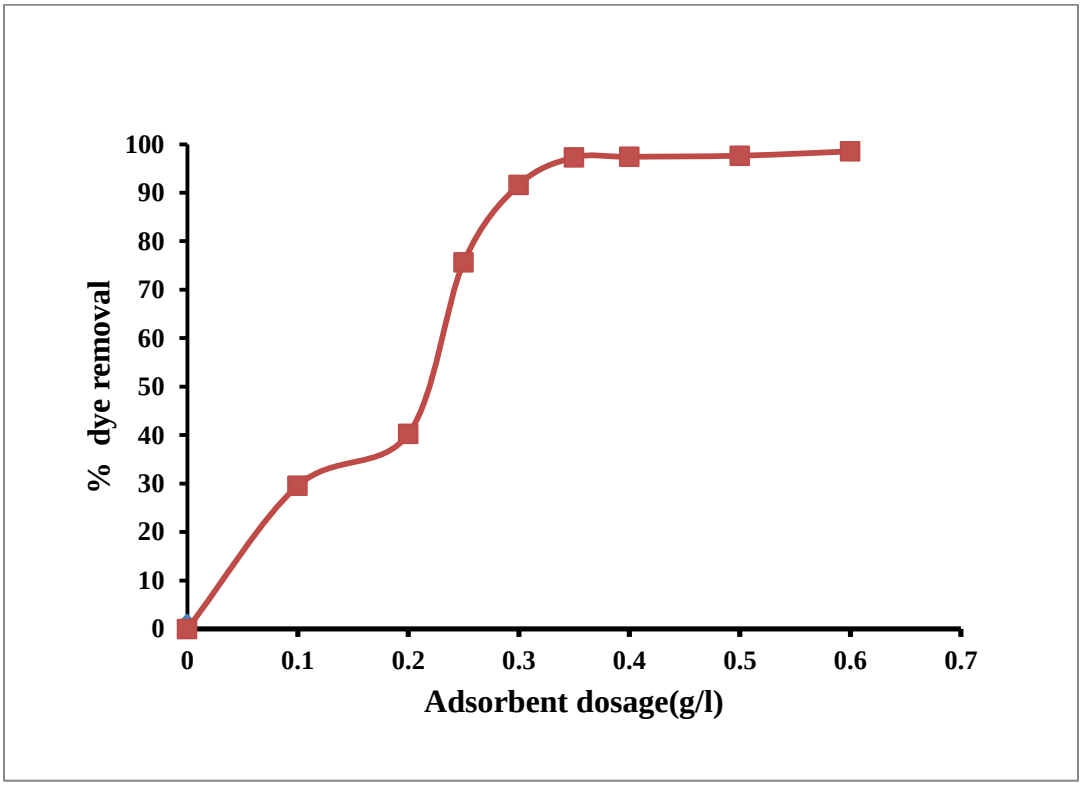


Figure 5.4: Effect of adsorbent dosage on the dye removal by originally modified nanoclay (Cloisite 15A) as an adsorbent (T = 303 K, C_0 = 100mg/l, t = 50min, pH = 5.6)

5.4 EFFECT OF INITIAL pH (pH_i)

Fig. 5.5 and 5.6 shows the effect of pHi on the removal of Reactive Black 5 from aqueous solution by organically modified nanoclay (cloisite 15A).The pH study was carried out in the initial pH range (pH_i) of 3 to11 at 303K. 1 N aqueous solution of either HCl or NaOH was used to adjust the pH of RB5 solution. During pH study the adsorbent dosage was kept contact. The maximum removal of Reactive Black 5 were attained at pH_i= 3 and pH_i = 5, respectively, while low removal occurred at pH_i = 11. The maximum removal capacity was 99.74% and 98.38% and they were obtained at pH_i = 3 and pH_i= 5, respectively. The pH_i= 5 was taken as optimum pH (pH_{opt}) for further studies because there were no significant differences in the removal of RB5 at pH_i = 3 and pH_i = 5.At a

high pH_i solution the percentage of RB5 removal was lower while at low pH_i solution the percentage of RB5 removal was higher. It means the Adsorption capacity can vary strongly with pH.

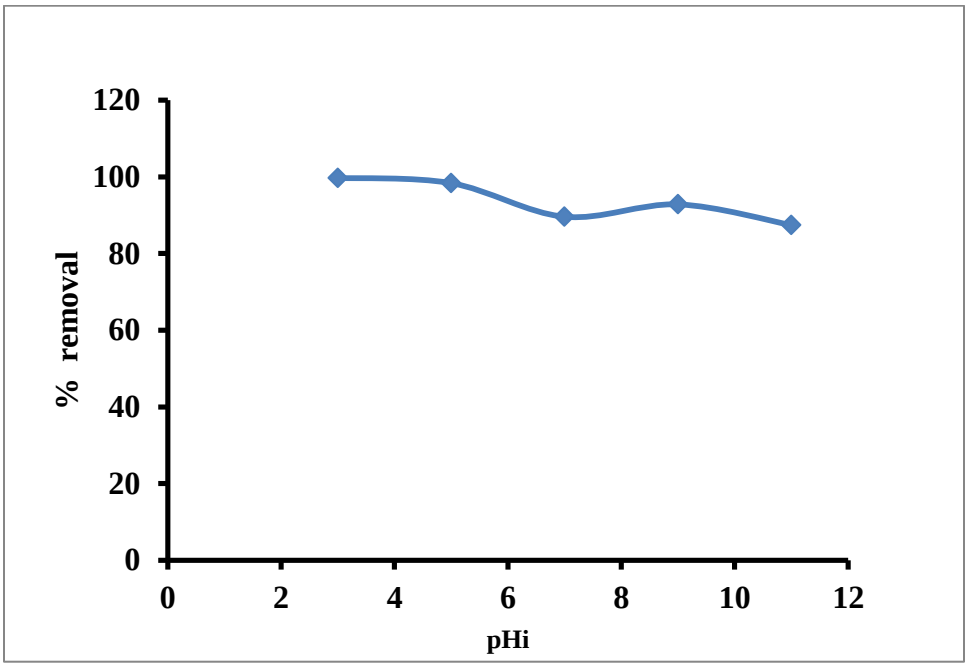


Figure 5.5: Effect of initial pH (pH_i) at color removal (wavelength 597)

