MODELING OF GAS PHASE SURFACE MODIFICATION OF POLYMER

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
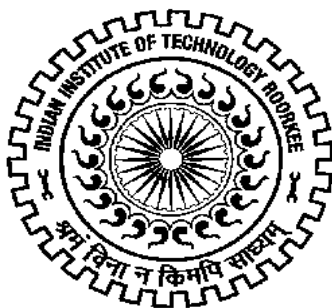*in*

CHEMICAL ENGINEERING
(With Specialization in Computer Aided Process And Plant Design)

By

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DECLARATION

I hereby declare that the work being presented in the seminar report entitled **"Modeling of gas phase surface modification of polymer"** in partial fulfillment of the requirements for the award of the degree of M. Tech. (With Specialization in Industrial Pollution Abatement) and submitted in the department of Chemical Engineering of the Indian Institute of Technology Roorkee. This is an authentic record of my own work carried out during the period from June, 2012 to June, 2013 under the supervision of **Dr. Shishir Sinha**, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India. The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

The present research work is concerned with the study and model development of modified resins. Mainly these resins are ion exchange resins which are modified through the gas phase nitration technique. In these nitration techniques mainly NO_x gas is used and this NO_x gas is very good for making the modified resin. Here two main ion exchange resin are taken for the kinetic model development, the exchange capacity of the different resins PMMA-EGDM and PS-EGDM are taken from two different papers, these paper give the information of exchange capacity of two different polymer resins at different temperature and time and with the use of these paper development of the mathematical model for the determination of rate constant is done. Both the model are developed at two different orders of the reaction and the model, for determination of rate constant give a very similar result to the experimental value given in the paper.

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1 INTRODUCTION

Owing to major significance in various industrial and household applications, developments of polymeric materials has received considerable attention. Polymer has not been discovered overnight. They came out of long and continuous studies by a host of motivated scientists whose work has enriched human life. Today the overall insight into polymer science and technology is so deep that a material scientist can make many limitless new materials. Just as an architect chooses bricks, stones, woods etc. of varying shapes, sizes and patterns to make or create a design, similarly a chemist can produce an innumerable plastics, rubber, foams by combining different type of chemicals to react under a desired given conditions [Govariker, 2005].

Polymers are complex and giant molecules and are different from low molecular weight compounds like common salt. Polymer are big molecules or 'macro molecules' are made up of much smaller molecules. These small molecules can be one or more same or different molecules. These small molecules can be one or more same or different molecules from which the polymers formed are known as monomers and the process by which monomer molecules forms big molecule or polymer is called 'polymerization'. Polymers are higher molecular weight materials consisting of several repeating units bounded together by covalent bonds. Polymers are natural and synthetic. Natural polymers are shellac, amber, cellulose, protein, silk and nucleic acid etc. Synthetic polymer can be classified as elastomers, fibers and plastics. Synthetic polymers are Bakelite, Neoprene, Nylon, PVC, Polystyrene, Polyacrylonitrile and Teflon.

Depending upon the use and strength of the polymer, Polymer is having three main forms as Elastomers, fibers and plastics. If polymer is formed into tough and hard utility articles by the application pressure and heat, it is called plastics. Examples are PVC, Polystyrene. When the polymer material vulcanized into rubber products of good elongation and strength then they are called elastomers. Examples are various rubbers like natural, synthetic and silicon rubber. If the polymer drawn into a long filament like materials, whose length is n above 100 times polymer diameter,, then it is called the polymer have been changed into fibers. Examples are Nylon and Terylene. Polymer extensively used in clothing, oil recovery, food and flavors, agriculture, packaging, consumer items, automotive parts, industries(pipes, parts, additives etc.), electronics, medicine and medical devices. An important application of polymeric material is ion exchange.

For this particular purpose many polymer based ion exchange resins are generally used. Ion exchange resins are used in many unit operations such as water softening, water purification, juice purification, sugar manufacturing, and pharmaceuticals and in form of catalyst in many catalyze organic reaction. Many copolymer based ion exchange resins are used in these application. e.g. PMMA-Polystyrene based copolymer, PMMA-di vinyl benzene based copolymer, PMMA-EGDM copolymer etc.. We can say that the ion exchange resins are the polymer which is having different functional groups attached on it. They are having some ions which they can exchange with the ions which they are working. In these days various work and research is going on the synthesis of copolymer based ion exchange resins. The conventional ion exchange resin is not having some appropriate physical and chemical properties so they are modified some degree to achieve the desirable extent of physical and chemical properties. For this modification purpose gas phase surface modification of polymer is a good technique.

Ion exchange resins are covalently cross linked, having a very high ionic character and they are insoluble polyelectrolyte. They are supplied as form of beads. The beads are mainly two types. In one type the bead have a dense internal structure means they are not having discrete pores and in another one they are in the form of porous, multichannel structure. The first one is called gel resins or microporous resins and the second one is macroporous resins. Ion exchange resins have also classified based on the charge on the counter ion which they can exchange (cation exchanger or anion exchanger) and based on ionic strength (strong exchanger or weak exchanger).

Suspension and emulsion polymerization are the two main techniques for the preparation of ion exchangers. In suspension polymerization technique water insoluble monomer and initiator are charged to a reactor which is usually a batch reactor and the reactor is fitted with mechanical agitator. Mechanical agitator and chain transfer agent controls the molecular weight of the prepared polymer. This technique generally used in free radical polymerization reaction. Many ion exchange resin based styrene copolymer beads, different injection molding grades of PVC, Polystyrene- acrylonitrile etc. are produced by this technique. In emulsion polymerization water and monomer charged in a reactor with water soluble initiator, chain transfer agent and a surfactant which is a salt of long chain fatty acid. In emulsion polymerization water act as a heat transfer agent. In emulsion polymerization initiator is water soluble, this is the main difference between suspension and emulsion polymerization.

1.1 ION EXCHANGE

Ion exchange contains the interchangeable ion which they can exchange between the two phases. Ion exchange is defined as the process where an insoluble substance remove ions of positive and negative charge from an electrolyte solution and release other ions of the same charge into solution in a chemically equivalent amount. The extent of ion exchange depends on the concentration of the ions in solution and the affinity of the ions for the insoluble phase with respect to the solution phase. Ion exchange resins are mainly two types, cation- and anion-exchange resins. The different ion-exchange resins consist of different covalently bonded polymers and legands. Ion-exchange resins are useful because they are having insoluble resin phase. After the exchange the resin can be separated with the use of filtration method. They are also used in continuous processes involving columns and chromatographic separations. They are environmental friendly because of their insolubility, they can be repeatedly used. The process of loading, regeneration and reloading allows them to use many times. Ion-exchange resins have been used in water softening, water purification, removal of toxic metals from water , wastewater treatment, sensors, chromatography, hydrometallurgy and bio-molecular separations. They have also been used as catalysts, both in the form of homogeneous catalysts such as sulfuric acid and to immobilize metallic catalysts [Alexandratos, 2009].

The exchange capacity is the important term in the ion exchangers. It is defined as number of counter ion equivalent to given amount of material. The exchange property of the exchanger is due to presence of the functional groups. These functional groups are created on the cross linked polymer by using many liquid and gas phase modification techniques.

1.2 IMPORTANCE OF POLYMERIC SURFACE

Polymers are being used in many industries due to its wide range of applications. So it is important to see the effect of environment on the surface of the polymers and it can be see through the surface characteristics of the polymer. By controlling the surface properties one can enhance or inhibit the various reaction systems. So it is important to control and understand the behavior enable to design or modify the polymer surface.

The surface properties of any polymeric surface depend upon the surface composition and surface structure of the outermost surface layer. Both the things play a important role in

performance of the polymeric material. There are some forces which act on the surface of polymer. One of them is Vanderwaal's force, which depend on the distance between the polymeric molecules. Force acting on the polymer surface is electrostatic force. A net charge on the surface of materials is acting due to several different mechanisms. Some of them are rubbing or contact electrification in air and ionizing of suitable groups in water or high di- electric constant solvent. Physiological capabilities, frictional behavior, wetting and coating characteristics are some examples of such surface properties.

1.3 POLYMER SURFACE MODIFICATION

In many applications, it is very difficult to find a material which has appropriate surface and bulk properties. So it is a necessary requirement to combine the surface properties of one material to bulk properties of other material for a desired property. In the polymeric material this can be done by surface modification. In surface modification surface properties can be change by changing the chemical structure of the polymer without altering the bulk property of the polymeric material. Several methods of surface modification are discussed below.

1.3.1 Physical Surface Modification Techniques: These methods can be categorized into two categories. The first one involved the chemical altering of the surface layers and the second one involved the depositing an extraneous layer on the top of the existing surface of the material to generate a sharp surface. These techniques require high energy species, e.g. radicals, ions, molecules, in excited electronic states etc. Various physical modification methods are discussed below. [Garbassi et al., 1994].

1.3.1.1 Flame Treatment: Flame treatments are widely applied in surface modification to introduce oxygen- containing functions at polyolefin's surfaces, mainly to improve prontability or paint-ability. Flame treatments deal with surface characterization of treated polymer trying to investigate which functional group have been created by the treatment and how do tbey affect either printability and adhesion.

1.3.1.2 Corona Treatment: Corona treated Polyolefin's films have enhanced adhesion properties and printability. XPS studies showed that corona treatment were capable to introduce hydroxyl, carbonyl, carboxyl and amide groups on the corona treated polymer surface. In this

technique a low energy (1 to 4 KHz) is applied to a polymer film which is move between an electrode and an earthed roller. Corona treated polymer films should be immediately used for the further application like printing, adhesion and sealing.

1.3.1.3 UV Treatment: The basic principal of UV treatment based on the photons(high energy species) which is used to activate many chemical reactions. It is firstly used in electronic industry. In UV treatment the presence of initiator and sensitizers are required because they absorb the UV radiation and excited to a short lifetime singlet state to more excited triplet state. In UV treatment the UV irradiation is absorbed only by initiator so the bulk properties of the polymer are not altered after the treatment.

1.3.1.4 Gamma Ray Treatment: In this method 100 to 300 KV energy electrons are used for treatment of the polymer and the mechanism is free radical mechanism. This lead to a introduction of the oxygenated species on the polymer surfaces, which gives the desired property like increase in the adhesion and enhanced mechanical properties. It is used for crosslinking of polymeric coatings and formation of thin polymeric film of desired properties. FTIR measurement showed that carbonyl, hydroxyl and vinyl groups could be introduced onto HDPE, LLDPE and VLDPE surface via this technique.

1.3.1.5 Electron Beam Treatment: The basic principal of electron beam treatment is based on accelerated electron which carries high amount of energy and this energy causes excitation of molecules. This electron only accelerated in the vacuum therefore both work chamber and electron beam equipment must be evacuated. The main reaction based on the formation of the free radicals. This method is not required any type of photo initiators because high speed electron bombarding molecules cause them to form radicals to initiate and propagate polymerization. It requires larger capital cost and more investment and precaution.

1.3.1.5 Ion Beam Treatment: Ion beam can be used in two different purposes one is to directly alter the surface composition of the polymeric material or other is to sputter off the target species which are then deposited to the surface. In this technique the treatment is generally done 20 to 200 KV. At low energies, ions do not penetrate the polymeric surface and at high energies it goes

several micrometers deep to the polymeric surface. The penetration power depends on the energy and mass of the ions. High energy and low mass ion can go very deep to the polymeric surface. XPS studies showed that surface oxidation and crosslinking of PS and PP films occured due to ion implantation on the presence of oxygen and argon.

1.3.1.6 Plasma Treatment: Plasma treatment is the technique in which glow discharge provides ionization of gas species that contains electrons, ions, exited molecules and radicals. This method is done in low temperature and low pressure. This technique improves the printability, sealibility and adhesion power with the enhance polymer resistance to mechanical failures. Plasma treatment can be categorized in two category hot plasma and cold plasma. Hot plasma generated at atmospheric pressure and very high temperature. Cold plasma required very low pressure. Hot plasma mainly used in mechanical and metallurgical operations.

1.3.1.7 Laser Treatment: In laser treatment an atom is excited from its ground state to higher energy state. In this technique higher voltage is used for this. During excitation the atoms lost electrons and on losing electron they becomes positively charged and move to negative electrode, the cathode and the electrons move to positive electrode, the anode. This technique is very efficient technique; in this technique surface modification can be done on any location and ate any distance. It modifies the surface without any energy being lost. Due to tunability and monochromatic property lasers are very efficient and offer precise control over the surface being modified. They can be used to promote crosslinking effect.

1.3.1.8 Metallization: In metallization coating is done on the polymer surface of metal species and this can done by electron beam excitation coating. The deposition is done by evaporation induced by Joule effect or electron beam excitation. It is mainly used for aluminum coating on plastic films for capacitor or decorative and barrier application.

1.3.1.9 Sputtering: In sputtering very high temperature and high vacuum used to evaporate atoms or molecules off a material surface. In sputtering, the target material and substrate should be in a vacuum chamber. The target is cathode and substrate is attached to the anode and voltage is applied between them. Plasma is created by sputtering gas (chemically heavy gas like argon).

The sputtering gases bombard the target and sputter off the material which we want to deposit. It is mainly used to produce inorganic coating where evaporation is not possible.

1.4 CHEMICAL SURFACE MODIFICATION TECHNIQUES

In this polymer modification technique the polymer surface is modified by means of chemical modification method. In this method the chemical composition of the polymeric material can be modified either by chemical reaction of the polymeric surface with a given solution which is called wet treatment or with gas phase which is called dry treatment. In this method is called chemical modification is also done by covalent bonding of the suitable macromolecule chains on the sample surface which is called surface grafting. Various treatments have been discussed in following subsection.

1.4.1 Wet Treatments

In surface modification technique, wet treatment is first method to improve the surface, properties of polymer. This is based on liquid polymer iteration. Mainly the polymer surface is heterogeneous in nature. Polymer surface rarely have homogeneous nature but the surface composition is constant throughout the surface. The surface is either amorphous or Crystalline in structure. There are various wet treatment method are discussed below.

1.4.1.1 Etching: This modification technique mainly applied to that polymer surface which has poor surface properties to adhesion. This is mainly used for flouro-polymers because they have very low surface tension so they are partially wetted by the liquids. But surface modification is difficult because of their inertness toward the chemicals. The strong reducing agent Polytetraflouroethylene (PTFE) react to the surface and lead to dark colored porous surface which can be glued successfully and early. The most common reducing agent is sodium which can be used either in liquid ammonia solution or as a complex with naphthalene which is solvated by excess of glycol diethyl ether. This treatment involves the dipping of flouro – polymer in the liquid solution for few minutes and after that the reaction occurs and breaking of carbon fluorine bond occurs and new bond formation takes place and the new bond is between sodium and fluorine so this is called sodium fluoride and recombination of carbon radicals to yield unsaturated hydrocarbon chains.

1.4.1.2 Surface Oxidation: Surface oxidation technique is used on various polymers for good to polymer adhesion. This technique is mainly used in electroplating industry. For example a sulphuric acid solution saturated with chromium trioxide at 80 C and it is adhesive between Acryl nitric butadiene styrene (ABS) and polypropylene surface.

1.4.1.3 Hydrolysis: In The modification technique, the attack of nucleophile agent can be NaOH (sodium hydroxide) is attacked on PET (polyethylene terephthalate) which is increases the number of hydrophilic groups and after the wetting property of the polymer also increases.

1.4.1.4 Functionalization: In Functionalization of polymer surface the creation of surface layer of well define functional groups takes place. In this way the created surface have the controlled properties or have a right substrate of controlled chemical reactivity.

1.4.2 Dry Treatment

1.4.2.1 Oxidation: In oxidation of polymers mainly nitrogen dioxide and dioxides are used in very less consumption of time or compare to conventional technique **[Pifer and Sen (1998)]**. The reaction involves the oxidation of polymers, copolymers, polymeric membranes and composites of functionalization, surface grafting without affecting the mechanical strength of the polymer. For example polysulfone ultrafiltration memberane is modified by gas phase nitration using mixture of NO and NO_2 which is called NO_x . From this membrane is functionalized by aminated route becomes hydrophilic in nature **[Chowdhury et al. 2001].**

1.4.2.2 Surface Grafting: The polymer surface grafting is the method to modify the polymer by the covalent bonding of new macromolecules on the substrate. A fundamental step in grafting is the creation of reactive groups on substrate in grafting is the creation of reactive group on substrate surface. Grafting can be done along two major parts, viz. free radical and ionic. Graft polymer is branched molecules and it has a main chain which is made entirely of one repeat unit and branched chains which is made of another repeat units. In Free radicals surface grafting primary homopolymer and co-monomers react in presence of free radical initiator and

polymerized thermally. Graft polymer has the potential to separate mixture Alcohol-water and salt water mixture is the main repeated mixture is also made by graft polymerization. Conducting polymer process able is also made by graft polymerization and these conducting polymer have application as a ion sensors, glucose sensors.

1.4.2.3 Bulk modification: Apart from previously discussed modification technique , this is about to modification of surface structure arising in multicomponent polymeric system. Here the emphasis is on relationship between the bulk and surface structure of heterogeneous, macromolecular system. Surface composition is due to effect of the presence of a free surface on component of the system.

Although all polymers are multicomponent even a pure homo polymer is composed of chain of different length whose distribution affects the properties of system, by multicomponent polymeric system we mean those materials made by different (blends) or by macromolecules containing block of different repeating units in the same chain (block polymer).

1.5 APPLICATION OF MODIFIED SURFACES

1.5.1 Wettability: Wetting is the key phenomena in many technological fields e.g. gluing, painting, washing etc. In these application a good contact between liquid and solid is sought other application are waterproofing and anti-sticking or anti-adherent coating.

1.5.2 Adhesion: Adhesion is a surface property relevant in many applications of polymeric materials. These are few applications like ink on shopping bags; paint on car parts and in engineering plastics applications. Adhesion is the joining together of two dissimilar materials and cohesion is the joining together of two different portion of same materials.

1.5.3 Barrier properties: Barrier is related to permeability with in turn is the combination of permanent diffusion and solubility in the polymer. Lowering one or both of them results in improve barrier properties are very important in packaging application like food, pharmaceuticals, cosmetic, fine chemicals etc. Tube and hoses for gasoline, fluorocarbons vapors etc. which are important in automotive and appliance application, requires solution to improve

barrier. Depending upon the application barrier can be classified into 3 groups-barriers to inert gases (e.g. Oxygen, nitrogen) barrier to chemically active gases (e.g. water carbon di-oxide) and barrier to liquids and vapors (e.g. aromas, fire chemicals, gasoline etc.)

1.5.4 Bio-medical materials:

1.5.4.1 Intra corporeal devices

1.5.4.1.1 Temporary devices: Surgical dressing

1.5.4.1.2 Simple semi-permanent devices: Tendons, joint reconstruction, bone cement heart valves, tubular devices (vascular grafting, oesophageal prosthetics etc .),soft tissue replacement materials for cosmetic reconstruction, Intraocular and cosmetic reconstruction, Intraocular and contact lenses, drug delivery implants.

1.5.4.1.3 Complex devices stimulating physiological process

- Artificial kidney/ blood dialysis, artificial lungs/ blood oxygenator
- Artificial heart
- Artificial pancreas, insulin delivery system.

1.5.4.2 Para corporeal or extracorporeal material

- Sterile and non-sterile packaging material
- Surgical Instrument
- Syringes
- Tubing
- Pharmaceutical containers
- Blood bags
- Catheters

1.5.5 Friction and Wear- Friction and wear are complicated phenomena which depend on bulk and surface properties. They are bulk dependent in that frictional forces depend on contract area, which in turn effected by the materials mechanical properties and by viscoelastic behavior. They are surface dependent in that the changes in surface energy.