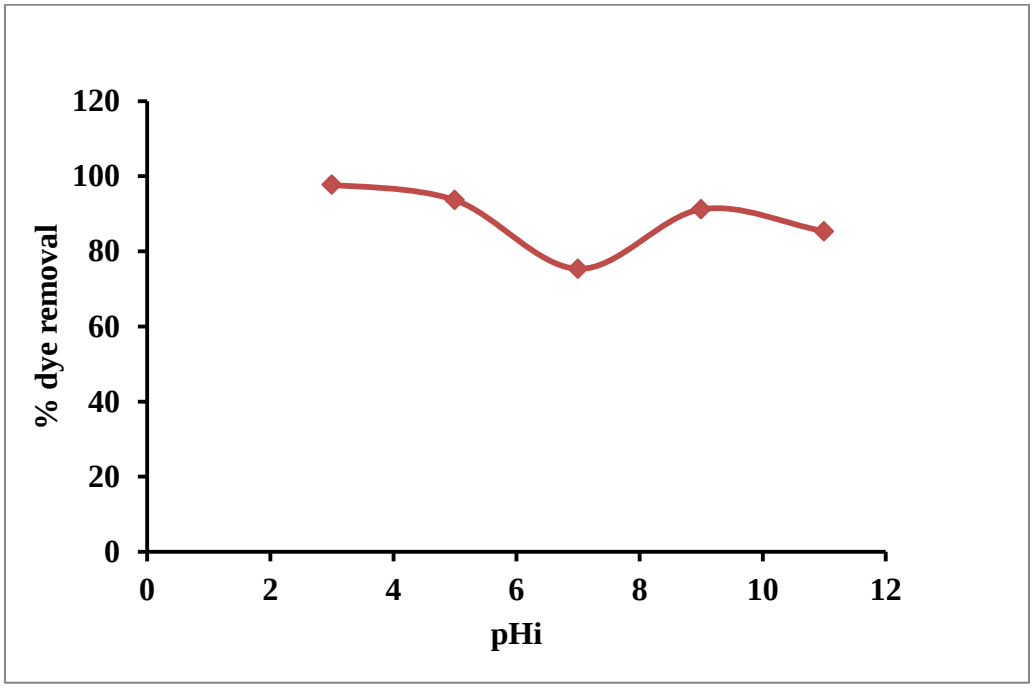


Figure 5.6: Effect of initial pH (pH_i)at dye removal (wavelength 312)

The result shows that the percentage of color removal of Reactive Black 5 was higher than dye removal. It means the effect of pH was more in case of colour removal than that of dye removal onto Cloiste 15A.

5.5 EFFECT OF TIME

Figure 5.7 and 5.8 shows theeffect of time on the color and dye removal by originally modified nanoclay (Cloisite 15A) as an adsorbent (T = 308 K, C_0 = 50 to 300 mg/l, t = 35 min, pH = 5). The equilibrium studies were performed at various dye concentration (C_0 = 50, 100, 150, 200, 250, 300 mg/l), ma_d= 0.35 g/l and at optimum pH = 5 (pH_{opt} = 5). The effect of time on the adsorption of RB5 was analysed at time interval of 0 to 35 min. After 35 min, the removal efficiency was almost constant. Therefore 35min (t = 35min) was found to be optimum time for the adsorption of Reactive black 5 onto organically modified nanoclay (Cloisite 15A). So 35 min was selected for all further studies for the adsorption of RB5.

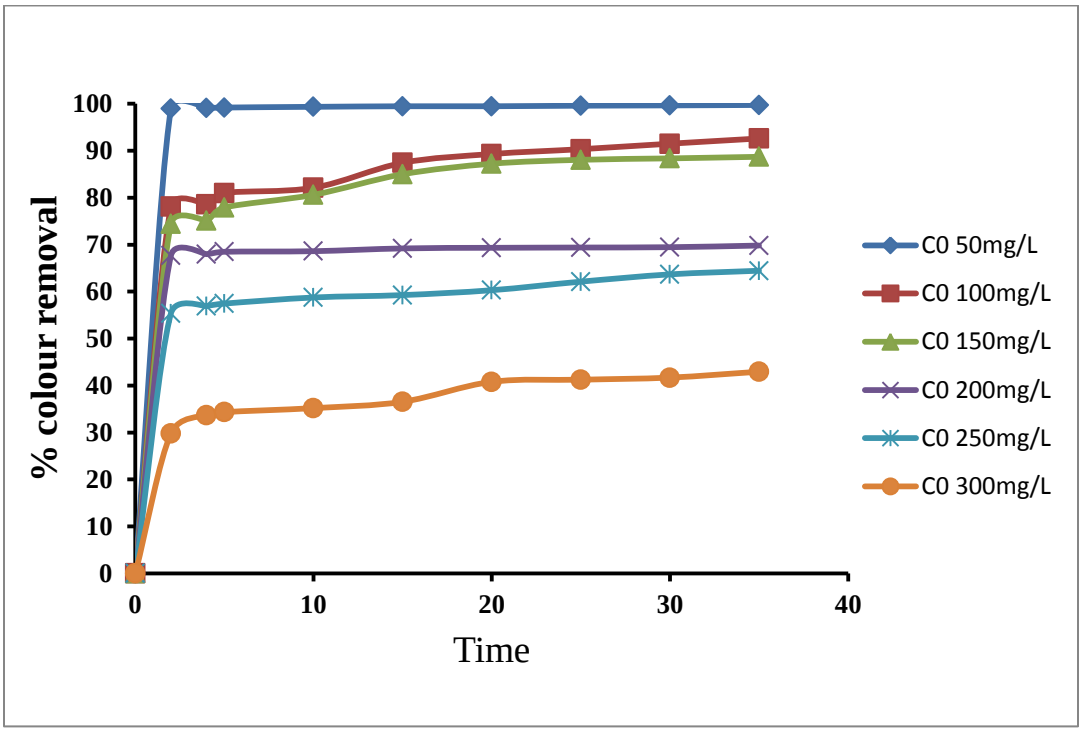


Figure 5.7: Effect of contact time on the color removal by originally modified nanoclay (Cloisite 15A) as an adsorbent (T = 308 K, C_0 = 50 to 300 mg/l, t = 35 min, pH = 5).

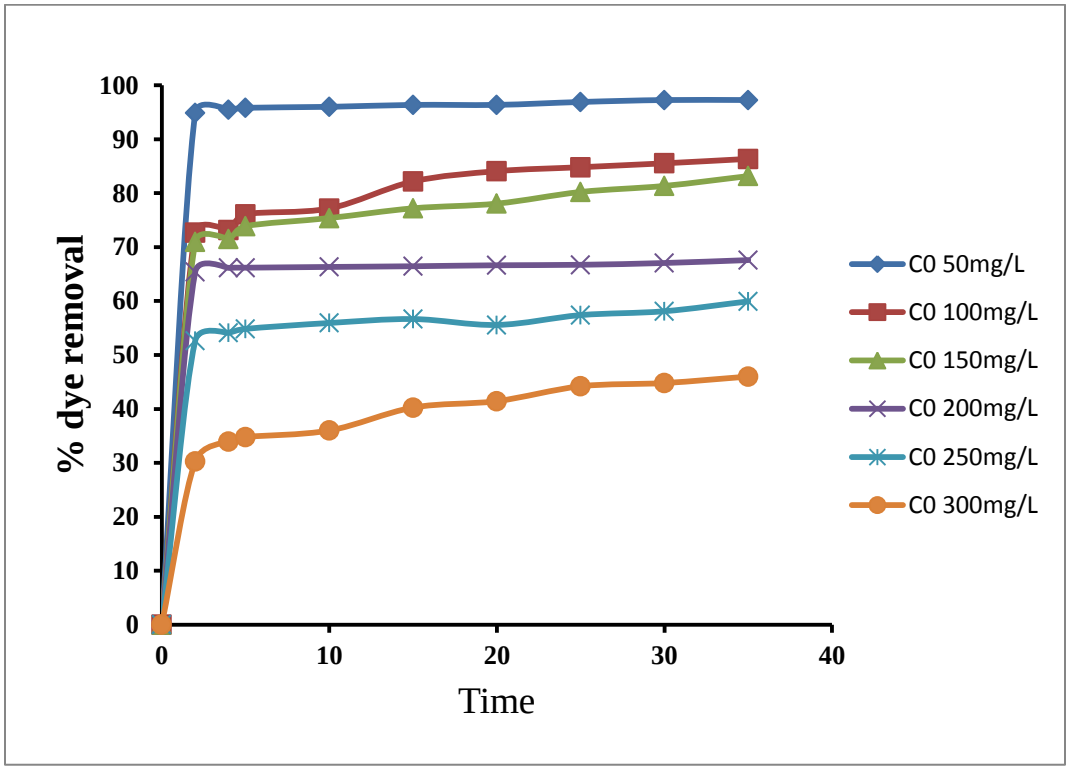


Figure 5.8: Effect of contact time on the dye removal by originally modified nanoclay (Cloisite 15A) as an adsorbent (T = 308 K, C_0 = 50 to 300 mg/l, t = 35 min, pH = 5).

5.6 EFFECT OF INITIAL RB5 DYE CONCENTRATION

Reactive Black 5 solution with different initial dye concentration (C_0 = 50 to 300 mg/l) was taken to see their effect on the removal of RB5 by organically modified nanoclay (cloisite 15A). The result shows that the adsorption of Reactive Black 5 was decreased when the initial RB5 dye concentration was increased. It means removal of RB5 is highly dependent on the initial dye concentration.

5.7 ADSORPTION KINETICS

Pseudo-first-order kinetic model and Pseudo-second-order kinetic model were used to study the adsorption kinetics by using experimental data. The pseudo-first-order and

second-order correlation coefficients, model parameters and MPSD error best fit values are given in **Table 5.1 and 5.2.**

The pseudo-second-order model fitted well with all experimental data and achieved highest correlation coefficient compare to pseudo-first-order model. Therefore the pseudo-second-order model is more suitable than the pseudo-first-order kinetic model. The k_2 and $q_{e(cal)}$are determined from the intercept and the slope from a linear plot of t/qt vs t. The pseudo second-order model fitting with all experimental data is shown in **Fig. 5.9 to5.14** by solid line for the removal of Reactive Black 5 by Cloisite 15A**.**The highest R^2 (R^2 = 1) values was obtained at temperature 308 K and 313 K (C_0=50 mg/L) for color removal and at 313 K for dye removal.

The color removal and dye removal results of second order model shows that: At T=30^0C, the qe value increases with an increase in the C_0while k_2 decreases with an increase in C_0but K_2 value again increases with C_0=250 mg/L .At T=35^0C, the qe value increases with an increase in the C_0 while k_2 decreases with an increase in C_0 and At T=40^0C,the qe value increases with an increase in the C_0 while k_2 decreases with an increase in C_0. Thus the adsorption of Reactive black 5 is limited by the concentration in the solution. MPSD error values are very small for pseudo second order model.

5.8 KINETIC PARAMETERS FOR THE REACTIVE BLACK 5 REMOVAL (t = 35 min, C_0=50-250 mg/L, m=0.35 g/L).

Table 5.1: PSEUDO-FIRST-ORDER MODEL

Percentage of color removal at wavelength 597

Temperature (T=30^0C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_1 (min^{-1})	R^2	MPSD
50	14.23	1.04	0.228	0.49416	31.24
100	25.25	8.99	0.156	0.90727	23.42
200	36.59	22.75	0.100	0.85027	16.09
250	42.71	19.11	0.097	0.83874	22.12

Temperature (T=35^0C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_1 (min^{-1})	R^2	MPSD
50	14.25	0.60	0.160	0.40136	32.19
100	26.46	9.47	0.114	0.86136	24.05
200	39.16	16.01	0.107	0.87034	22.74
250	46.41	20.05	0.091	0.85684	23.40

Temperature (T=40^{0}C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_1 (min^{-1})	R^2	MPSD
50	14.26	0.90	0.386	0.5131	31.39
100	28.18	3.53	0.127	0.63774	30.17
200	42.07	3.94	0.088	0.36808	31.25
250	49.37	14.90	0.128	0.85569	25.38

Percentage of dye removal at wavelength 312

Temperature (T=30^{0}C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_1 (min^{-1})	R^2	MPSD
50	13.84	1.96	0.227	0.66058	28.35
100	23.86	7.058	0.131	0.8462	25.49
200	35.55	25.47	0.132	0.92788	12.15
250	40.21	18.91	0.096	0.74689	21.18

Temperature (T=35^{0}C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_1 (min^{-1})	R^2	MPSD
50	13.89	1.23	0.140	0.4718	31.06
100	24.67	8.89	0.125	0.88389	23.76
200	38.15	15.75	0.091	0.8164	23.48
250	42.81	17.39	0.094	0.8529	22.85

Temperature (T=40^{0}C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_1 (min^{-1})	R^2	MPSD
50	13.94	1.52	0.30	0.49638	30.08
100	27.66	3.66	0.10	0.5523	30.22
200	40.89	3.63	0.094	0.38877	31.31
250	47.60	16.23	0.069	0.66917	26.04

TABLE 5.2: PSEUDO-SECOND-ORDER MODEL

Percentage of color removal at wavelength 597

Temperature (T=30^{0}C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_2 (g/mg min)	R^2	MPSD
50	14.23	14.30	1.063	0.99995	0.0094
100	25.25	25.52	0.076	0.99962	0.30
200	36.59	37.14	0.014	0.99014	0.41
250	42.71	42.95	0.020	0.997	1.33

Temperature (T=35^{0}C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_2 (g/mg min)	R^2	MPSD
50	14.25	14.26	2.63	1	0.01
100	26.46	26.70	0.049	0.99869	0.03
200	39.16	39.52	0.026	0.99776	0.07
250	46.41	46.66	0.018	0.9963	0.17