Their applications are in-

- Packaging machines
- Automotive applications

1. Wind shield blades
2. Lining
3. Car tires etc.

- Magnetic storage media e.g. floppy, CD.

1.6 Ion exchange resins:

Ion exchange resins are cross-linked polymer which has some ions which they can exchange with solution medium ions. Ion exchange ruins are cross-linked polymers which contains some ions(cat ions or anions)which can be exchanged by the medium ions

- Cation exchange run(which has cation to exchange with)
- Anion exchange run((which has anion to exchange with)
- Amphoteric exchange anion(cation and anion both are present to exchange)
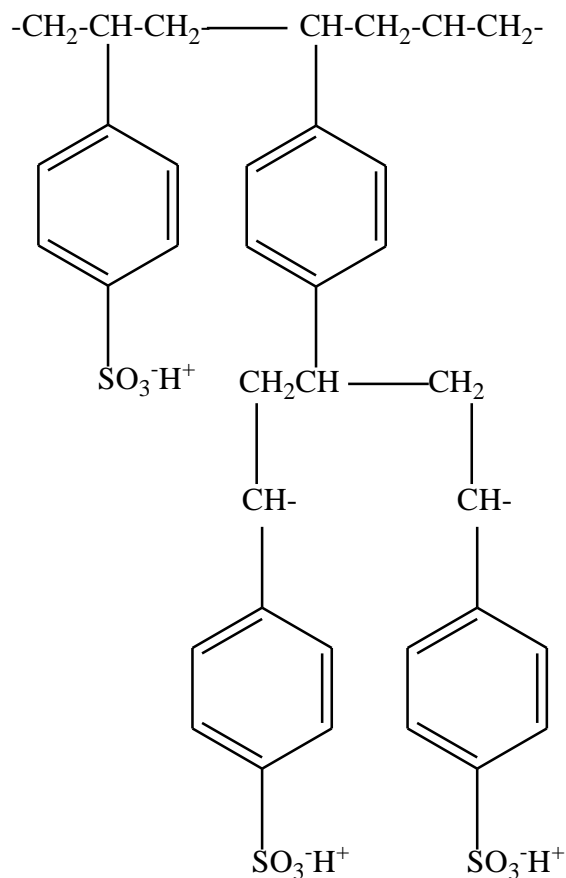
Figure 1.1 - Cation Exchange Resin

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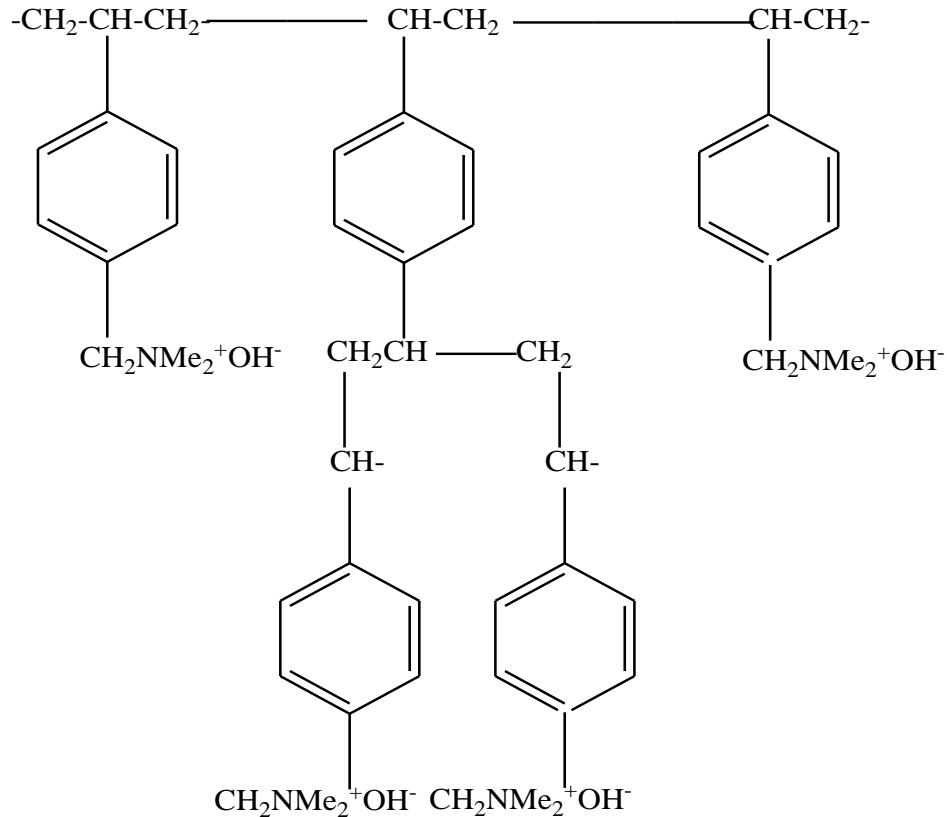
Figure 1.2- Anion Exchange Resin

1.6.1 Ion exchange

Ion exchange is define as the process where an insoluble substance removes ions of positive and negative charge from an electrolyte in a chemically equivalent amount. There is no structure change /diffuse into the network of resin.

$$nRA^+ + B^{n+} \Leftrightarrow R^{n-}B^+ + nA^+$$
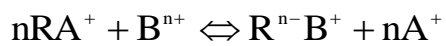
R^-, anion groups attached to the ion exchange resin, A^+ and B^{n+} are ions in solution.

$$K_{A^+}^{B^{n+}} = \frac{[R^{n-}B^+]_R [A^+]_s}{[R^-A^+]_R [B^{n+}]_s}$$

$[R^{n-}Bn+]_R$ Activity of B^{n+} in the resin

$[B^{n+}]_s$ Activity of B^{n+} in the solution.

1.6.2 Respective quotient or separation factor(Q_s):

The preference of the ion exchange one in relative to other.

$$Q_s = \frac{[R^{n-}B^+]_R [A^+]_s}{[R^-A^+]_R [B^{n+}]_s}$$

The affinity of an ion for a resin can be generated by the following-

1. Ions of high valance are preferred over ions of low valance $Fe^{3+}>Mg^{2+}>Na^{+}$, $PO_4^{3-}>So_4^{2-}>NO_3^{-}$ This is preferred increase with a decrease in the total ionic conc. In the solution.

2. For ions of some valances, the exchange reaction increased with decreasing hydrated radius and increasing atomic no. ($Ca^{2+}> Mg^{2+}>Be^{2+}$, $K^{+}>Na^{+}>Li^{+}$).

3. For a solution which has high total ionic conc. The extent of the exchange reaction follows no general rule and often of the exchange reaction follows no general rule and is often reversed. This type of response is the basic for the reversibility of regeneration.

4. The relationship between the degree of crosslinking and the size of the hydrated ion may affect the extant of the crosslinking the ion may be too large to penetrate into the material of the resin.

1.7 Advantage and disadvantage of choosing a resin with a high affinity for the ion to be exchanged

Advantages

1. Sharp break through curve
2. Shorter ion exchange column
3. Greater flow rate applied to ion exchanged column

Disadvantage:

High regenerants concentration required.

1.8 Type of ion exchange resin

1. Cation exchange resin
a. strong – acid exchange resin(SAC)
b. weak-acid exchange resin(WAC)
2. Anion exchange resin
a. strong – base exchange resin(SBA)
b. weak-base exchange resin(WBA)

Weak acid based resin- Function group derived from a weak acid carboxylic or phenolic **,** weak out in low pH range(below pH=7).

a) $R\text{-}SO_3^-$: H^+ +Nacl→HCl + $R\text{-}SO_3\text{-}:Na^+$

b) $2R\text{-}SO_3^-$: Na^+ + NaCl → $2R\text{-}SO_3^-:H^+$ + Na_2SO_4

Weak acid exchange resin-

a) $RCOO^-$ H^+ + NaHCO→$RCOO^-$ Na^+ + H_2CO_3 -> CO_2 + H_2O

b) $RCOO^-Na^+$ + HCl→RCOO : H^+ + NaCl   Regeneration 100% H

Strong base exchange resin-

a) $R\text{-}NR_3^+OH^-$ + NaCl → $R\text{-}NR_3^+$ + Cl^- + NaOH

b) $R\text{-}NR_3^+OH^-$ + HCl→$R\text{-}NR_3^+$ + Cl^- + H_2O

c) $R\text{-}NR_3^+OH^-$ +NaOH→$R\text{-}NR_3^+$ +OH^- + NaCl   Regeneration 30-50% H

Weak Base exchange resin-

a) $R\text{-}NH_2$ + HCl →$R\text{-}NH_2.HCl$

b) 2 $R\text{-}NH_2\text{-}HCl$ + Na_2CO_3→2 $R\text{-}NH_2$ +2NaCl +H_2CO_3→CO_2 + H_2O

c) RNH_2HCl +NH_4OH→$R\text{-}NH_2$+ NH_4Cl + H_2O

Regeneration→100% H , pH value , less than 7

Ion exchange capacity- Ion exchange capacity is a measure of the total quantity of the ions which theatrically can be exchange (no. of ionizable group) per unit or volume of resin meq/L or meq/gm.

X = [No. of equivalent of the ion of interest applied to the column]/ Resin volume

  - [No. of equivalent of the ion interest passing through the column]/ Resin volume

1.9 SUMMARY AND OBJECTIVE

According to the given introduction the gas phase modification technique for the modification of ion exchange resin is a very suitable technique to modify the ion exchange resin and the present work on this area has the following objectives.

- To study of different polymer modification techniques and use of these techniques to develop a modify the ion exchange resins.

- To study the gas phase modification technique to develop modified ion exchange resins.

- To develop a kinetic model for PMMA-EGDM(Poly methlmethacrylate - ethylene glycol di methacrylate) resin.

- To develop a kinetic model for PS-EGDM(Poly Styrene - ethylene glycol di methacrylate) resin.

2 LITERATURE REVIEW

Ion exchange is a surface phenomenon in which polymer surface resins have a very high affinity towards the solution ions in which they are put in. A lot of studies are done in the field of ion exchange resins and many studies also done to observe the activity of modified polymer surface of resins. In this chapter, a review of available literature on the synthesis, modification of surfaces characterization of the polymer resins and applications of their resin has been carried out. For some application the polymer surface has not that type of strength which is required. To obtain this type of chemical and mechanical strength the methodology of surface modification is to be implemented [Penn and Wang (1994)]. Hefferich (1992) classified the ion exchange in origin, inorganic and synthetic groups. In inorganic ion exchanges clays and glauconitic are important. Organic ion exchanger such as Humic acids and zeolites are weak in mechanical strength. The synthetic polymer PS-DVB, PMMA-EGDM, PS-EGDM have the same property to natural occurring ion exchangers. Here some literature has given related to this topic.

Alexandratos (2009)

His review provides a show of the work in the field of ion exchange resins through publications appearing in Industrial & Engineering Chemistry Research journal. His review proposed that the different ion-exchange resins consisted of different types of polymers and ligands and they were covalently bound to the polymers. Because of the insolubility of the resin phase they are very useful in many applications. They can be separated by filtration after the ion exchange is over. They are environmentally compatible because of their reproducibility. They have used as catalysts in place of homogeneous catalysts such as sulfuric acid and to immobilize metallic catalysts. He emphasis that the research with ion-exchange resins is as fertile today as it was when it all first began or in the past. They are used in water and wastewater treatment to remove both ions and molecules, and on catalytic applications. An important need is for the ability to design ion-exchange resins on their selectivity for targeted substrates. For this a better understanding of substrate - ligand interactions and the influence of the polymer support on those interactions are required. He said that Hard-soft acid-base theory was of great value as an

organizing principle but a basic understanding of the effects of polarizability and molecular structure would require more research with molecular orbital theory. In the area of bead formation also research required so that they are easily handled and they have stability in it. For this monoliths provide an interesting alternative as do membranes and linear polymers.

Xiong et al. (2009)

They performed experiment to investigate the recuperation of nickel (II) form weak acid resin which is macro porous in nature. The reaction was performed at three different temperatures 288K, 298K, and 308K respectively. At the ph of 6.9 optimal removal of ion has been recovered optimum in nature. They also performed the kinetic modeling by fitting the first and second order curve to the experimental value obtained from sorption analysis. For doing the experiments they initially made the buffer solution by maintaining the ph of the solution between 3.5 to 6.9. For determining the concentration of the nickel they used UV spectrophotometer. They performed different set of experiments at constant temperature and amount of adsorb component with time to investigate the ion exchange capacity of the nickel (II). After performing the experiment they gave the conclusions that the ion exchange property depend on the initial ph of the solutions. Contact time also plays the important role in the adsorption of the nickel ion. They showed that influence of metal ion has no any significant on the removal of nickel (II).

Lee et al. (2007)

They proposed that the ion exchange process was very important process to remove heavy metal ions from the sludge and the waste water. Both ions and the resins have a equilibrium relationship. They analyzed the different sets of equilibrium of the ion exchange such as Cu^{2+}/H^+, Zn^{2+}/H^+ and Cd^{2+}/H^+. They used the system Aberlite IR-120. The approach to study the equilibrium relationship was the langmuir isotherm, Freundlich isotherm and different type of selectivity approaches. They also calculated different type of thermodynamics properties such as Gibbs free energy change and enthalpy change. They compare the selectivity coefficients and according to that the sequence to IR-120 was $Cu^{2+}>Zn^{2+}>Cd^{2+}>H^+$. They also studied the ion-exchange kinetics. They were regressed the ion exchange kinetic data by different models such

as pseudo first order, second order and reversible order. The activation energy calculated from the rate coefficient at different temperature. They resulted that Langmuir isotherm fits better than frendlich approach.

Pugazhenthi et al. (2005)

They studied the removal of hexavalent chromium by carbon membrane. Mathematical modelling was also done. Carbon membrane was prepared through nitration followed by amination. It was also observed that the water flux in case of modified membrane was double in compare to unmodified membrane. Also losses in rejection were obtained only 12% in case of modified membrane. In the modeling section the solution of difficult non linear equation was solved by using poisson-boltzmen equation. Also the model proved to be helpful to find pore size.

Bhattacharya and Mishra (2004)

They reviewed the past research on the modification technique through polymer grafting. They gave the brief discussion of various initiation of Graft co-polymerization. They also discussed various controlling factor of grafting and various application of graft copolymer. They tried to cover two important applications of grafting technique viz. conducting polymers and membranes separation science. In review they concentrated on two important grafting methods, (i) grafting with a single monomer and (ii) grafting with a mixture of two or more monomers. They gave the information of different type of graft polymerization techniques which include radiation, photochemical, chemical, plasma-induced techniques and enzymatic grafting. They also gave the information about several variables that control the grafting includes the nature of the backbone, monomer, solvent, additives, initiator and temperature etc. They also showed that membrane grafting had the potential to separate mixtures viz. salt-water mixtures, alcohol-water mixture. Grafting techniques also used for making conducting polymer processable and they are used as a ion sensors, glucose sensors etc.

Chen et al. (2004)

They prepared a new type of composite proton exchange members which was by polystyrene sulfonate solution with suspended micron sized particles was the particles of cross linking polystyrene sulfonate. Through the experiment it had seen that resin/PSS composite membranes have greater ion exchange capacity than normal PSS member but ion conductivity of both the membranes was same. The composite membranes have the greater chemical stability than the PSS membranes in the fuel cell.

Neelakandan et al. (2003)

They prepared the PMMA -EGDM (poly methyl methacrylate-ethylene glycol di-methacrylate) copolymer. Ultra filtration membrane from the monomers in two stages. For this they used gas phase nitration scheme NOx at 800C . they also performed the separation. Experiments on the chromium(V1) salt solution at low pressures this chemical modification result increase in the pore size as well as hydrophobicity of membrane. This chemical modification membrane then used for separation of chromium(VI) and they showed that modification membrane gave much high permeable flux with same rejection when they compared it to the un-modified membrane. They also results that the flow of the pure water through modified membrane was much better than the unmodified membranes.

Murakami et al. (2002)

They reported the surface modification of polystyrene with aromatics rings and Polymethylmethaacrylate with no aromatic rings for the surface modification they used the ozone aeration, UV irradiation (ozone/UV) in distilled water. They also investigated the surface stage of the polymers through contact angel, Atomic force microcopy (AFM) and FTIR. According to them the contact angle of ultrapure water decreased with an increase in elapsed time of treatment in Ps films. Through these surface modification technique the surface became rough. The ozone/UV treatment introduce -OH and -CO groups on the film and surfaces of polystyrene.

Sinha and Kumar (2002)

They prepared PolyStyrene-DivinylBenzene based ion exchange resin by suspension polymerization using gelatin as a stabilizer and toluene as porogon which was subsequently nitrated by a mixture of NO and NO_2 (called NO_x) in a gas phase nitration. This was aminated by reducing the nitrate groups using hydrazine hydrate, and the resultant weak base anion exchange resin was shown to have one-time exchange property because of its inability to be regenerated. In the same study the chloroethylated PS-DVB resin was prepared by reacting aminated resin with dichloroethane, and was shown that two molecules of the latter reacted with every amine group. The regenerable strong-base anion exchange resin was then prepared by quarternizing it with tartiary (trimethyl and triethyl) amines and triphenyl phosphine, and it was shown that these gegen ions had a considerable effect on the exchange ability of the resin.

Sinha et al. (2002)

They prepared the Poly (methyl methacrylate)-ethylene glycol dimethyl acrylate resin. For making of this they used suspension polymerization method and gelatin was the key compound to decide the size of the polymer particles. To prepare the modified weak base PMMA-EGDM resin, resin 1 which was PMMA-EGDM resin was nitrated using NO_x gas. The modified PMMA-EGDM resin was nitrated using NO_x gas. The modified PMMA-EGDM resin (resin 2) was reduced to NH_2 groups and after that the exchange capacity of the modified resin was determined. This resin was the resin 3. After that they examined the exchange capacity of the resin 3. It was found in experiment that exchange capacity first increased with the increase in the extent of nitration. This exchange capacity was maximum for 4.8 meq/gm of wet resin with 78% moisture for 8 hours of nitration and after that for a longer nitration time as a result of polymer degradation. These results were compared with commercial resin, which had exchange capacity of 1.68 meq/gm of wet resin with 43% moisture content. They also devised three stages of moisture remove for assessing the salvation ability of the modified PMMA-EGDM resin. Their experiment showed that high capacity of the modified PMMA-EGDM resin may attributed high salvation ability.

Chowdhury et al. (2001)

They have proposed a new gas phase modification technique. This technique includes gas phase nitration scheme for polysulfone membranes. In this technique a mixture of NO and NO_2 gas are used (which is generally called NO_x). This nitration followed by amination of the nitration followed by amination of nitrated functional groups. For the amination process hydrazine hydrate are used. After the nitration it has been that the strength of the polymeric material has not changed and its surface becomes more hydrophilic in nature. The paper shows that for the experimental exchange capacity of the modified membrane, all membranes should have at least two amine groups attached to its every repeat unit. His ultrafication experiment shows that the rejection capacity of membranes increase for nano-electrolyte solutions through its modification. In this experiment it has seen that the separation characteristics of black liquor shows two times increase of rejection at every dilution for the modified membranes compared to unmodified membranes.

Kichatov et al. (2001)

They performed the experiment to investigate the variation of size distribution of the particles of polymer with respect to stirring rate and time of compound to stabilize in the emulsion. For this experiment they used 10 m^3 volume of reactor which consists of three stirring blade in which synthesis of poly styrene was performed by suspension polymerization method. By using baffles in the reactor the axial flow rate of the compounds were increased. Water used in the reactor was 2.4 m^3 and styrene was 4.25 m^3 benzoyl peroxide and dicumyl peroxide was also used in amount of 3.5 kg and 7.8 kg respectively, Iso pentene was also added to the reaction mixture as a foaming agent. The reactions of the reactants were performed at 108c and the pressure was maintained at 4.5 KPa. The size of the particles of polymer was determined by using the sieve method. They also studied the variation of time to the polymer emulsion by adding the stabilizer to the reactor. Surface forces play the important role in maintaining the stability of the polymer product, they found out that when they increase the viscosity of the reaction mixture the polymerization favors on the other hand by producing very high surface tension helps the droplets of the polymer to gain it in the spherical shape.