Temperature (T=40^{0}C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_2 (g/mg min)	R^2	MPSD
50	14.26	14.26	52.53	1	0.02
100	28.18	28.19	0.26	0.99994	0.08
200	42.07	41.92	0.21	0.99987	0.07
250	49.37	49.77	0.039	0.99953	0.20

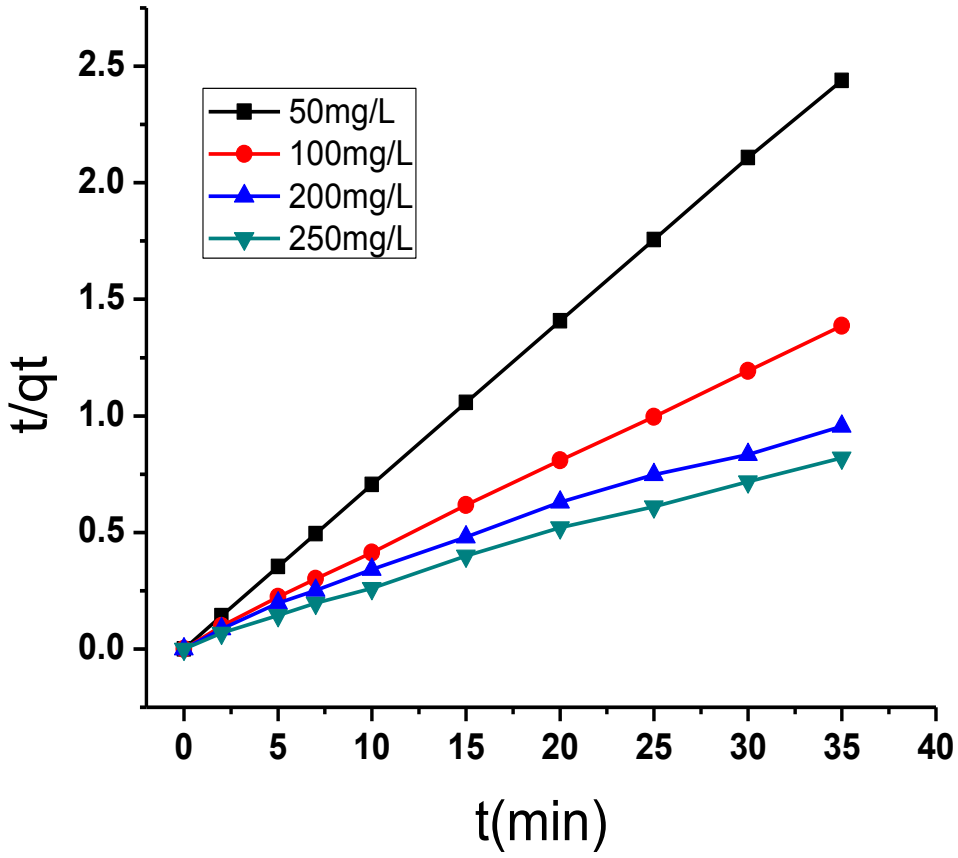


Figure 5.9: Effect of contact time on the color removal by cloisite 15A nanoclay. Experimental data points given by the symbols and the lines predicted by the pseudo second-order model. T = 303 K, m $_{ad\text{-}opt}$ = 0.35 g/l.

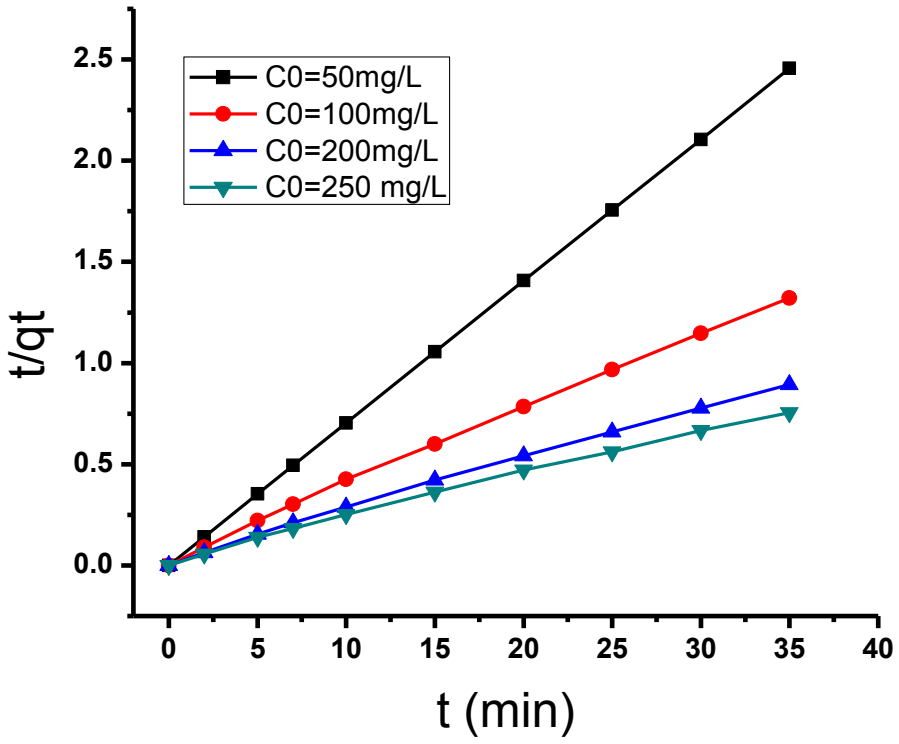


Figure 5.10: Effect of contact time on the color removal by cloisite 15A nanoclay. Experimental data points given by the symbols and the lines predicted by the pseudo second-order model. T = 308 K, $m_{ad\text{-}opt}$ = 0.35 g/l.

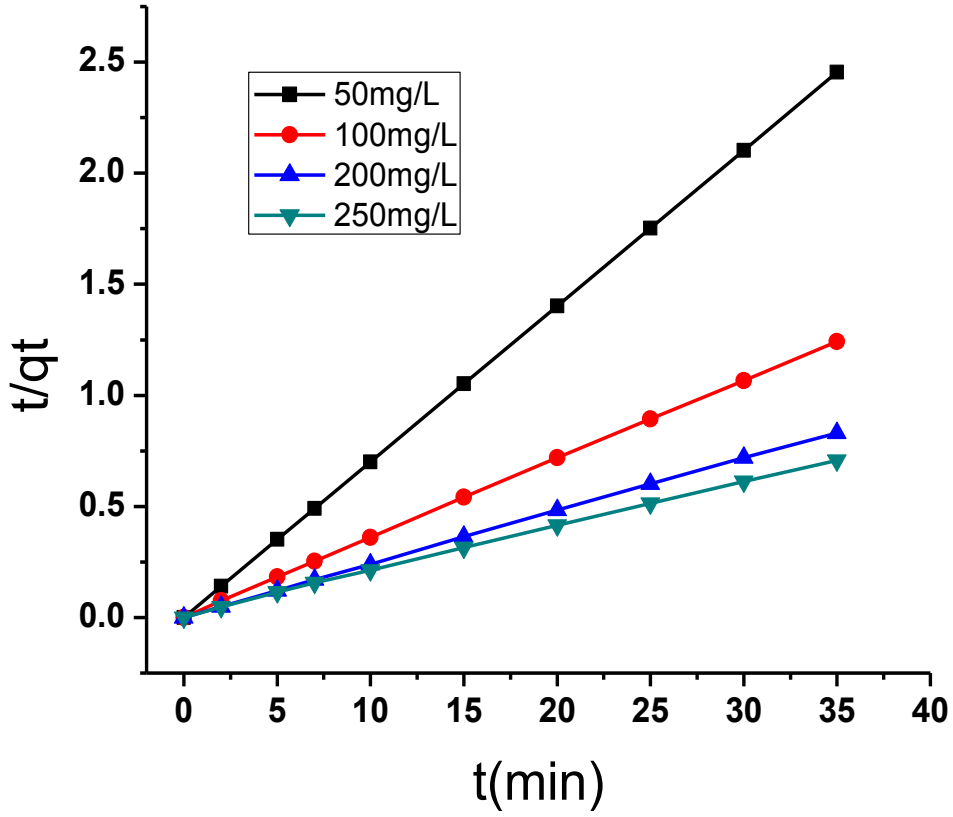


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Figure 5.11: Effect of contact time on the color removal by cloisite 15A nanoclay. Experimental data points given by the symbols and the lines predicted by the pseudo second-order model. T = 313K, $m_{ad\text{-}opt}$ = 0.35 g/.

Percentage of dye removal at wavelength 312

Temperature (T=30^{0}C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_2 (g/mg min)	R^2	MPSD
50	13.84	13.87	0.82	0.99999	0.009
100	23.86	24.03	0.087	0.99964	0.28
200	35.55	36.79	0.014	0.99355	0.36
250	40.21	40.17	0.020	0.99317	0.12

Temperature (T=35^{0}C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_2 (g/mg min)	R^2	MPSD
50	13.89	13.90	0.81	0.99997	0.02
100	24.67	24.96	0.055	0.9989	0.10
200	38.15	38.24	0.024	0.99619	0.09
250	42.81	43.10	0.02	0.9977	0.28

Temperature (T=40^{0}C)

C_0 (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_2 (g/mg min)	R^2	MPSD
50	13.94	13.95	2.24	1	0.02
100	27.66	27.60	0.2	0.99987	0.03
200	40.89	40.79	0.22	0.99991	0.07
250	47.60	47.59	0.028	0.99817	0.06

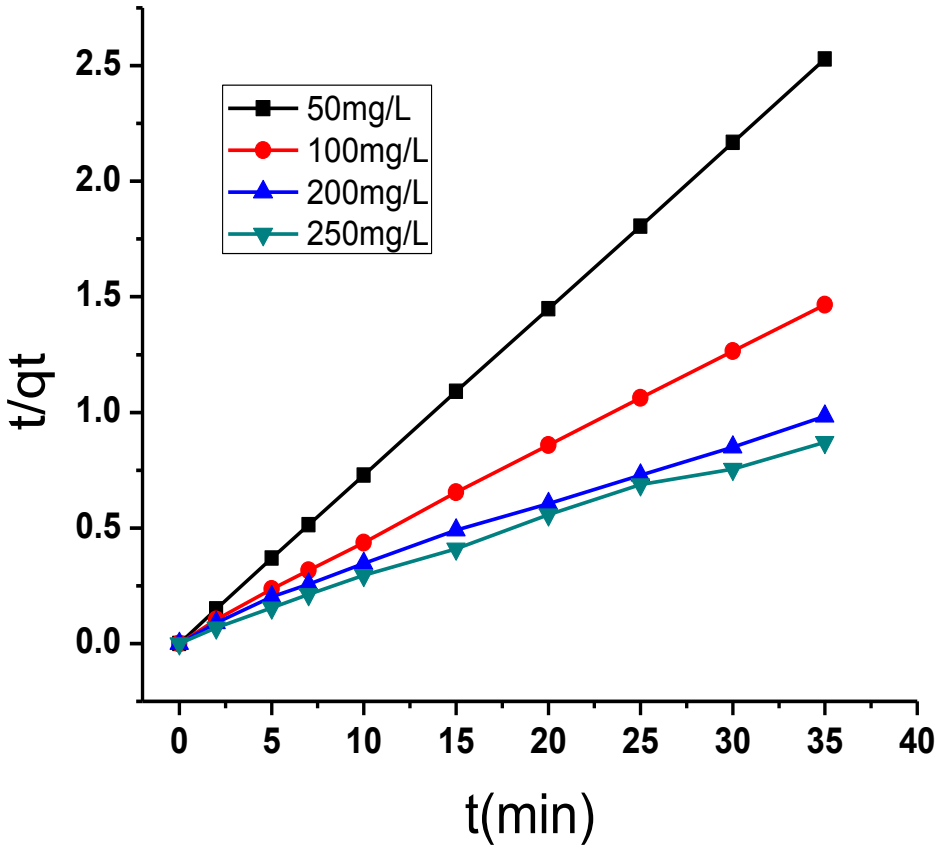

Figure 5.12: Effect of contact time on the dye removal by cloisite 15A nanoclay. Experimental data points given by the symbols and the lines predicted by the pseudo second-order model. T = 303 K, m $_{ad\text{-}opt}$ = 0.35 g/