Amor et al. (2000)

They studied XPS analysis of plasma treated and alumina coated PMMA. Two objects of study which are completed in this paper are - XPS study of plasma treated PMMA (poly methyl methacrylate), study of PMMA and thin film of alumina inter phase. The modifications which were observed on PMMA surface were obtained when polymer was plasma treated. By these modifications substrate and alumina interaction increases. Alumina carboxylate was found at inter phase and no evidence was observed to have covalent bonds among polymers and alumina film.

Jayaswal et al. (2000)

They prepared Polystyrene-Di Vinyl Benzene in the laboratory using suspension polymerization and they used gelatin and toluene as porogen. This polymer was nitrated by a mixture of Na and NO2 (called NOx). The analysis has done through this test the covalent bonding between the nitrogen and carbon has demonstrated. This polymer resin then aminated by reducing nitrogen group. With use of hydrazine hydrated. This resin was a weak base anion exchange and which had one time exchange capacity because it is not possible to regenerate further by the usual ASTN procedure. After that the aminated resin was converted to chloroethylated PS-DVB with using di chloro ethane. The generable strong base anion exchange resin is then prepared. Which is called gegen ions. They had the considerable exchanging ability of the resin It was found that for any gegenion , the exchange capacity firstly increase for short times of exchange capacity firstly for short times of nitration these after reaching maxima falls larger time of nitration then after of slight degeneration from this experiments found that for the resin with tri phenyl phosphine gives the highest exchange capacity and the resin with tri-methyl gave the lowest exchange capacity.

Marais et al. (1999)

They studied modification of UPR film by using tetrafluoromethane microwave plasma. The surface which was treated, investigated through atomic force microscopy and contact angle. By the measurement of permeation, it was shown that the surface energy was decreased when it was treated with carbon tetrafluoromethane plasma. This was because of increase in hydrophobic

property. Water content by UPR film was decreased by surface modification done by fluoronation, also diffusion coefficient decreased. It was clearly observed that various effects were improved by tetrafluoromethane treatment.

Ghosh et al. (1998)

They studied polymerization of methyl methacrylate. With the help of experimental data of polymerization of methyl methacrylate parameters were tuned. The experiment was conduct in a stainless steel reactor which was controlled by computer. The polymerization reaction was conducted at temperatures 50 and 70 degree centigrade. The benzoyl peroxide was used to initiate the polymerization. The gravimetric analysis was used to measure conversion of monomer and viscosity molecule weight was measured by viscometer. Also the applications in non isothermal reaction were also studied.

Chan et al. (1996)

 They gave information about the modification of polymer through plasma and protons. In plasma treatment there are many different type of gases are used such as argon, oxygen, nitrogen, fluorine, carbon di oxide and water and these different gases introduce different type of polymer surface for various application. They cracked the effect of different gases effects on surface. They have been that oxygen could increase the surface energy of polymer, Florien could decrease the surface energy and improve the chemical inertness. For introduction of cross linking the surface inert gas is used in plasma treatment. The main disadvantage of this technique is the high operation cost They demonstrate that the plasma polymerized surface have very good barrier properties. So these are very useful for biometric application and in the microelectronized industry They also check the UV radiation technique foe surface modification of polymer and it has seen that UV irradiation increase the hydrophobicity and photo are the polymer surface. They also discussed the different modification technique which was at those days.

Kang et al. (1996)

They studied the surface modification of poly tetra fluoro ethylene (PTFE). The modification was done by graft co polymerization near to ultra violet light. In this process acrylic acid, sodium salt and other chemicals are used. The characterization of modified film was done by using XPS (x-ray photoelectron spectroscopy). The graft was improved when using Ar plasma pretreatment and concentration of monomer. Initially trypsin immobilization on PTFE films was increased by WSC (water soluble carbodimide). The activity of enzyme was increased with concentration of grafted surface but after some time got saturated.

Arshady (1992)

He gave a methological description of heterogeneous polymerization. This included suspension, precipitation, and emulsion and dispersion polymerization. They distinguished the above polymerization techniques according to four criteria, initial state of polymerization mixture, and kinetics of polymerization, mechanism of particle formation and shape and size of the final polymer particles. The discussion focused on the parameter influence polymer particle morphology such as emusifier, stabilizer, reactor design and stirring speed. He also discussed some special topic such as emulsifier free emulsion polymerization, seeded polymerization and formation of the core shell particles.

Briggs D. (1984)

He studied new developments in the analysis of polymer surface. It was found that in case of polymer surface and characterization, advantages of XPS are its quality to find out elements and present data which is easily qualified. The functional groups which are specific in chemical shift are limited and this is controlled by using these factors. Imaging, fingerprints are main advantages of SIMS. When we use XPS and SIMS in combined form, it gives better result.

IKada Y.(1984)

They studied surface modification of polymers. It is very rare for the materials which are used as biomaterials that these materials follow properties, surface and bulk. So the material which have already bio functionality and bulk properties in a good amount, they can be used to develop

surface to make them useful as biomaterials. In the paper surface modification is done by using grafting technique of polymer. These techniques are already used in polymer chemistry but need to be applied in biomaterials. It is shown that by graft polymerization of monomer graft surface might be obtained or same object can also be achieved by using covalent coupling reaction on polymer molecules. The surface properties which are to be modified have two types of biocompatibility. First one includes least foreign body reaction. Second one includes capability of cell and tissue bonding. In this paper possible ways of producing bio specific surfaces are explained
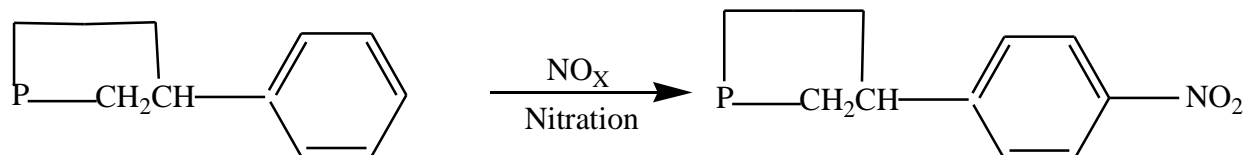
3.1 METHODOLOGY AND MODEL DEVELOPMENT

3.1.1 Synthesis of macroporous PS-EGDM anion exchange resin by gas phase modification using NO_X
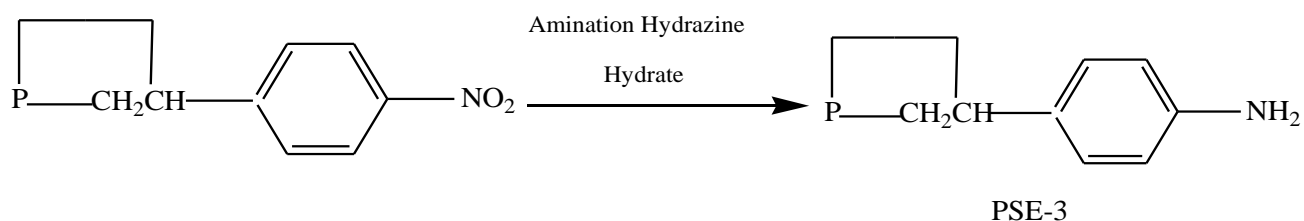
3.1.1.1 The synthesis of polystyrene- ethylene glycol di methacrylate(PS-EGDM) resin is done by suspension polymerization technique. This PS-EGDM polymer then goes through the chemical modification. In the suspension polymerization process, the reaction carried out by the mixing of organic phase. The components of the organic phase were suspended in inorganic phase. Some stabilizer also be in the solution to control the particle size of the polymer. The resin prepared through suspension polymerization was very hard and processed high mechanical strength. The very hard and process high mechanical strength. The size of resin found to be uneven with the average particles size 0.5 - 1 mm.


styrene

Ethylene Glycol Di methacrylate

Suspension Polymerization
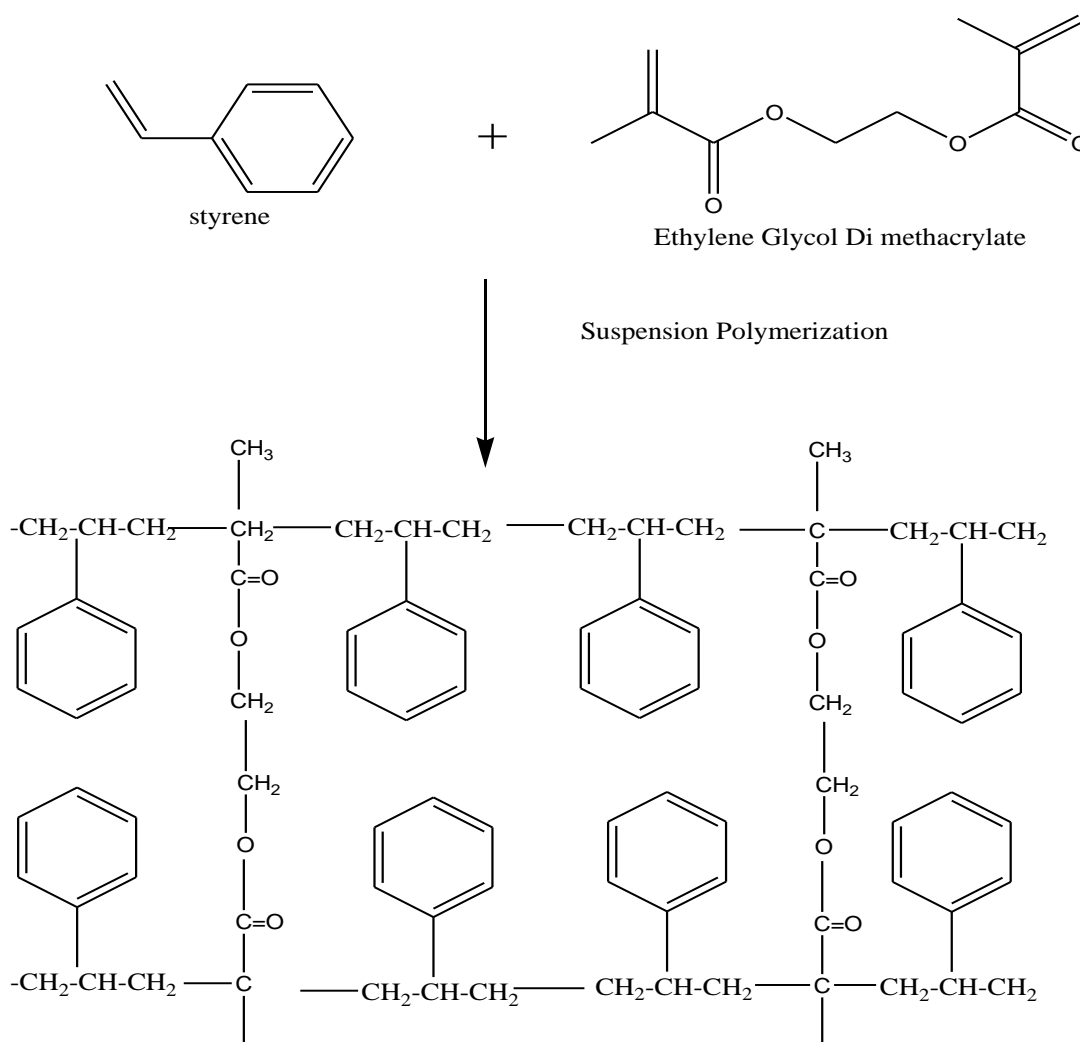
3.1.1.2 After the synthesis, the synthesized resin(PSE-1) was surface modification by gas phase nitrate using NO_x.

3.1.1.3 For the use of PS-EGDM resin as ion exchange resin the nitrated resin (PSE-2) was modified with use of hydrazine hydrate.
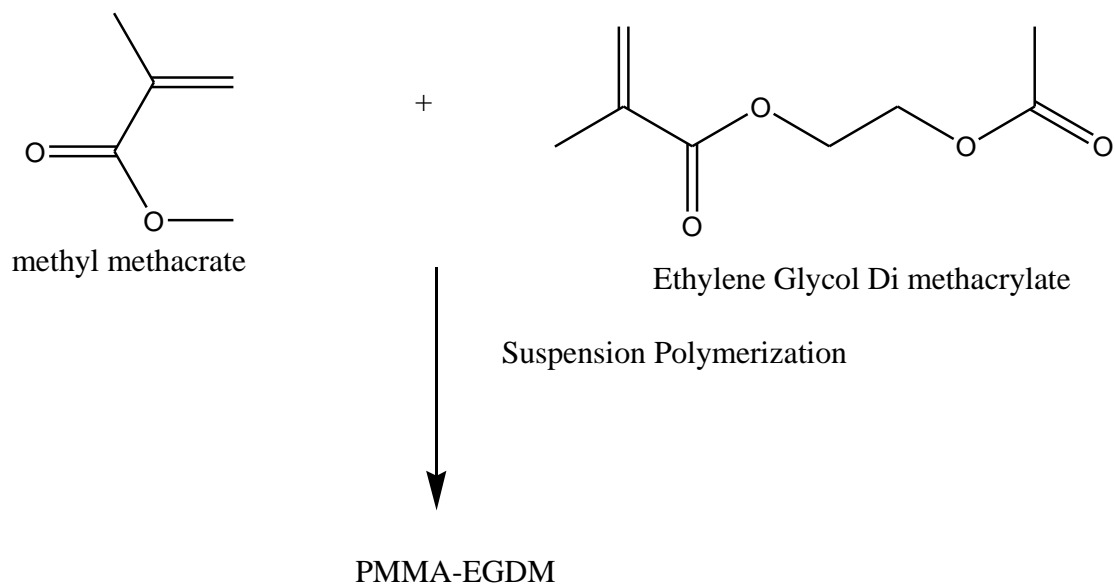

PSE-3

3.1.1.4 The resin (PSE-3) on reaction with HCl was likely to give an exchange ion. The reaction mechanism is as follows.
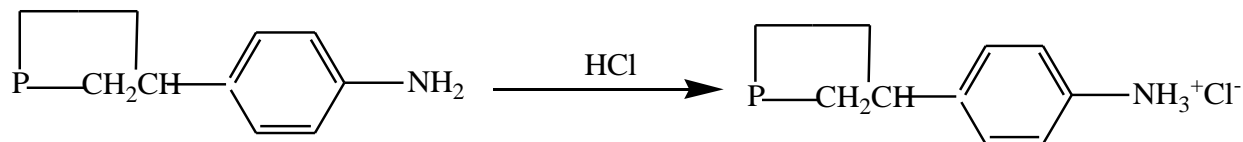

3.1.2 Synthesis of macroporous PMMA-EGDM anion exchange resin by gas phase modification using NO_X
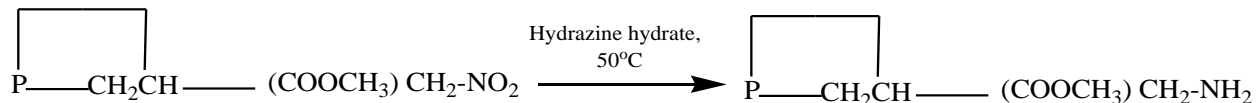
3.1.2.1 The synthesis of polymethylmethacrylate- ethylene glycol di methacrylate(PMMA-EGDM) resin is done by suspension polymerization technique. This PMMA-EGDM polymer then goes through the chemical modification. In the suspension polymerization process, the reaction carried out by the mixing of organic phase. The components of the organic phase were suspended in inorganic phase. Some stabilizer also be in the solution to control the particle size of the polymer. The resin prepared through suspension polymerization was very hard and processed high mechanical strength. The very hard and process high mechanical strength. The size of resin found to be uneven with the average particles size 0.5 - 1 mm.

methyl methacrate

+

Ethylene Glycol Di methacrylate

Suspension Polymerization

PMMA-EGDM

3.1.2.2 After the synthesis, the synthesized resin (Resin 1) was surface modification by gas phase nitrate using NO_x

$$P\text{---}CH_2CH\text{---}(COOCH_3)\ CH_3 \xrightarrow{NO_x,\ 120^oC} P\text{---}CH_2CH\text{---}(COOCH_3)\ CH_2\text{-}NO_2$$
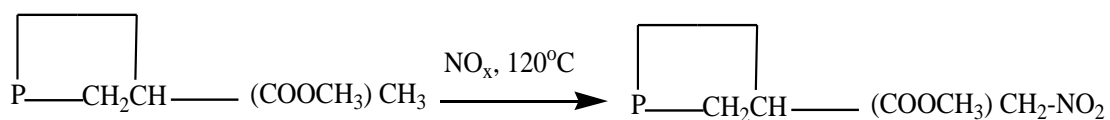
3.1.2.3 For the use of PMMA-EGDM resin as ion exchange resin the nitrated resin (Resin 2) was modified with use of hydrazine hydrate.

$$P\text{---}CH_2CH\text{---}(COOCH_3)\ CH_2\text{-}NO_2 \xrightarrow[50^oC]{\text{Hydrazine hydrate,}} P\text{---}CH_2CH\text{---}(COOCH_3)\ CH_2\text{-}NH_2$$

3.1.2.4 The resin (Resin 3) on reaction with HCl was likely to give an exchange ion. The reaction mechanism is as follows.

$$P\text{---}CH_2CH\text{---}(COOCH_3)\ CH_2\text{-}NH_2 \xrightarrow{HCl} P\text{---}CH_2CH\text{---}(COOCH_3)\ CH_2\text{-}NH_3^+Cl^-$$
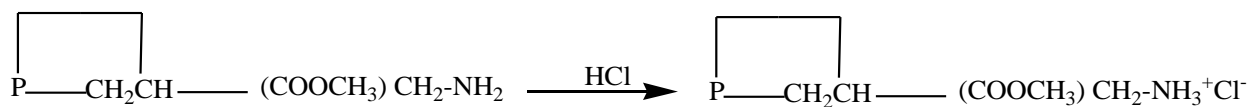
3.2 EXPERIMENTAL SETUP

This experimental setup contains a large water bath in which a reactor is placed, the water bath have a temperature controller device to adjust the temperature of the system of water bath. This water bath also contains a reactor with stirrer; this reactor is used for making a polymer resin with the use of suspension polymerization technique. To control the temperature of the water bath, it can be operated to the temperature controller. This temperature controller device contains a thermocouple which checks the temperature of the water bath. The water bath also contains a stirrer to maintain uniformity of the temperature of the water bath. The stirrer of the reactor and the water bath both are connected through to the mains which controls the speed of the reactor.
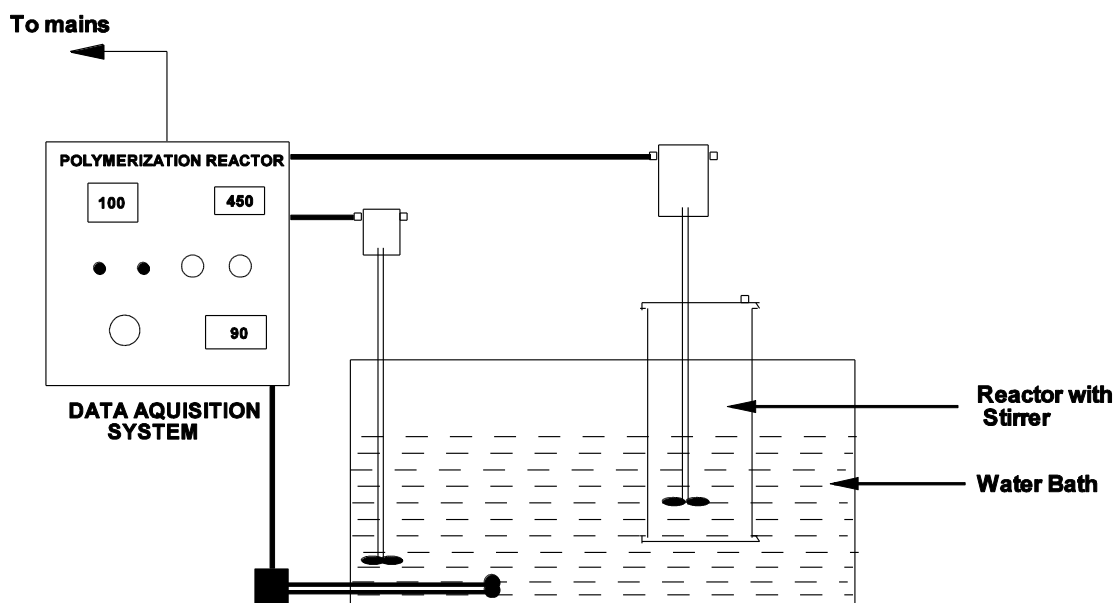