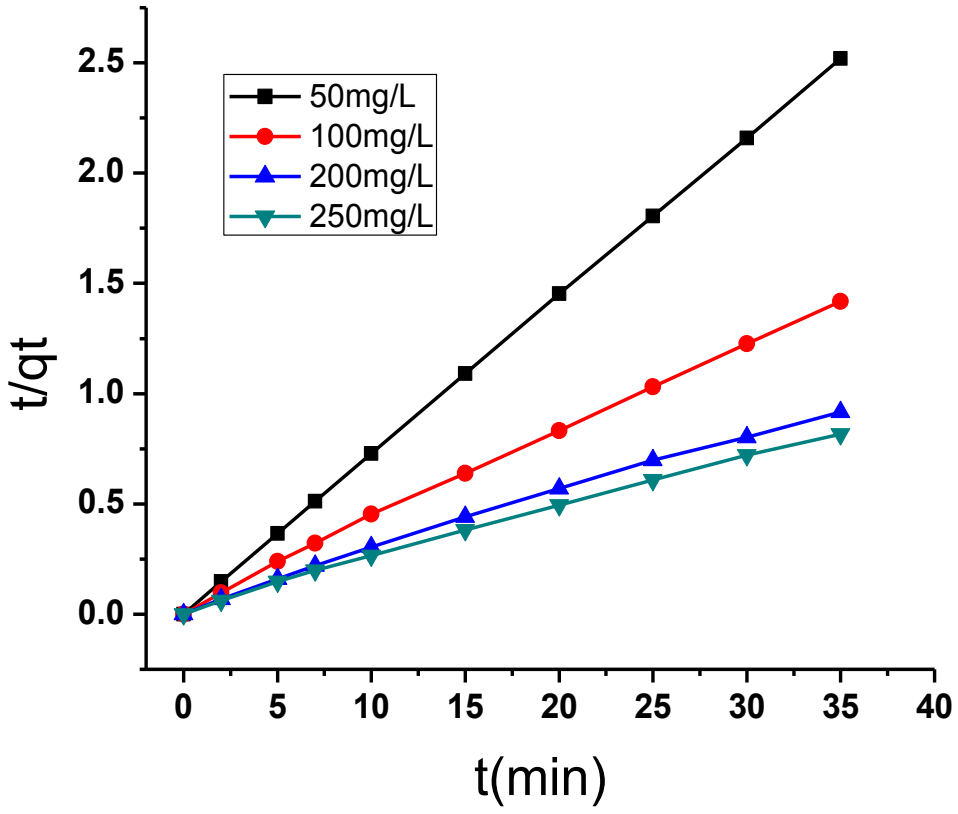

Figure 5.13: Effect of contact time on the dye removal by cloisite 15A nanoclay. Experimental data points given by the symbols and the lines predicted by the pseudo second-order model. T = 308 K, $m_{ad\text{-}opt}$= 0.35 g/l.

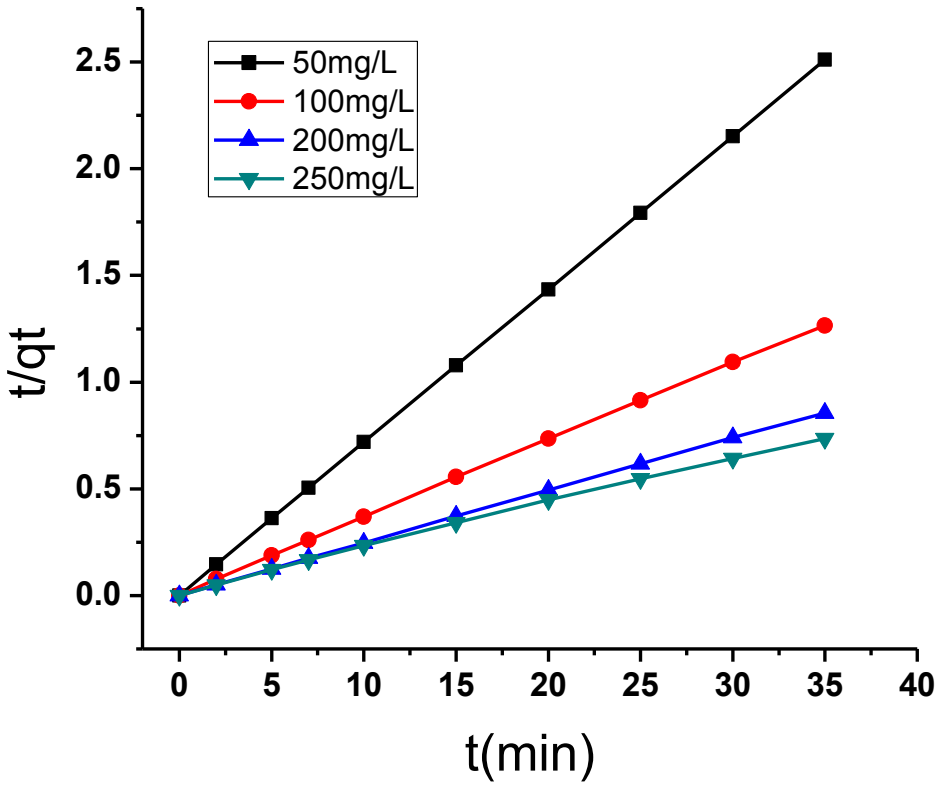

Figure 5.14: Effect of contact time on the dye removal by cloisite 15A nanoclay. Experimental data points given by the symbols and the lines predicted by the pseudo second-order model. T = 313K, $m_{ad\text{-}opt}$ = 0.35 g/l.

5.9 ADSORPTION ISOTHERM

5.9.1 Effect of temperature

Temperature has a major effect on the adsorption capacity of the adsorbent. The effect of temperature on the adsorption of dye was studied by taking different temperature range (293, 303 and 313 K). The adsorption of Reactive Black 5 was increases with increasing temperature. Thus the adsorption of RB5 onto Cloisite 15A is an endothermic in nature.

5.9.2 Isotherm modeling

Table 5.3 and 5.4 shows the isotherm parameters of various models like Langmuir, Freundlich and Temkin isotherm model. R^2 and CH^2 are the two parameters of these three models. In table **5.3 and 5.4**, it is found that there are very small differences in CHI^2 values for Langmuir, Freundlich and Temkin isotherm. The equilibrium adsorption of Reactive Black 5 was studied to calculate the adsorption capacity and affinity. To determine the suitability of the isotherms the R^2 values at different temperature were analyzed. The data in the **table 5.3 and 5.4**show that Langmuir model obtain highest R^2 values (R^2 = 0.98438 and 0.9894) for color and dye removal at temperature 313 K.K_F indicate the adsorption capacity and 1/n indicate adsorption intensity. K_F values increases with increase in temperature for both color and dye removal. q_m indicate the higher affinity. q_m values increases with increase in temperature for both cases. Cloisite 15A shows a higher adsorption capacity at higher temperature. The experimental data points for color and dye removal onto organically modified nanoclay (Cloisite 15A) is shown in **figure 5.15 to 5.20.**

TABLE 5.3: ISOTHERM PARAMETERS FOR THE REACTIVE BLACK 5 ADSORPTION BY CLOISITE 15A NANOCLAY (t= 30min, $pH_{i\text{-}opt}$= 5, m_{ad}= 0.35g/l, WAVELENGTH 597)

Percentage of color removal

Langmuir	$q_e = q_m K_L C_e / 1 + K_L C_e$			
T(K)	**q_m (mg/g)**	**K_L (1/mg)**	**R^2**	**CHI^2**
293	**40.29**	**0.277**	**0.98139**	**0.352**
303	**41.54**	**0.339**	**0.98303**	**0.367**
313	**47.64**	**0.738**	**0.98438**	**1.364**

Freundlich	$q_e = K_F C_e^{1/n}$			
T(K)	**1/n**	**K_F(mg/g)**	**R^2**	**CHI^2**
293	**0.18404**	**17.80**	**0.8586**	**0.026**
303	**0.16855**	**19.87**	**0.93398**	**0.021**
313	**0.16351**	**25.40**	**0.97068**	**0.000093**