Figure 3.1 Experimental Setup for Preparation of Different Resins

3.2.1 Determination of ion exchange capacity

The exchange capacity of polymer resin is determined by two methods:

1.   Titration method

2.   Gravimetric method (standard ASTM method)

3.2.1.1 Titration method: In this method [Jayaswal et al.(2001)] about 1.5 gm of resin were placed in a 250 ms signal neck round bottom flack and this resin was then refluxed wit 0.1 N HCl in on oil both at a 50^0 C. The reaction was then filtrate was titrated with 0.1N NaOH which

contained of chlorine intake by resin and it is carried out using phenolphthalein indicator. The filtrate resin then washed carefully then dried. The dried resin was again refluxed with 0.1 NaOH for 4 hr 50^0C and the remaining with 0.1N NaOH concentration in resin was determined by filtrating the filtrate with 0.1 N HCl using phenolphthalein indicator. The capacity of resin is calculated by following relation.

$$N_{NaOH} = \frac{V_{HCl}}{V_{NaOH}} . N_{Hcl}$$

The capacity of resin in meq/gm $= \dfrac{50(0.1 - N_{NaOH})}{W}$

where W= weight of resin

3.2.1.2 Gravitational Method: In order to check the efficiency of titration values, the exchange capacity of aminated resin can be determined by using the method given in ASTM standards and BIS. In the recommended procedure two steps were followed as:

3.2.1.2.1 Gravitational Method: Firstly, the mixed acid was prepared by mixing H_2SO_4 (18.1 mL, sp. gr. 1.84) with HCl (27.5 mL, sp gr. 1.19) in 500 mL distilled water and then this mixture was brought up to 1000 mL volume by adding distilled water. Test water was prepared by diluting mixed acid with distilled water upto 1% concentration. This test water was then added to resin in the quantity of 100mL per gram of resin in a beaker (closed with lid) and the whole mass was kept for 24 hr at room temperature. After 24 hr the resin was filtered and washed with distilled water until the filtrate becomes neutral, i.e., when the methyl orange color, changes from orange red to orange yellow. Thus, the resin was freed from mixed acid and regenerated.

3.2.1.2.2 Determination of exchange capacity: The resin obtained from regeneration step was mixed with 0.1 N NaNO$_3$ solutions and kept for another 24 hr. Then the reaction mass was filtered and 1.7 g AgNO$_3$ with 2-3 drops of HNO$_3$ were added to the filtrate and the whole reaction mass is kept for another 24 hr. The chlorine ions present in the filtrate form AgCl, which were precipitated. The precipitate was removed by filtering through filter paper and weighed and the capacity of the resin was calculated.

$$Capacity, meq/g = \frac{Weight\ of\ the\ Precipitate}{Molecular\ Weight\ of\ AgCl}$$

3.2.2 Solid Phase Kinetic Modeling for Exchange Capacity:

Solid phase kinetic modeling is used to determine the rate constant of the ion exchange resin with use of the data of Exchange Capacity (Q) vs Time (t) data. From this kinetic modeling one can determine the value of rate constant and the best fit solid phase model for the same. The basic equation for the solid phase kinetic model is given below.

$$\frac{dC_A}{dt} = kC_A^n$$

where C_A = Concentration of the compound,

k = Rate Constant,

n = Order of the reaction.

Rate constant k also a dependable variable which depends Temperature, Activation energy and pre-exponential factor. This rate constant value can be given by the Arrhenius equation which is given below.

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right)$$

where k_0 = pre-exponential factor,

Ea = Activation energy,

R = Universal Gas Constant,

T = Temperature in Kelvin.

The unit of E_a is the energy per unit mole. The unit of pre exponential factor or frequency factor is the same as the unit of the Rate constant. A is also called the attempt frequency of any reaction. It can say that k is the number of collision per second in any reaction. A is the number of collisions in a reaction in a second and $\exp(-E_a/RT)$ is the probability of an collision likely to be occur.

3.2.2.1 For the first order reaction the integral equation can be written as

$$\frac{dC_A}{dt} = kC_A^n$$

For n=1,

$$\frac{dC_A}{dt} = k_1 C_A$$

$$\int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A} = \int_0^t k_1 dt$$

-ln(1-X$_A$)=k$_1$t

where $X_A = \dfrac{C_{A_0} - C_A}{C_{A_0}}$

For the solid phase kinetic modeling XA can be replaced with Q/Q$_\infty$. whwer Q is the exchange capacity and Q$_\infty$ is the Asymptotic exchange capacity.

So the Solid phase model equation can be written as

$$-\ln\left(1 - \frac{Q}{Q_\infty}\right) = k_1 t$$

3.2.2.2 For the second order reaction the integral equation can be written as

$$\frac{dC_A}{dt} = kC_A^n$$

For n=2,

$$\frac{dC_A}{dt} = k_2 C_A^2$$

$$\int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A^2} = \int_0^t k_2 dt$$

$$\frac{X_A}{1 - X_A} = k_2 C_{A_0} t$$

where $X_A = \dfrac{C_{A_0} - C_A}{C_{A_0}}$

For the solid phase kinetic modeling X_A can be replaced with Q/Q$_\infty$. whwer Q is the exchange capacity and Q$_\infty$ is the Asymptotic exchange capacity.

So the Solid phase model equation can be written as

$$\frac{Q/Q_\infty}{1-Q/Q_\infty} = k_2 Q_\infty t$$

3.2.2.3 For the first order reaction the integral equation can be written as

$$\frac{dC_A}{dt} = kC_A^n$$

For n=3,

$$\frac{dC_A}{dt} = k_3 C_A^3$$

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^t k_3 dt$$

$$\frac{2X_A - X_A^2}{(1-X_A)^2} = 2k_3 C_{A0} t$$

where $X_A = \dfrac{C_{A_0} - C_A}{C_{A_0}}$

For the solid phase kinetic modeling X_A can be replaced with Q/Q_∞. whwer Q is the exchange capacity and Q_∞ is the Asymptotic exchange capacity.

So the Solid phase model equation can be written as

$$\frac{(Q/Q_\infty)(2-(Q/Q_\infty))}{(1-Q/Q_\infty)} = 2k_3 Q_\infty^2 t$$

4 RESULTS AND DISCUSSION

4.1 Solid Phase Model Development for Aminated PMMA-EGDM Resin

For the solid phase model development for PMMA-EGDM resin, firstly the data is taken from the paper of Sinha et al. (2002) , this paper contains the results of experiment of modification of PMMA-EGDM resin. In these paper different values of the exchange capacity of modified PMMA-EGDM resin at different temperature and different time interval is given. For the preparation of the model equation firstly the order of the equation assumes and after that model is developed. Here sum of least square term is used which gives the information about the best fit of model function to a data set. For the development of the model tangent estimation method, newton method and forward derivation method is used and the solver set to the given different parameters which are given below.

- Maximum Time: 100 seconds
- Iterations: 100
- Precision: 0.000001
- Tolerance: 5 %
- Convergence: 0.0001

Table 4.1 Ion Exchange Capacity Q (meq/gm) of Aminated PMMA-EGDM Resin at different Temperature and Time (Sinha et al., 2002)

Time (hours)	Q, 60°C	Q, 70°C	Q, 80°C	Q, 90°C
0	0	0	0	0
2	0.38	0.49	0.49	0.76
4	0.47	0.34	0.34	1.48
6	0.19	0.71	0.71	1.77
8	0.56	0.87	0.87	1.9
10	0.78	0.91	0.91	1.96
12	0.64	0.99	0.99	1.84

4.1.1 Solid Phase Kinetic Studies for exchanger capacity, Q vs t data for PMMA-EGDM:

4.1.1.1 For Solid Model 1 (n=1)

Table 4.2 Calculations of Solid Phase Model Development for First Order, (PMMA-EGDM)

$-\ln\left(1-\dfrac{Q}{Q_\infty}\right) = k_1 t$							
Temp.	Time	Q_{exp}	Q_∞	k_1	SSE	Q_{model}	R^2 (Qmodel:Qexp)
60°C	0	0	2.9341	0.0205	0.0343	0	0.661
	2	0.38				0.1179	
	4	0.47				0.2311	
	6	0.19				0.3397	
	8	0.56				0.4439	
	10	0.78				0.5440	
	12	0.64				0.6400	
70°C	0	0	1.1336	0.1722	0.1782	0	0.903
	2	0.49				0.3303	
	4	0.34				0.5643	
	6	0.71				0.7301	
	8	0.87				0.8477	
	10	0.91				0.9310	
	12	0.99				0.9900	
80°C	0	0	2.1287	0.0760	0.07693	0	0.913
	2	0.58				0.3003	
	4	0.69				0.5582	
	6	0.83				0.7797	
	8	0.97				0.9700	
	10	1.18				1.1334	
	12	1.09				1.2738	
90°C	0	0	2.0541	0.3083	2.1265	0	0.983
	2	0.76				0.9453	
	4	1.48				1.4556	
	6	1.77				1.7311	
	8	1.90				1.8797	
	10	1.96				1.9600	
	12	1.84				2.0033	

Table 4.3 Calculated Data for estimation of k_o and E_a

Temp (K)	k_1	$k_0 exp(-E_a/RT)$	SSE	k_0	E_a
$k_1 = k_0 exp(-E_a/RT)$, where R=82.05746 cm^3-atm-k^{-1}-mol^{-1}					
333	0.0205	0.1443			
343	0.1722	0.1443	0.0477	0.1443	1.0050
353	0.0760	0.1443			
363	0.3083	0.1443			

4.1.1.1.1 Regression analysis

In regression analysis, here non linear regression analysis is used for the development of the solid phase model. From the regression analysis following result is obtain, which has shown through the various graphs and table. Here the value of R square gives the information about the goodness of fit. The R square value is also called the value of the correlation coefficient and this value give the information about the nearness of the predicted value through the model to the experimental value or the given value.
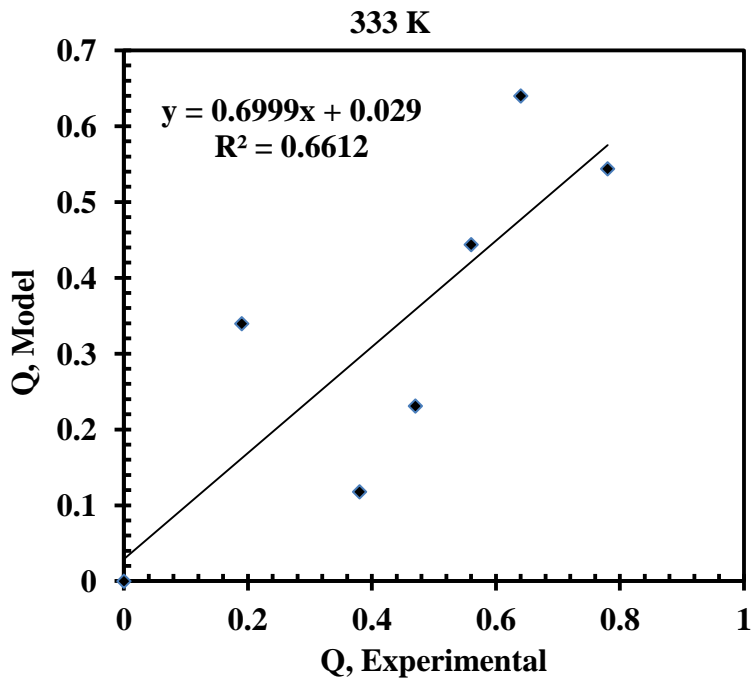
Figure 4.1 A curve between model and experimental value at 333 K

343K

y = 0.949x + 0.0433
R² = 0.9035
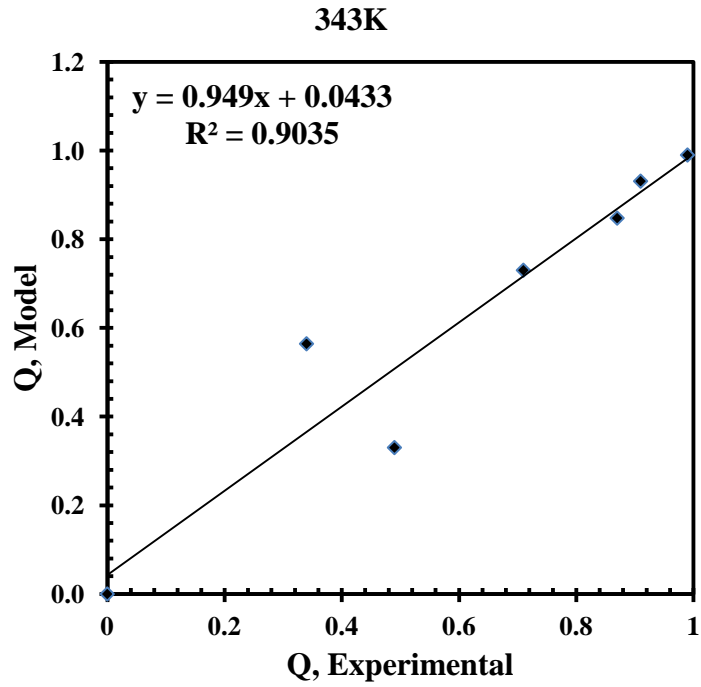
Figure 4.2 A curve between model and experimental value at 343 K

353K

y = 1.1034x - 0.1252
R² = 0.9139
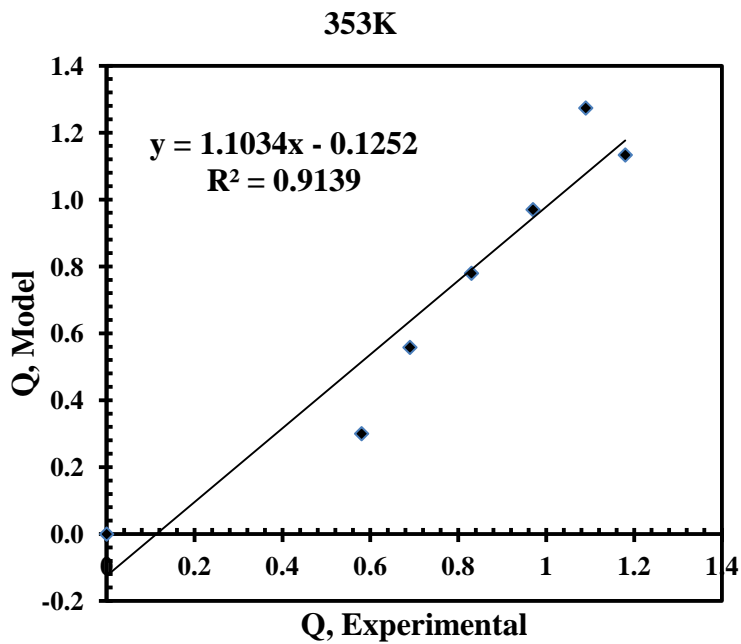
Figure 4.3 A curve between model and experimental value at 353 K

363K

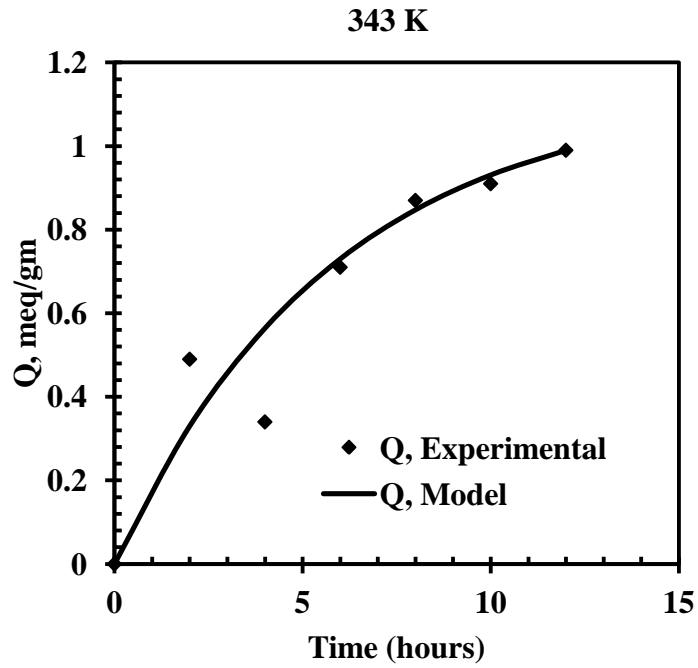y = 0.9786x + 0.0675
R² = 0.9837

Q, Model

Q, Experimental
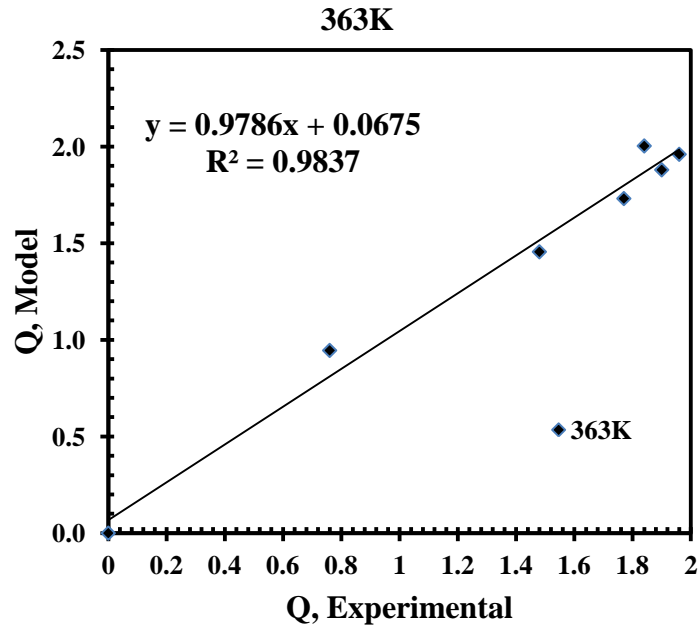
◆363K

Figure 4.4 A curve between model and experimental value at 363 K

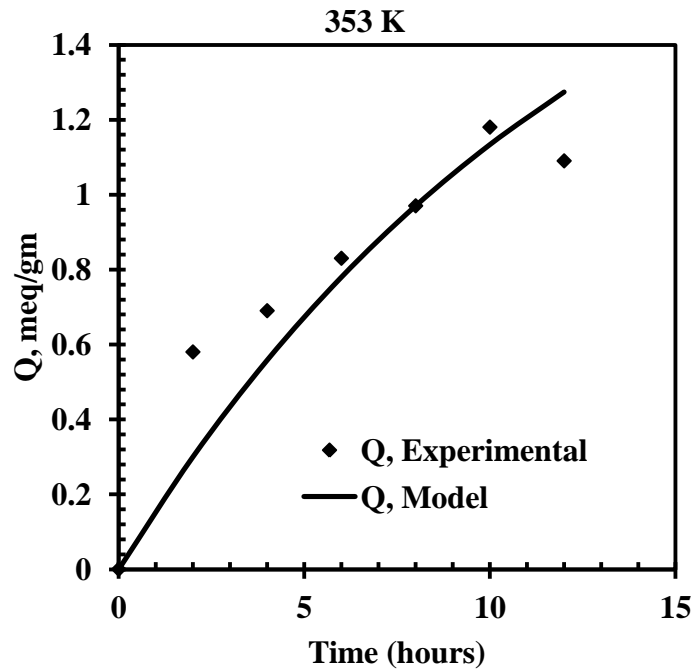### 4.1.1.1.2 Comparison between Q_{model} and $Q_{experimental}$

333 K

Q, meq/gm

Time (hours)

◆ Q, Experimental
── Q, Model
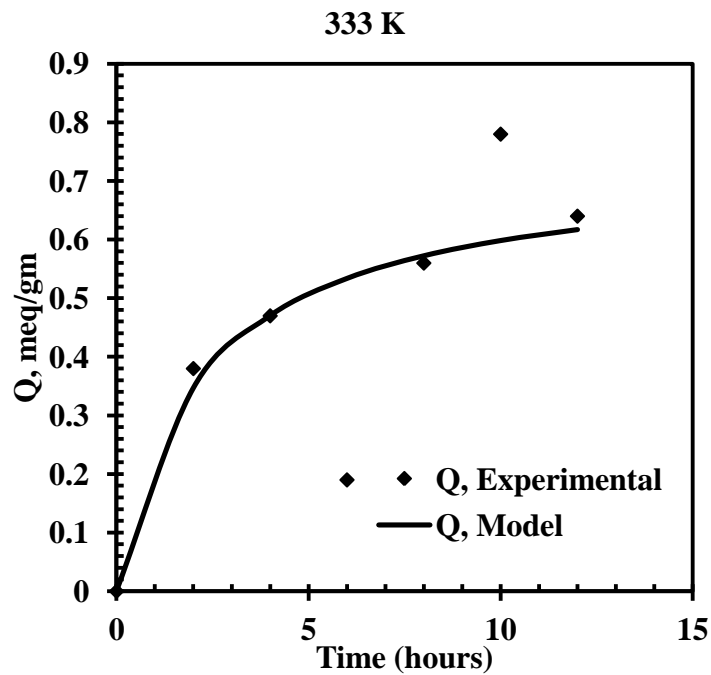
Figure 4.5 A curve between model and experimental value Vs Time at 333 K

Figure 4.6 A curve between model and experimental value Vs Time at 343 K

Figure 4.7 A curve between model and experimental value Vs Time at 353 K
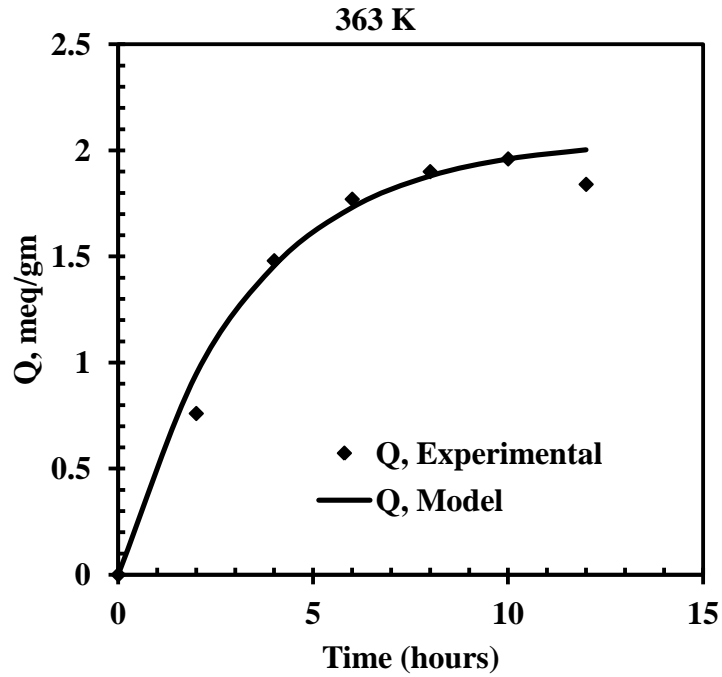
Figure 4.8 A curve between model and experimental value Vs Time at 363 K
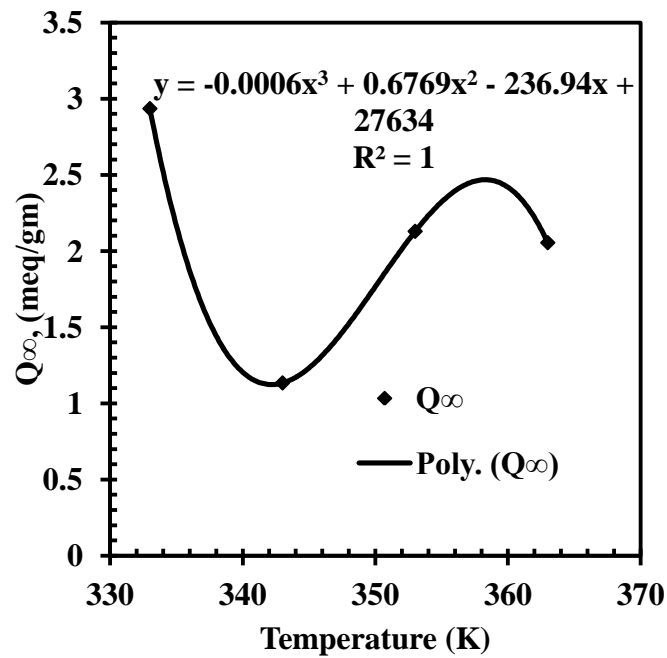
Figure 4.9 The curve between Q∞ and Temperature in Kelvin

For Solid Model 1 (n=1)

$$-\ln\left(1-\frac{Q}{Q_\infty}\right) = k_1 t$$

Best fit rate constant

$$k_1 = 0.1443 \exp\left(\frac{-0.0122}{T}\right)$$

where $Q_\infty = 0.676 * T^2 - 236.9 * T + 27634$

4.1.1.2 For Solid Model 1 (n=2)

Table 4.4 Calculations of Solid Phase Model Development for First Order, (PMMA-EGDM)

$Q = \dfrac{k_2 Q_\infty^2 t}{1 + k_2 Q_\infty t}$							
Temp.	Time	Q_{exp}	Q_∞	k_2	SSE	Q_{model}	R^2 (Qmodel:Qexp)
60°C	0	0	0.7311	0.6156	0.1198	0.0000	0.649
	2	0.38				0.3463	
	4	0.47				0.4700	
	6	0.19				0.5335	
	8	0.56				0.5722	
	10	0.78				0.5982	
	12	0.64				0.6169	
70°C	0	0	1.1469	0.3116	0.1180	0.0000	0.859
	2	0.49				0.4780	
	4	0.34				0.6748	
	6	0.71				0.7821	
	8	0.87				0.8497	
	10	0.91				0.8961	
	12	0.99				0.9300	
80°C	0	0	1.3429	0.2421	0.0346	0.0000	0.966
	2	0.58				0.5292	
	4	0.69				0.7592	
	6	0.83				0.8878	
	8	0.97				0.9700	
	10	1.18				1.0270	
	12	1.09				1.0689	
90°C	0	0	2.5048	0.1441	0.1270	0.0000	0.967
	2	0.76				1.0503	
	4	1.48				1.4800	
	6	1.77				1.7137	
	8	1.90				1.8606	
	10	1.96				1.9615	
	12	1.84				2.0351	

Table 4.5 Calculated Data for estimation of k_o and E_a

$k_1=k_0\exp(-E_a/RT)$, where R=82.05746 cm^3-atm-k^{-1}-mol^{-1}					
Temp (K)	k_1	$k_0\exp(-E_a/RT)$	SSE	k_0	E_a
333	0.0205	0.1443			
343	0.3136	0.3116	0.1253	0.3114	-15.1154
353	0.0760	0.3116			
363	0.1441	0.3116			

4.1.1.2.1 Regression Analysis

333K

y = 0.6562x + 0.165
R^2 = 0.6492

Q, Model
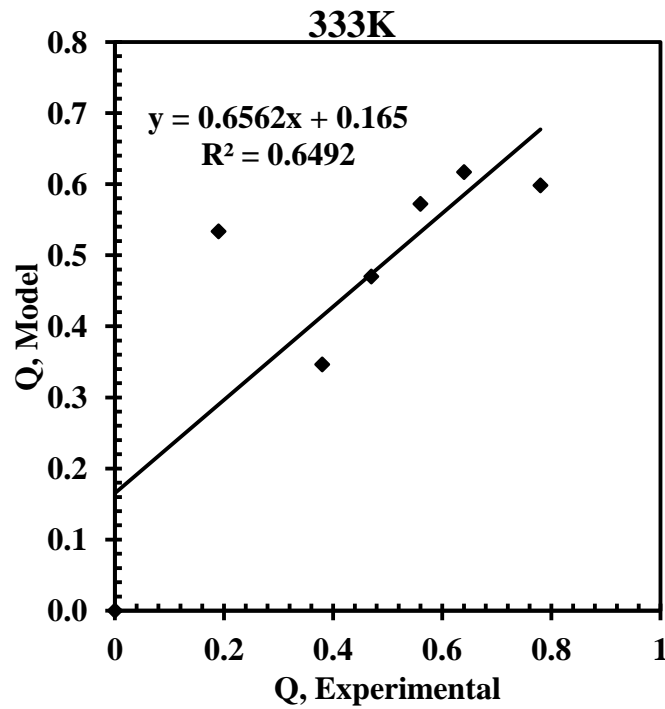
Q, Experimental

Figure 4.10 A curve between model and experimental value at 333 K

343K

y = 0.8499x + 0.1354
R² = 0.8591
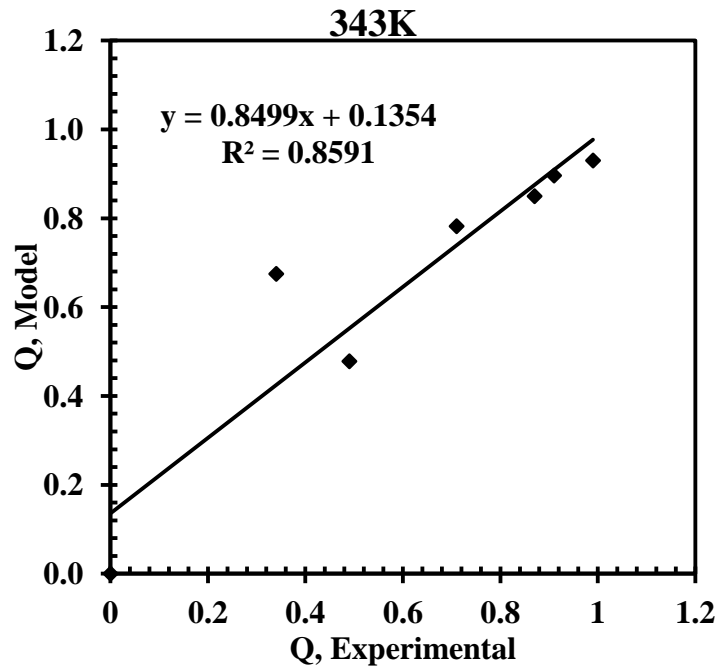
Figure 4.11 A curve between model and experimental value at 343 K

353K

y = 0.9341x + 0.0363
R² = 0.9661
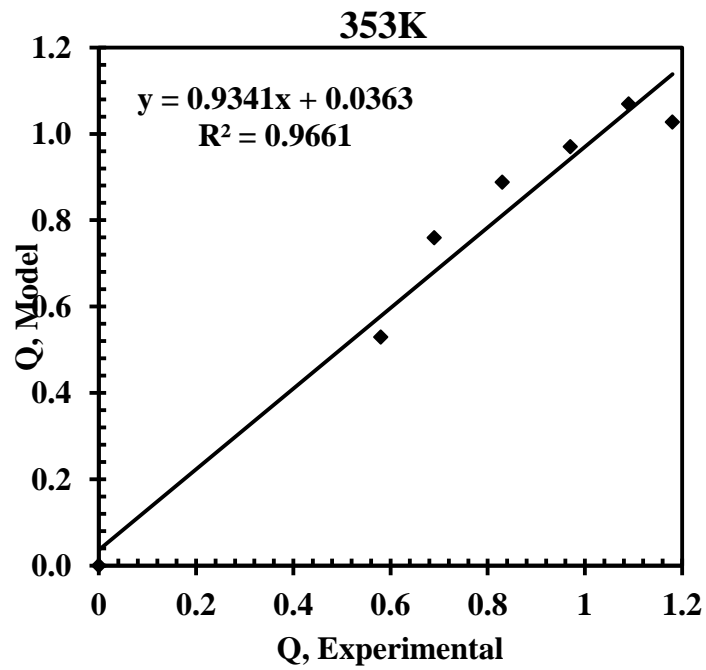
Figure 4.12 A curve between model and experimental value at 353 K
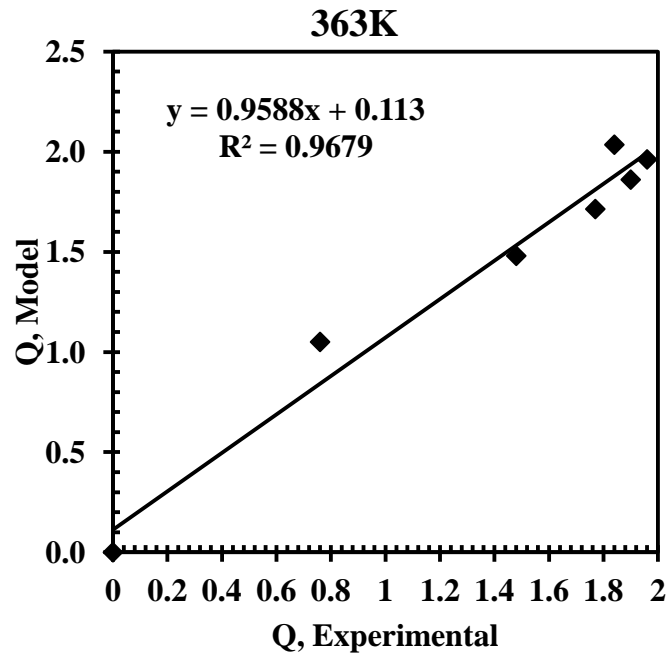
Figure 4.13 A curve between model and experimental value at 363 K

4.1.1.2.2 Comparison Between Q$_{model}$ and Q$_{experimental}$ -
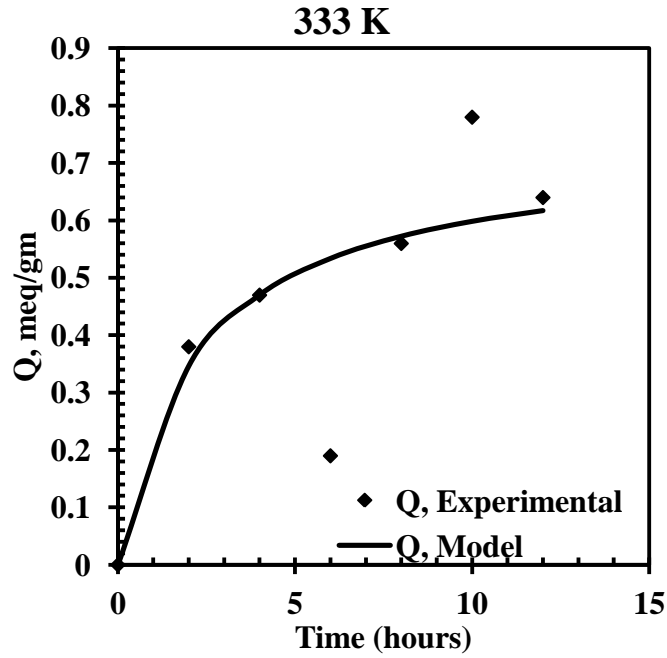
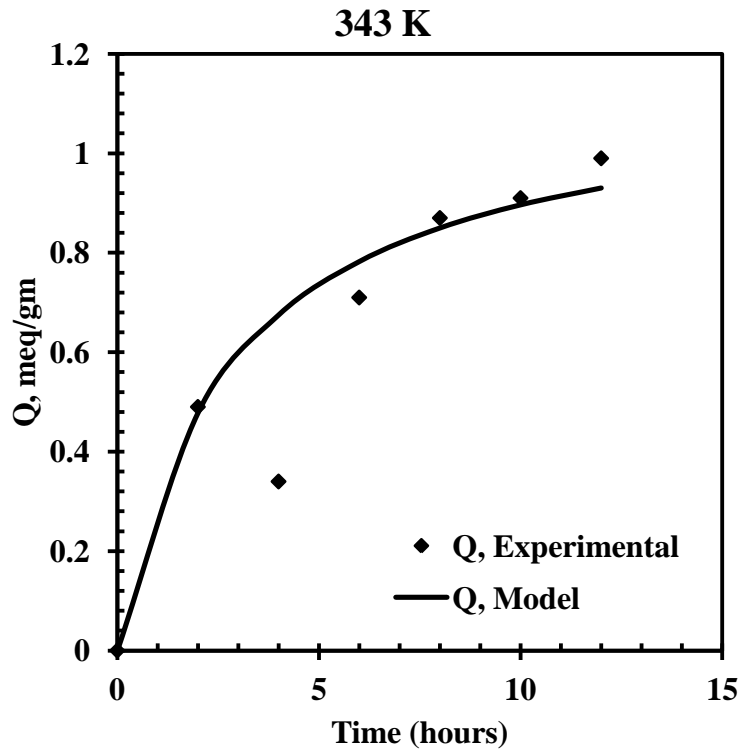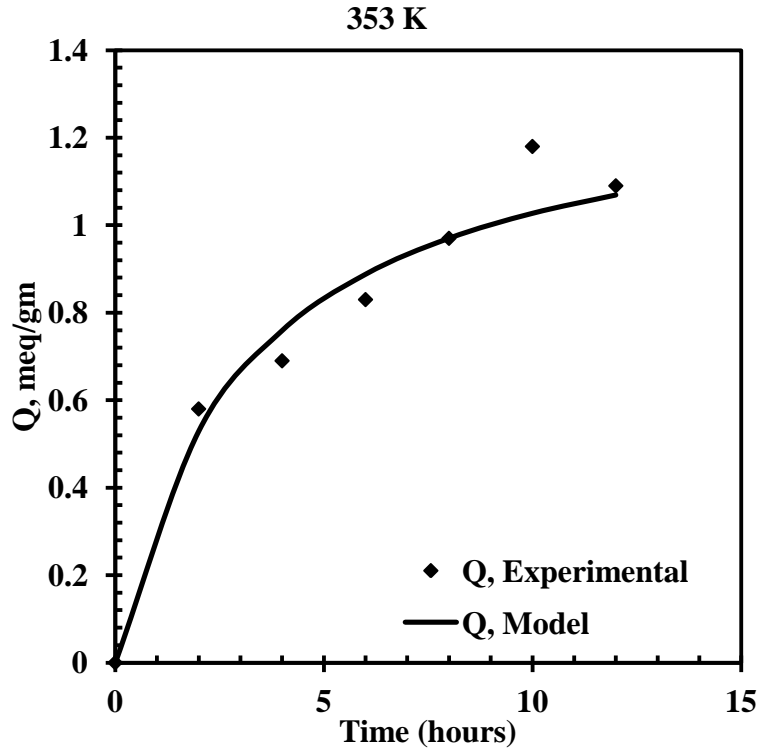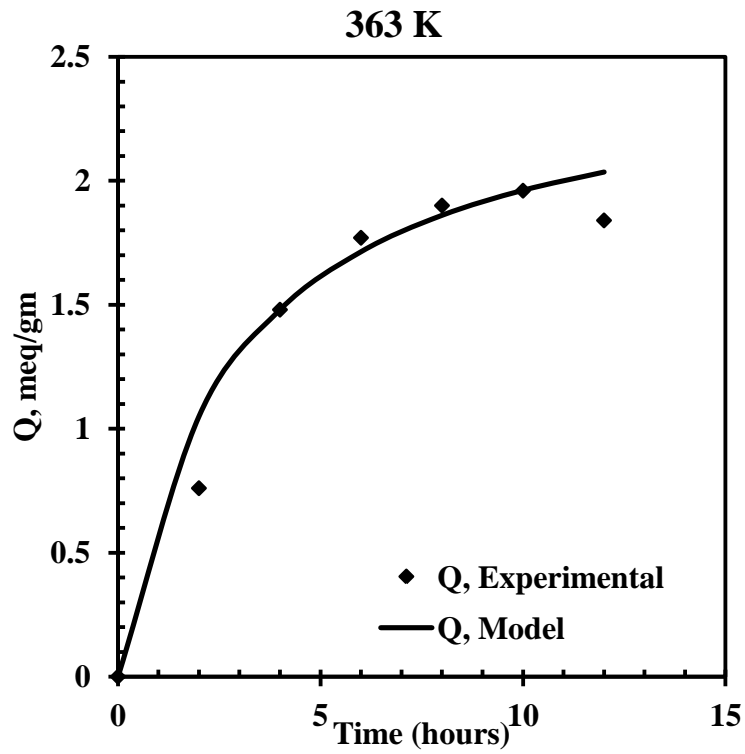**Figure 4.14 A curve between model and experimental value at 333 K**