Temkin	$q_e = B_T \ln K_T + B_T \ln C_e$			
T (K)	**K_T (l/mg)**	**B_T (kJ/mol)**	**R^2**	**CH^2**
293	**0.148**	**4.04**	**0.84679**	**0.0006**
303	**0.181**	**4.15**	**0.86916**	**0.0010**
313	**0.528**	**4.51**	**0.96851**	**0.0001**

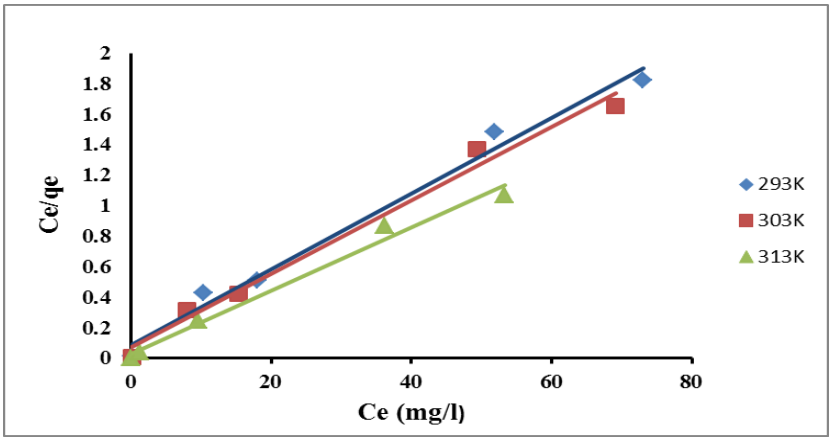

Figure 5.15: Equilibrium adsorption isotherms at different temperature for thecolor removal of RB5 by Cloisite 15A. Experimental data points given by symbols and the lines predicted by Langmuir isotherm model. t = 30 min, C_o = 50-300 mg/l, $m_{ad\text{-}opt}$ = 0.35 g/l.

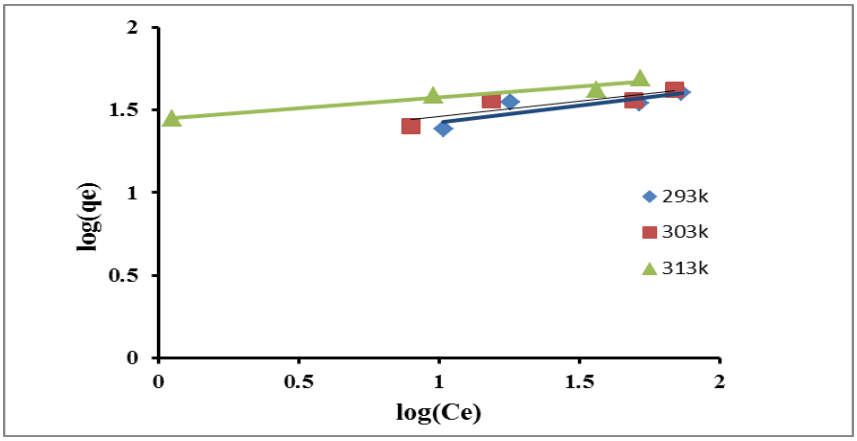

Figure 5.16: Equilibrium adsorption isotherms at different temperature for the color removal of RB5 by Cloisite 15A. Experimental data points given by symbols and the lines predicted by Freundlich isotherm model. t = 30 min, C_o = 50-300 mg/l, $m_{ad\text{-}opt}$ = 0.35 g/l

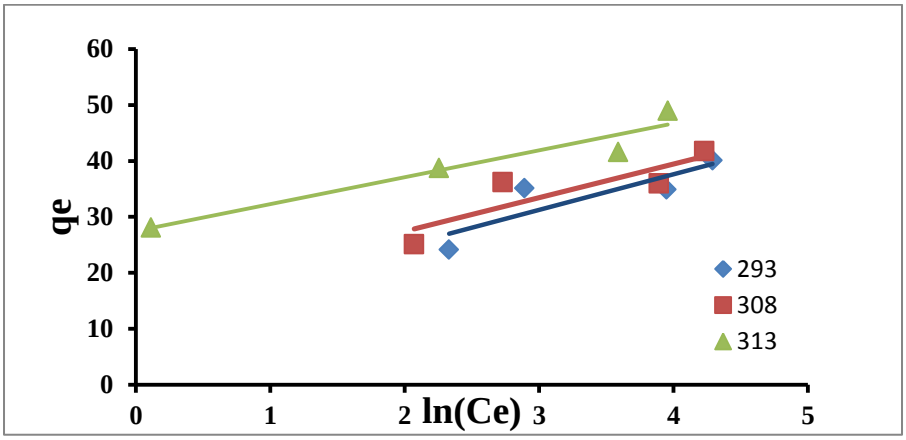

Figure 5.17: Equilibrium adsorption isotherms at different temperature for the color removal of RB5 by Cloisite 15A. Experimental data points given by symbols and the lines predicted by Temkin isotherm model. t = 30 min, C_o = 50-300 mg/l, $m_{ad\text{-}opt}$ = 0.35 g/l.

TABLE 5.4: ISOTHERM PARAMETERS FOR THE REACTIVE BLACK 5 ADSORPTION BY CLOISITE 15A NANOCLAY (T= 30min, $pH_{i\text{-}opt}$= 5, m_{ad}= 0.35g/l, WAVELENGTH 312)

Percentage of dye removal

Langmuir	$q_e = q_m K_L C_e / 1 + K_L C_e$			
T(K)	**q_m (mg/g)**	**K_L (1/mg)**	**R_2**	**CHI^2**
293	**39.61**	**0.185**	**0.98162**	**0.064**
303	**41.11**	**0.196**	**0.9864**	**0.051**
313	**46.97**	**0.371**	**0.9894**	**0.110**
Freundlich	$q_e = K_F C_e^{1/n}$			
T(K)	**1/n**	**K_F(mg/g)**	**R^2**	**CHI^2**
293	**0.25089**	**13.17**	**0.9056**	**0.0033**
303	**0.24929**	**13.87**	**0.94581**	**0.078**
313	**0.25289**	**17.48**	**0.87552**	**2.390**
Redlich-Peterson	$q_e = B_T \ln K_T + B_T \ln C_e$			
T (K)	**K_T (l/mg)**	**B_T (kJ/mol)**	**R^2**	**CH^2**
293	**0.0074**	**5.90**	**0.86856**	**0.000044**
303	**0.0084**	**6.00**	**0.91739**	**0.00022**
313	**0.0012**	**6.94**	**0.954712**	**0.01259**