Figure 4.15 A curve between model and experimental value at 343 K

Figure 4.16 A curve between model and experimental value at 353 K

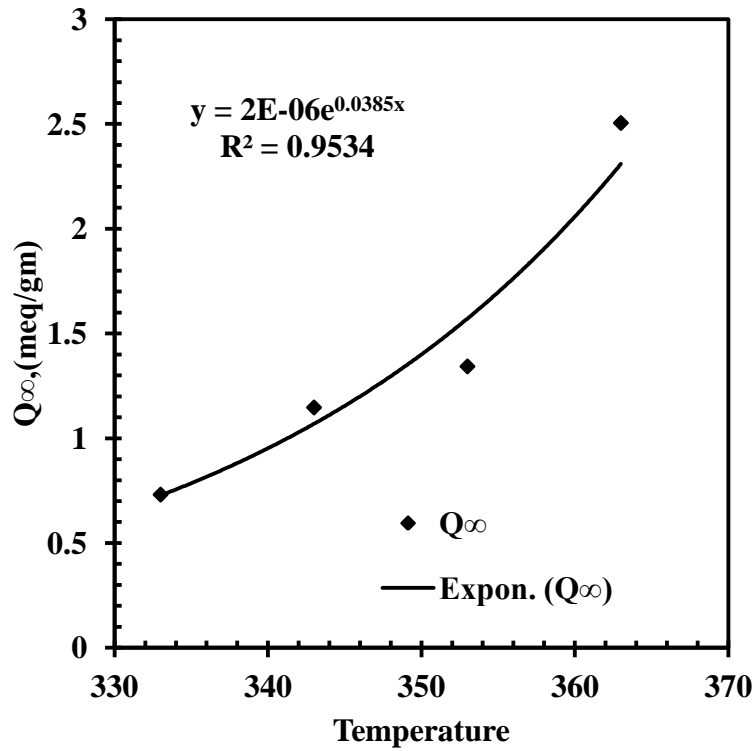**Figure 4.17 A curve between model and experimental value at 363 K**

Figure 4.18 A Curve between Asymptotic Value and Temperature

For Solid Model 2 (n=2)

$$Q = \frac{k_2 Q_\infty^2 t}{1 + k_2 Q_\infty t}$$

Best fit rate constant

$$k_2 = 0.3114 \exp\left(\frac{0.1842}{T}\right)$$

where, $Q_\infty = 2*10^{-6} \exp(0.038*T)$

4.2 Solid Phase Model Development For Aminated PS-EGDM Resin :

For the solid phase model development for PS-EGDM resin, firstly the data is taken from the PhD thesis of Mr. Gagnesh Sharma, Development of Surface modified macroporous PMMA-DVB and PS-EGDM based ion exchangers (2012) , this thesis contains the results of experiment of modification of PS-EGDM resin. In this paper different value of the exchange capacity of modified PS-EGDM resin at different temperature and different time interval is given. For the preparation of the model equation firstly the order of the equation assumes and after that model is developed. Here sum of least square term is used which gives the information about the best fit of model function to a data set. For the development of the model tangent estimation method, newton method and forward derivation method is used and the solver set to the given different parameter which is given below.

Maximum Time: 100 seconds

Iterations: 100

Precision: 0.000001

Tolerance: 5 %

Convergence: 0.0001

Table 4.6 Ion Exchange Capacity Q (meq/gm) of Aminated PS-EGDM Resin at different Temperature and Time

Time (hours)	Q (meq/gm)							
	$60^{o}C$	$70^{o}C$	$80^{o}C$	$90^{o}C$	$100^{o}C$	$110^{o}C$	$120^{o}C$	$130^{o}C$
0	0	0	0	0	0	0	0	0
3	0.74	0.88	1.11	1.54	1.74	1.88	1.84	1.65
4	0.96	1.18	1.37	1.76	2.03	2.32	2.24	1.92
5	1.51	1.73	1.89	2.12	2.52	2.68	2.57	2.22
6	2.02	2.24	2.4	2.54	3.05	3.26	3.13	2.64
7	2.18	2.42	2.43	2.8	3.06	3.5	3.31	2.94
8	1.97	2.36	2.46	2.58	3	3.2	3.03	2.86
9	1.83	1.89	2.07	2.43	2.75	3.17	3	2.49

4.2.1 Solid Phase Kinetic Studies for exchanger capacity PS-EGDM Resin, Q vs t data
4.2.1.1 For Solid Model 1 (n=1)
Table 4.7 Calculations of Solid Phase Model Development for First Order,(PS-EGDM)

$-\ln\left(1-\dfrac{Q}{Q_\infty}\right)=k_1 t$						
Temp.	Time	Q_{exp}	Q_∞	k_1	SSE	Q_{model}	R^2 (Qmodel:Qexp)
60°C	0	0	2.6	0.1830	0.769	0.000	0.871
	3	0.74				1.261	
	4	0.96				1.527	
	5	1.51				1.740	
	6	2.02				1.911	
	7	2.18				2.048	
	8	1.97				2.157	
	9	1.83				2.245	
70°C	0	0	2.9	0.1862	0.888	0.000	0.870
	3	0.88				1.407	
	4	1.18				1.703	
	5	1.73				1.941	
	6	2.24				2.131	
	7	2.42				2.284	
	8	2.36				2.406	
	9	1.89				2.504	
80°C	0	0	2.9	0.2104	0.883	0.000	0.915
	3	1.11				1.407	
	4	1.37				1.703	
	5	1.89				1.941	
	6	2.4				2.131	
	7	2.43				2.284	
	8	2.46				2.406	
	9	2.07				2.504	
90°C	0	0	3.1	0.2352	0.927	0.000	0.957
	3	1.54				1.504	
	4	1.76				1.821	
	5	2.12				2.075	
	6	2.54				2.278	
	7	2.8				2.441	
	8	2.58				2.572	
	9	2.43				2.677	

$-\ln\left(1 - \dfrac{Q}{Q_\infty}\right) = k_1 t$

Temp.	Time	Q_{exp}	Q_∞	k_1	SSE	Q_{model}	R^2 (Qmodel:Qexp)
100°C	0	0	3.5	0.2434	0.925	0.0000	0.953
	3	1.74				1.6981	
	4	2.03				2.0558	
	5	2.52				2.3425	
	6	3.05				2.5723	
	7	3.06				2.7565	
	8	3				2.9041	
	9	2.75				3.0224	
110°C	0	0	3.9	0.2393	0.775	0.0000	0.965
	3	1.88				1.8921	
	4	2.32				2.2908	
	5	2.68				2.6102	
	6	3.26				2.8663	
	7	3.5				3.0715	
	8	3.2				3.2360	
	9	3.17				3.3678	
120°C	0	0	3.7	0.2405	0.802	0.0000	0.963
	3	1.84				1.7951	
	4	2.24				2.1733	
	5	2.57				2.4764	
	6	3.13				2.7193	
	7	3.31				2.9140	
	8	3.03				3.0700	
	9	3				3.1951	
130°C	0	0	3.3	0.2324	0.894	0.0000	0.954
	3	1.65				1.6010	
	4	1.92				1.9383	
	5	2.22				2.2087	
	6	2.64				2.4253	
	7	2.94				2.5990	
	8	2.86				2.7381	
	9	2.49				2.8497	

Table 4.8 Calculated Data for estimation of k_o and E_a

Temp (K)	k_2	$k_0\exp(-E_a/RT)$	SSE	k_0	E_a
$k_2=k_0\exp(-E_a/RT)$, where R=82.05746 cm^3-atm-k^{-1}-mol^{-1}					
333	0.1830	0.2213			
343	0.1862	0.2213			
353	0.2104	0.2213			
363	0.2352	0.2213			
373	0.2434	0.2213	0.0043	0.2213	1.0000
383	0.2393	0.2213			
393	0.2405	0.2213			
403	0.2324	0.2213			

4.2.1.1.1 Regression Analysis:
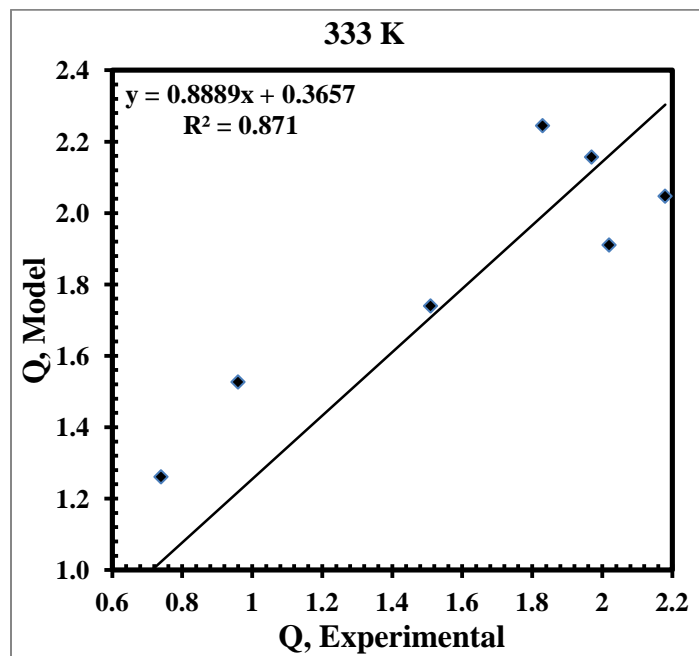
Figure 4.19 A curve between model and experimental value at 333 K
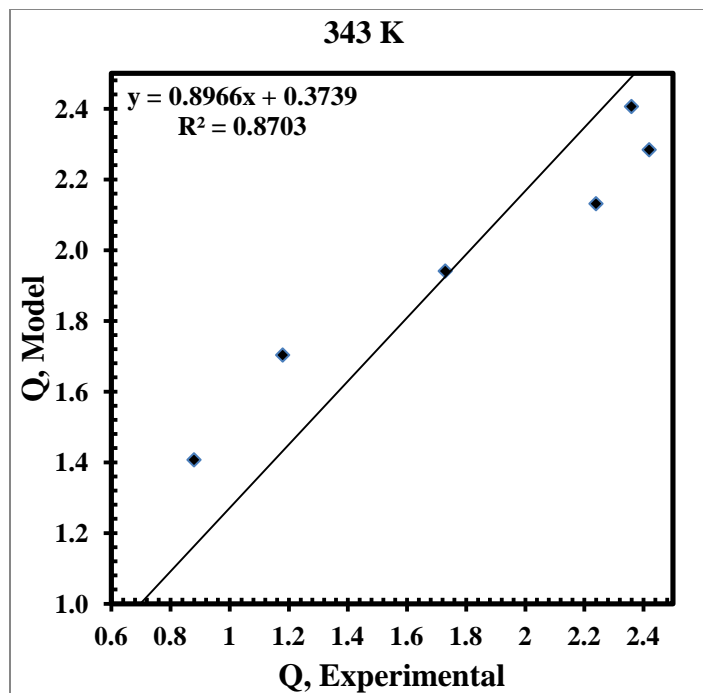
Figure 4.20 A curve between model and experimental value at 343 K
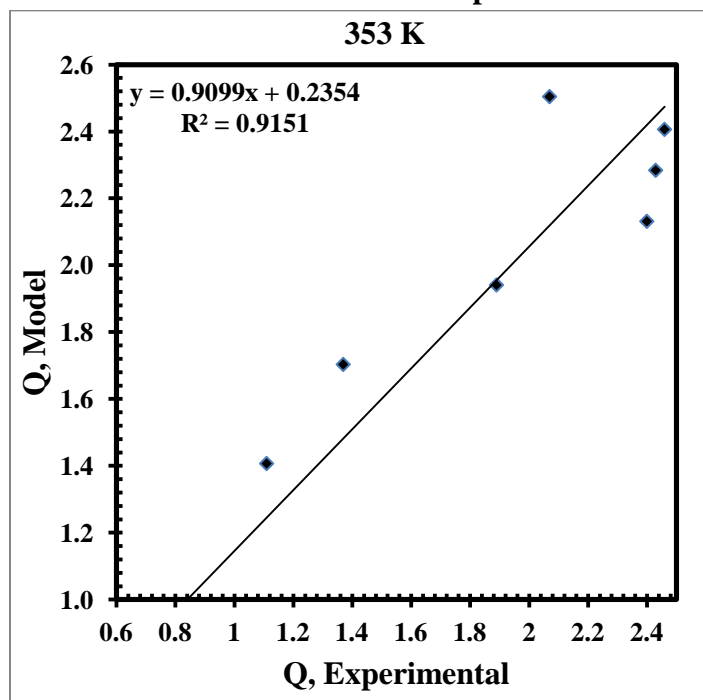
Figure 4.21 A curve between model and experimental value at 353 K
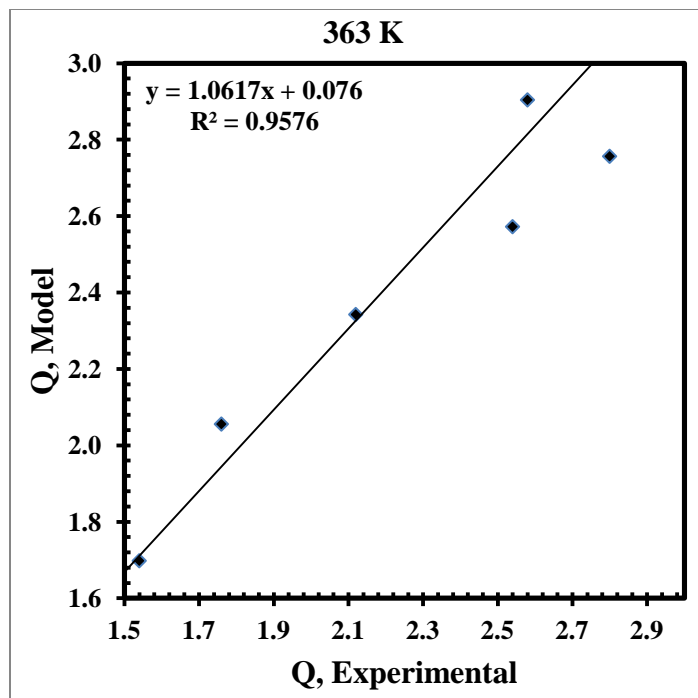
Figure 4.22 A curve between model and experimental value at 363 K
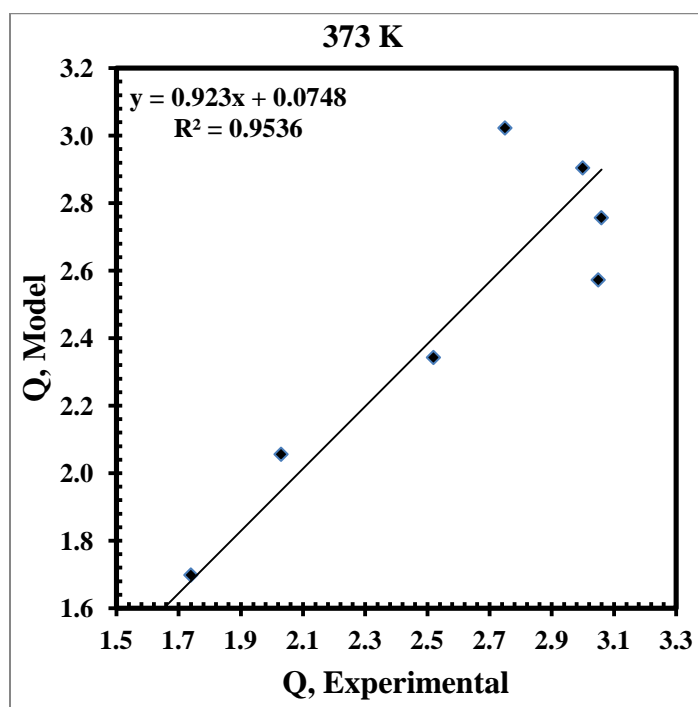
Figure 4.23 A curve between model and experimental value at 373 K
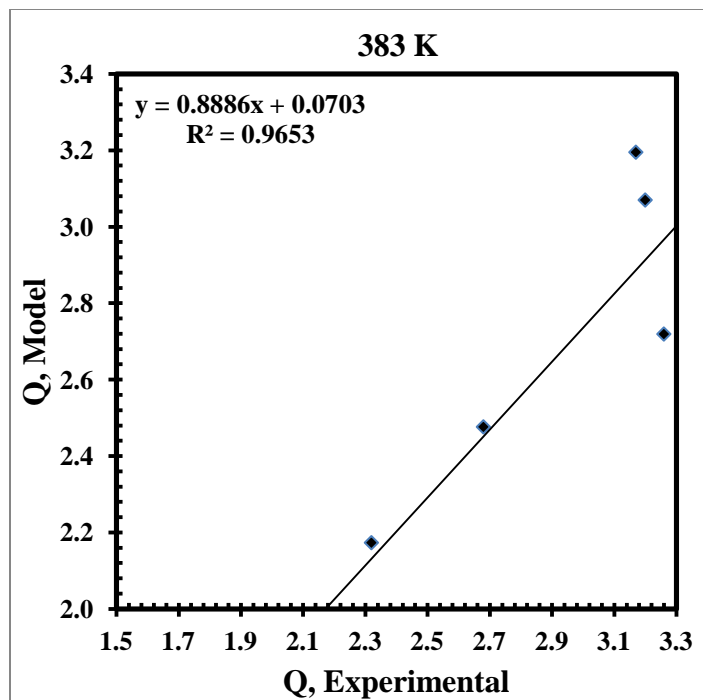
Figure 4.24 A curve between model and experimental value at 383 K
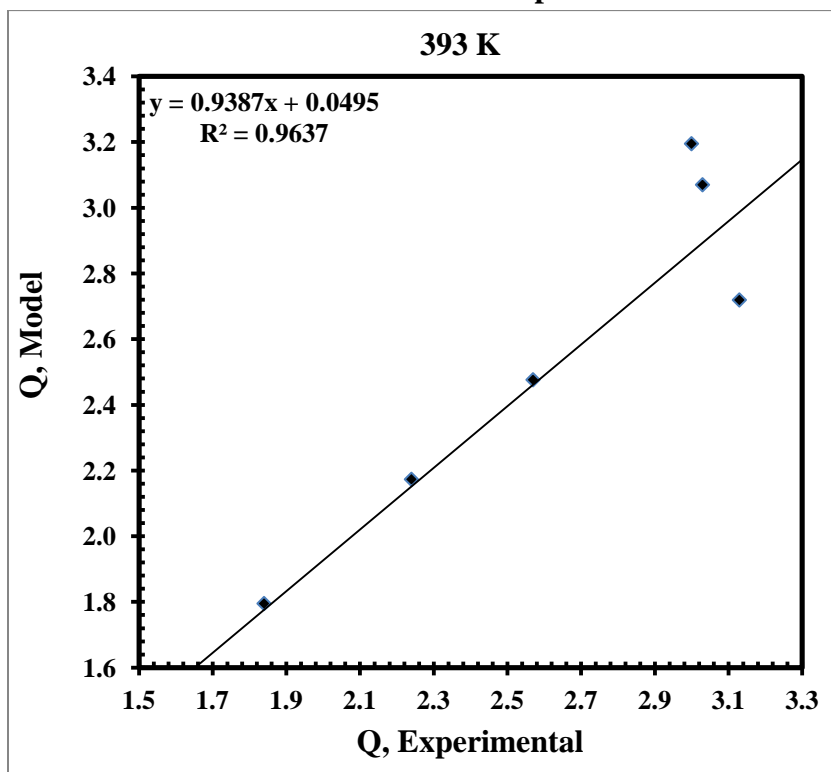
Figure 4.25 A curve between model and experimental value at 393 K

403 K

$y = 0.9466x + 0.0666$

$R^2 = 0.9541$

Q, Model
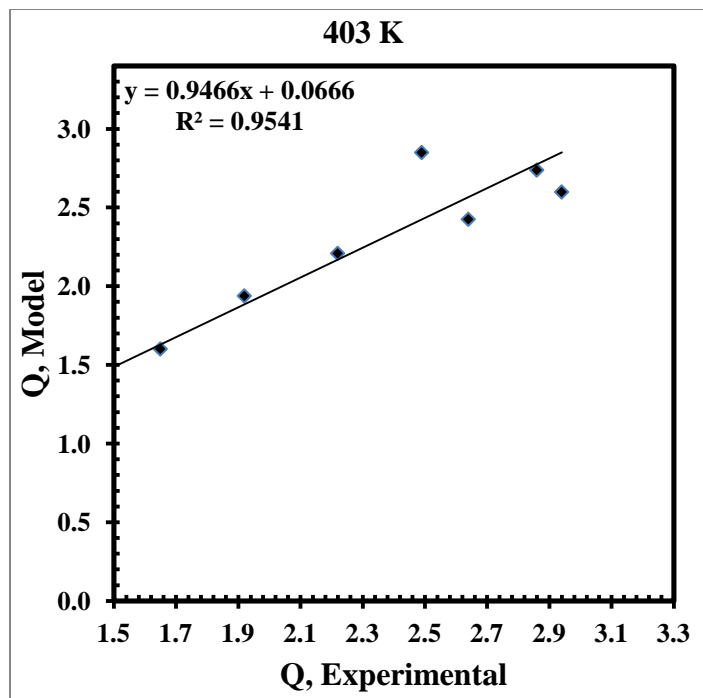
Q, Experimental

Figure 4.26 A curve between model and experimental value at 393 K

4.2.1.1.2 Comparison between Q_{model} and $Q_{experimental}$:
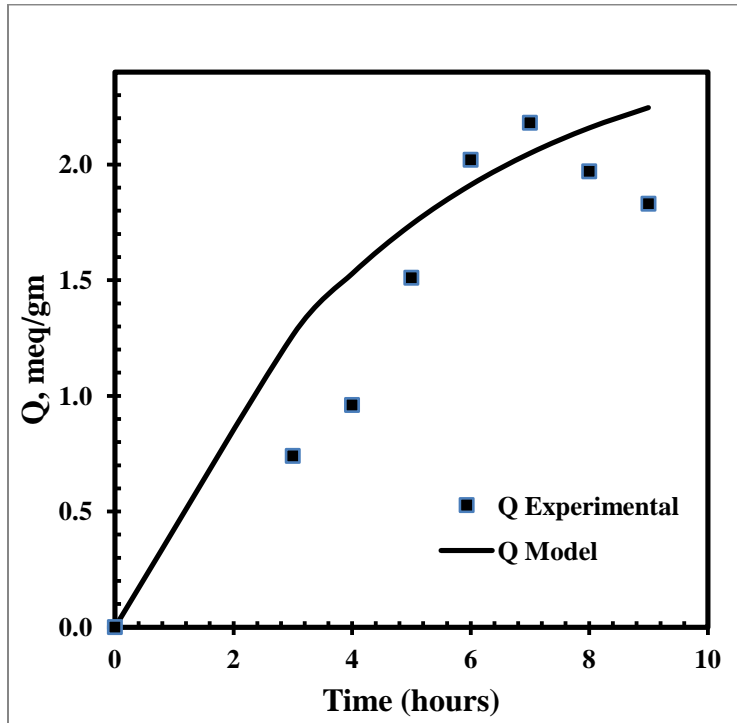
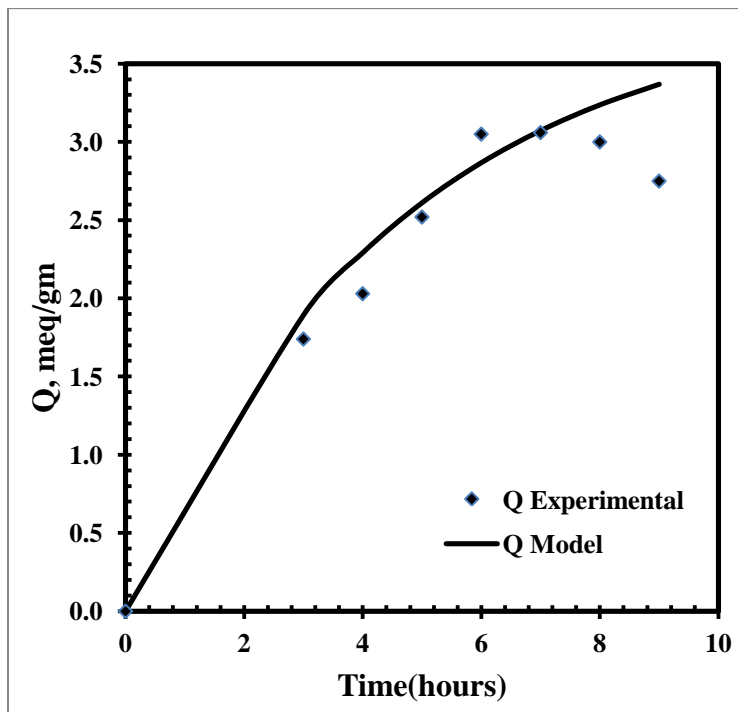**Figure 4.27 A curve between Q_{model} and $Q_{experimental}$ w.r.t Time at 333 K**
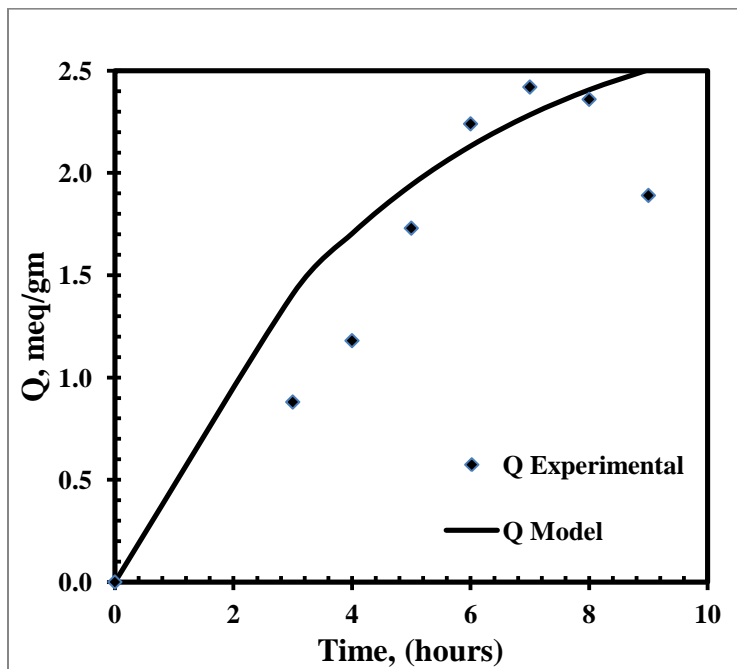
Figure 4.28 A curve between Q_{model} and $Q_{experimental}$ w.r.t Time at 343 K
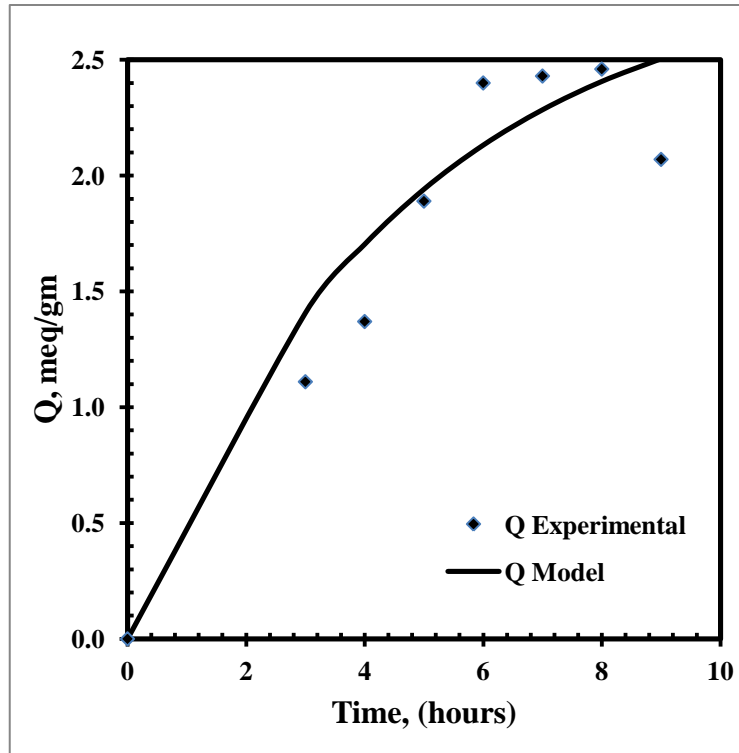
Figure 4.29 A curve between Q_{model} and $Q_{experimental}$ w.r.t Time at 353 K
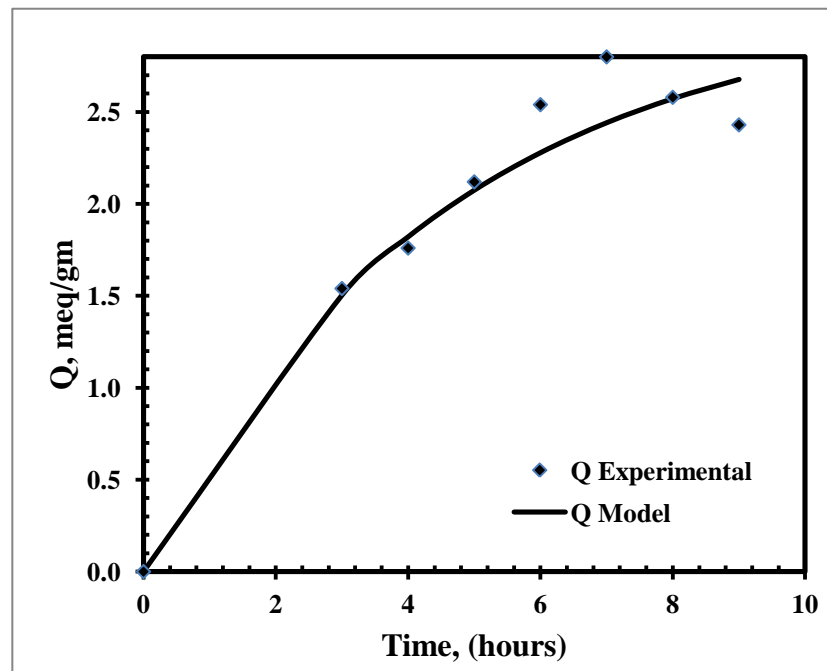
Figure 4.30 A curve between Q_{model} and $Q_{experimental}$ w.r.t Time at 363 K
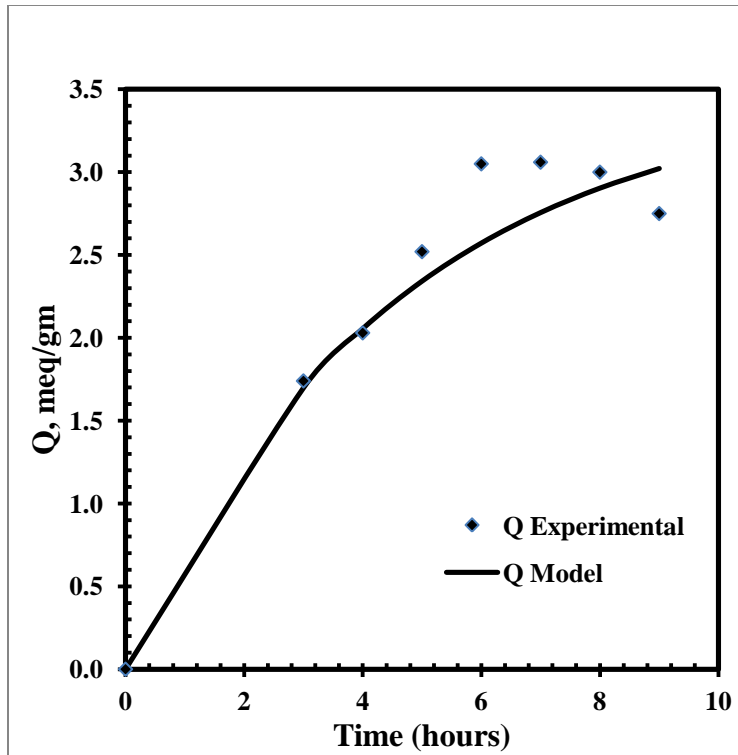
Figure 4.31 A curve between Q_{model} and $Q_{experimental}$ w.r.t Time at 373 K

Figure 4.32 A curve between Q_{model} and $Q_{experimental}$ w.r.t Time at 383 K

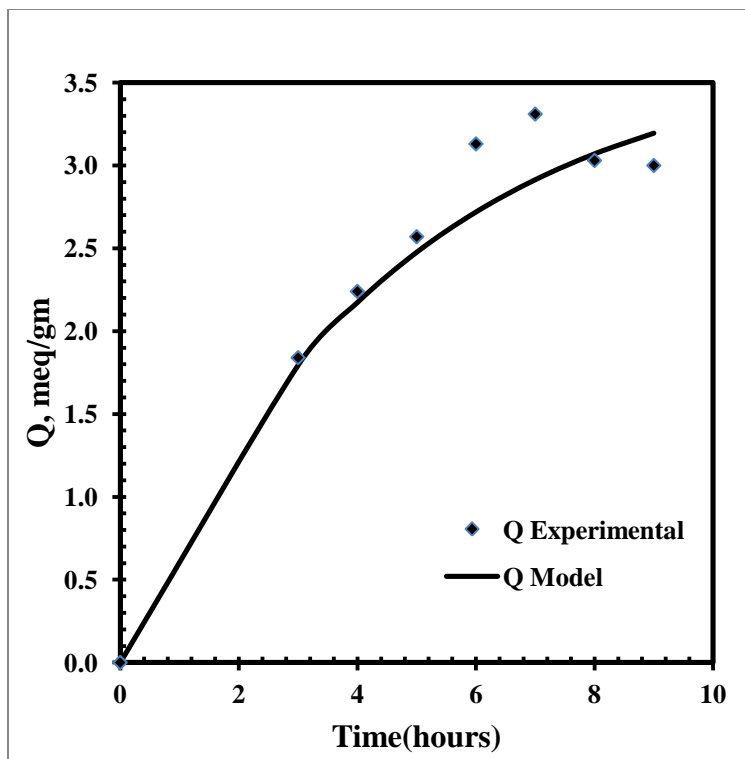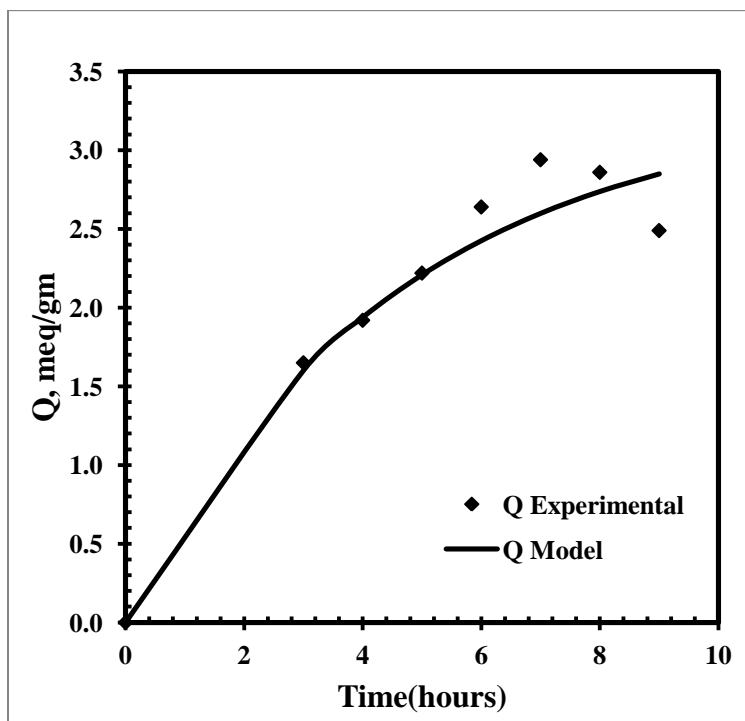**Figure 4.33 A curve between Q_{model} and $Q_{experimental}$ w.r.t Time at 393 K**

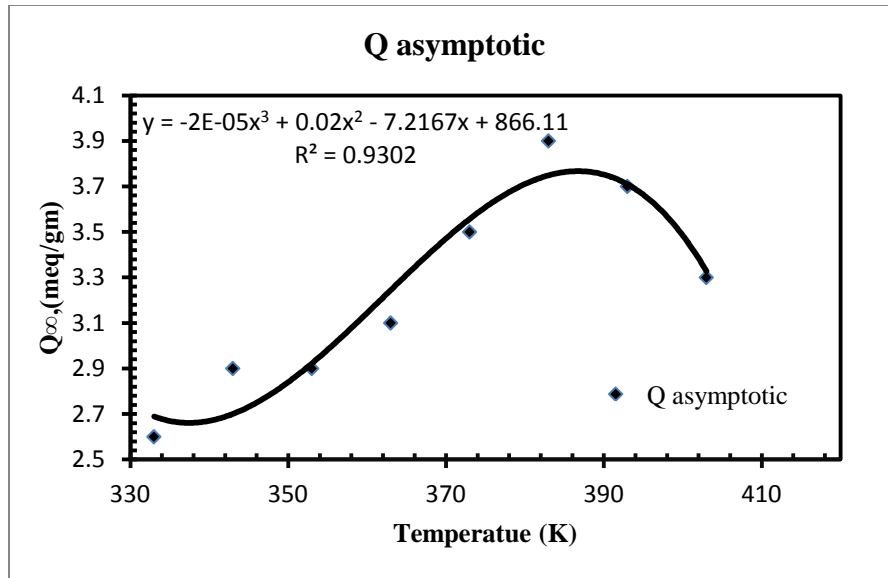**Figure 4.34 A curve between Q_{model} and $Q_{experimental}$ w.r.t Time at 403 K**