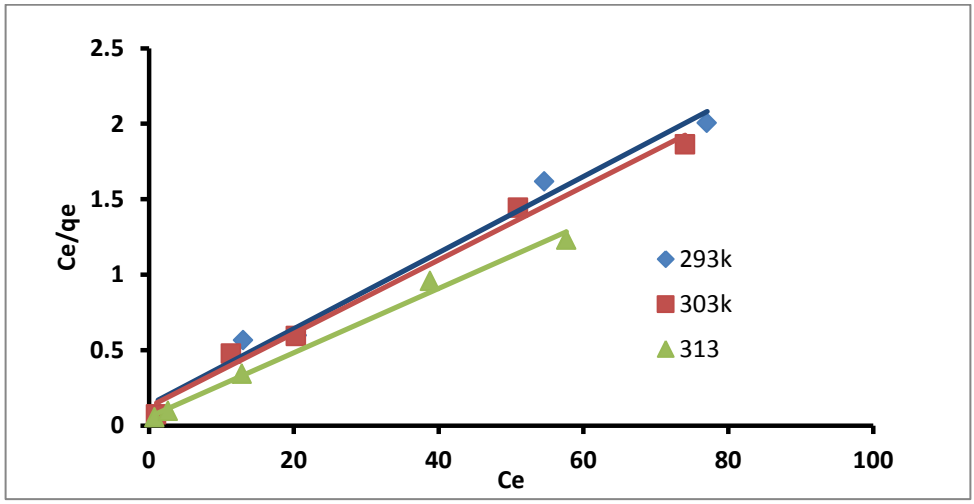

Figure 5.18: Equilibrium adsorption isotherms at different temperature for the dye removal of RB5 by Cloisite 15A. Experimental data points given by symbols and the lines predicted by Langmuir isotherm model. t = 30 min, C_o = 50-300 mg/l, $m_{ad\text{-}opt}$ = 0.35 g/l.

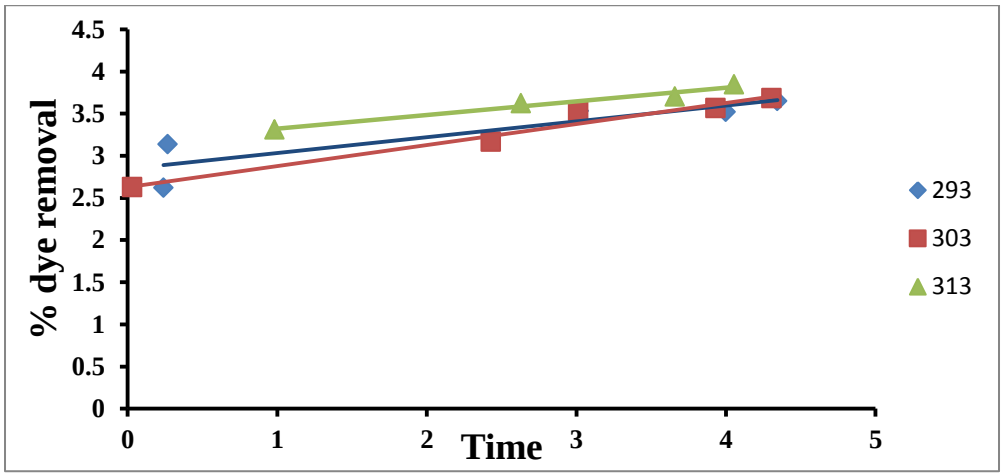

Figure 5.19: Equilibrium adsorption isotherms at different temperature for the dye removal of RB5 by Cloisite 15A. Experimental data points given by symbols and thelines predicted by Freundlich isotherm model. t = 30 min, C_o = 50-300 mg/l, $m_{ad\text{-}opt}$ = 0.35 g/l.

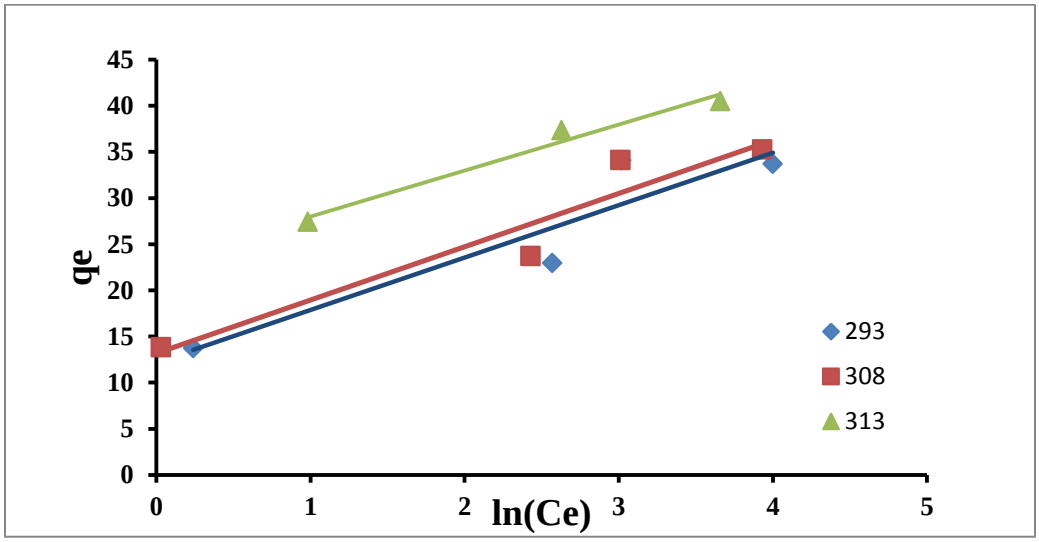

Figure 5.20: Equilibrium adsorption isotherms at different temperature for the dyeremoval of RB5 by Cloisite 15A. Experimental data points given by symbols and the lines predicted by Temkin isotherm model. t = 30 min, C_o = 50-300 mg/l, $m_{ad\text{-}opt}$ = 0.35 g/l.

CHAPTER – 6

CONCLUSIONS

On the basis of the results and discussion presented for the removal of Reactive Black 5 dye by adsorption process onto Cloisite 15A, the following conclusions are drawn:

- The optimum conditions for the removal of Reactive Black 5 dye by using Cloisite 15A nanoclay are:: adsorbent dose = 0.35 g/l, contact time = 35 min and pH = 5.
- The adsorption process is endothermic in nature. The color removal is more than dye removal.
- The pseudo-second-order model fits well with all experimental data.
- The color and dye removal results of pseudo second order model indicate that the q_e value increases with an increase in the C_0. Thus the adsorption of Reactive black 5 is limited by the concentration in the solution.
- The adsorption kinetic shows that the K_2 values decrease with an increase in temperature (20 to 40^0C) but at a temperature of 30^0C, the K_2 value again increases with C_0=250 mg/L.

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