Figure 4.35 A curve between Q$_{asymptotic}$ and Temperature (K)

For Solid Model (n=1)

$$-\ln\left(1-\frac{Q}{Q_\infty}\right)=k_1 t$$

Best fit rate Constant:

$$k_1=0.2213\exp(-0.0122/T)$$

where $Q_\infty= -2E\text{-}05*T^3 + 0.02*T^2 - 7.216*T + 866.1$

4.2.1.2 For Solid Model 2 (n=2)

Table 4.9 Calculations of Solid Phase Model Development for First Order, (PS-EGDM)

$Q = \dfrac{k_2 Q_\infty^2 t}{1 + k_2 Q_\infty t}$							
Temp.	Time	Q_{exp}	Q_∞	k_2	SSE	Q_{model}	R^2 (Qmodel:Qexp)
60°C	0	0	5.2	0.01517	0.0965	0.000	0.882
	3	0.74				0.935	
	4	0.96				1.177	
	5	1.51				1.392	
	6	2.02				1.586	
	7	2.18				1.761	
	8	1.97				1.919	
	9	1.83				2.064	
70°C	0	0	6	0.01259	0.0994	0.000	0.870
	3	0.88				1.222	
	4	1.18				1.526	
	5	1.73				1.794	
	6	2.24				2.031	
	7	2.42				2.243	
	8	2.36				2.433	
	9	1.89				2.605	
80°C	0	0	6	0.01383	0.0917	0.000	0.902
	3	1.11				1.233	
	4	1.37				1.538	
	5	1.89				1.807	
	6	2.4				2.045	
	7	2.43				2.258	
	8	2.46				2.449	
	9	2.07				2.621	
90°C	0	0	6.2	0.01533	0.0914	0.000	0.929
	3	1.54				1.319	
	4	1.76				1.642	
	5	2.12				1.925	
	6	2.54				2.175	
	7	2.8				2.397	
	8	2.58				2.596	

				$Q = \dfrac{k_2 Q_\infty^2 t}{1 + k_2 Q_\infty t}$			
Temp.	Time	Q_{exp}	Q_∞	k_2	SSE	Q_{model}	R^2 (Qmodel:Qexp)
100°C	0	0	7.2	0.01294	0.0953	0.000	0.929
	3	1.74				1.733	
	4	2.03				2.139	
	5	2.52				2.489	
	6	3.05				2.794	
	7	3.06				3.062	
	8	3				3.299	
	9	2.75				3.510	
110°C	0	0	7.2	0.01863	0.0953	0.000	0.945
	3	1.88				1.747	
	4	2.32				2.156	
	5	2.68				2.507	
	6	3.26				2.812	
	7	3.5				3.081	
	8	3.2				3.318	
	9	3.17				3.529	
120°C	0	0	7.2	0.01410	0.0981	0.000	0.941
	3	1.84				1.762	
	4	2.24				2.172	
	5	2.57				2.524	
	6	3.13				2.831	
	7	3.31				3.099	
	8	3.03				3.337	
	9	3				3.549	
130°C	0	0	6.6	0.01427	0.0946	0.000	0.929
	3	1.65				1.524	
	4	1.92				1.886	
	5	2.22				2.201	
	6	2.64				2.476	
	7	2.94				2.718	
	8	2.86				2.934	
	9	2.49				3.127	

Table 4.10 Calculated Data for estimation of k_o and E_a

$k_2=k_0\exp(-E_a/RT)$, where R=82.05746 cm^3-atm-k^{-1}-mol^{-1}					
Temp (K)	k_2	$k_0\exp(-E_a/RT)$	SSE	k_0	E_a
333	0.0152	0.0141			
343	0.0126	0.0142			
353	0.0138	0.0144			
363	0.0153	0.0145			
373	0.0129	0.0147	2.38E-05	0.00984	-0.0881
383	0.0186	0.0148			
393	0.0141	0.0150			
403	0.0143	0.0152			

4.2.1.2.1 Regression Analysis:

333 K

y = 0.8144x + 0.2131
R² = 0.8827
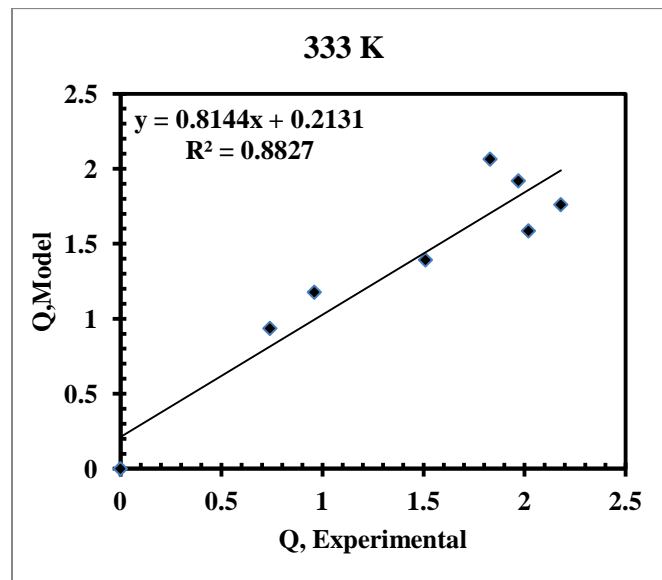
Figure 4.36 A curve between model and experimental value at 333 K
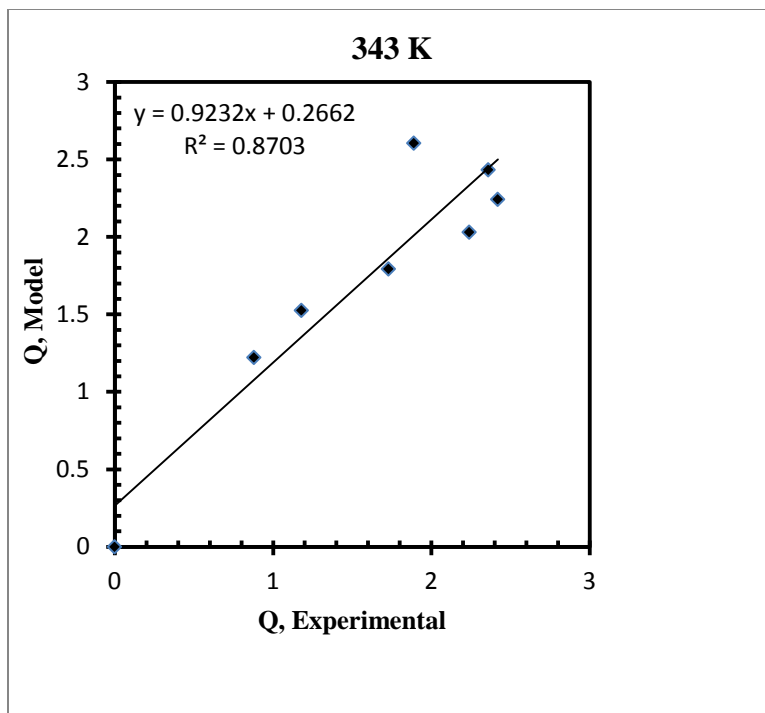
Figure 4.37 A curve between model and experimental value at 343 K
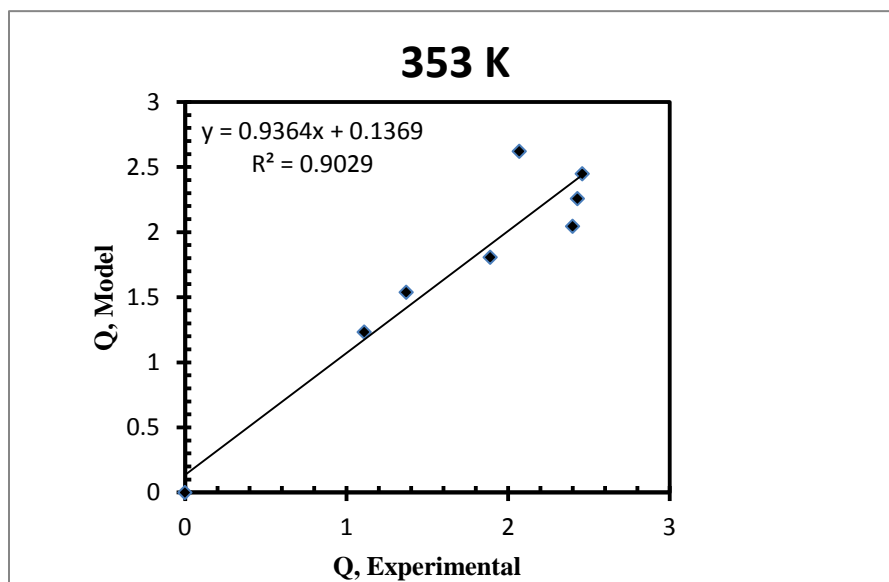
Figure 4.38 A curve between model and experimental value at 363 K
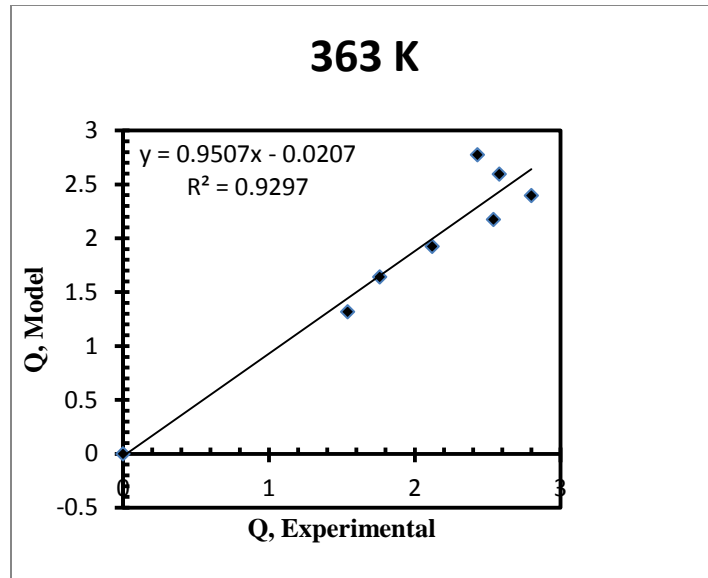
Figure 4.39 A curve between model and experimental value at 363 K
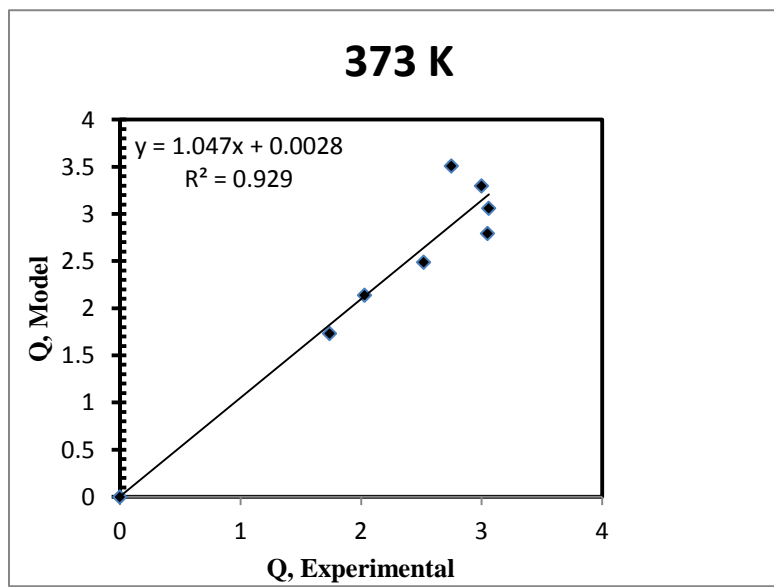
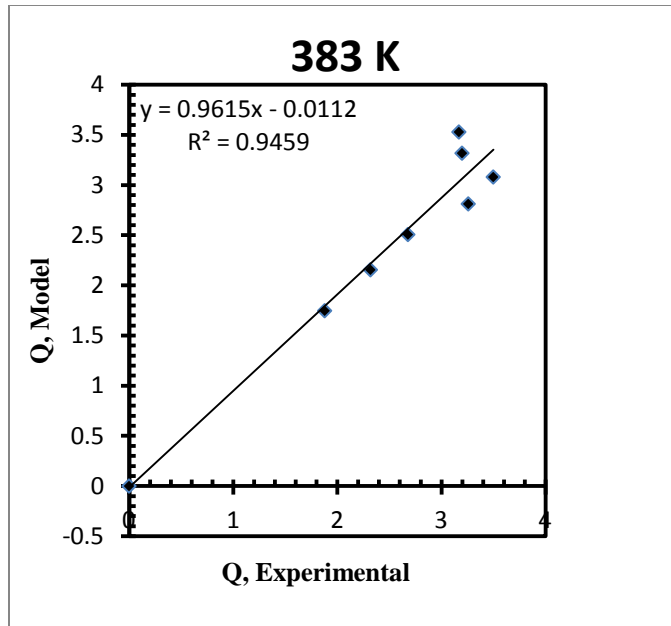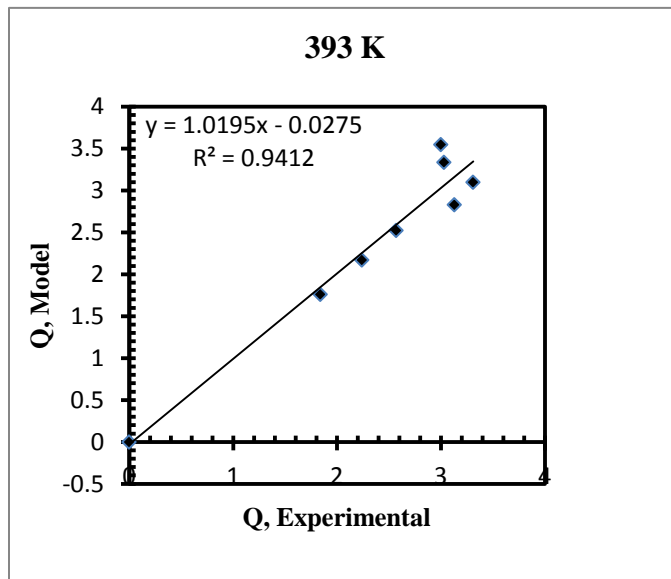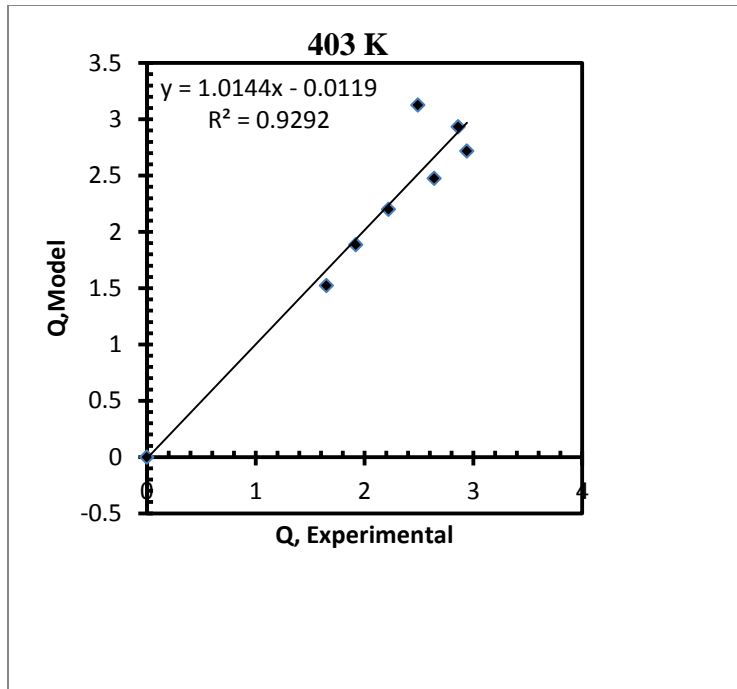**Figure 4.40 A curve between model and experimental value at 373 K**

383 K

y = 0.9615x - 0.0112
R² = 0.9459

Figure 4.41 A curve between model and experimental value at 383 K

393 K

y = 1.0195x - 0.0275
R² = 0.9412

Figure 4.42 A curve between model and experimental value at 393 K

Figure 4.43 A curve between model and experimental value at 403 K

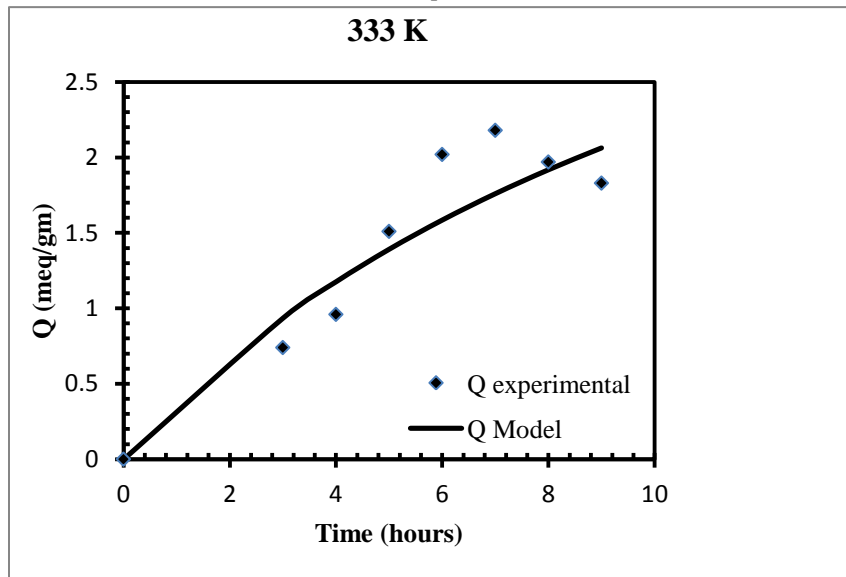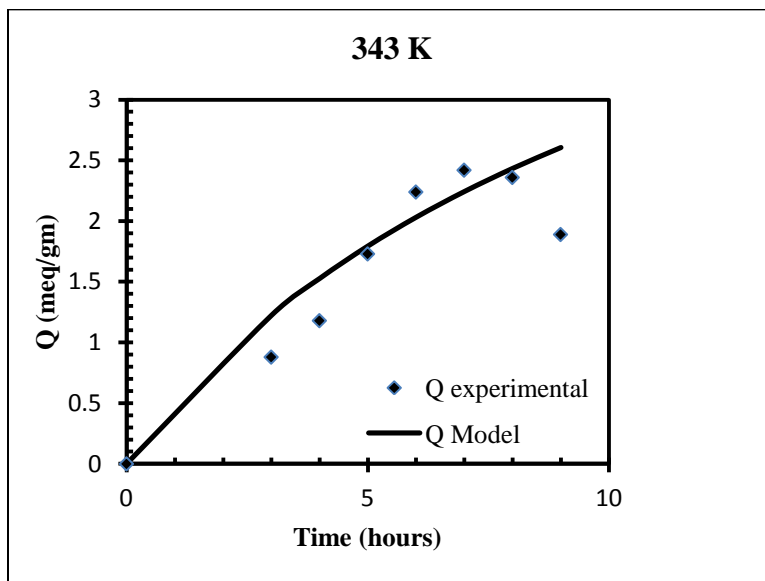**4.2.1.2.2 Comparison between Q_{Model} and $Q_{Experimental}$:**

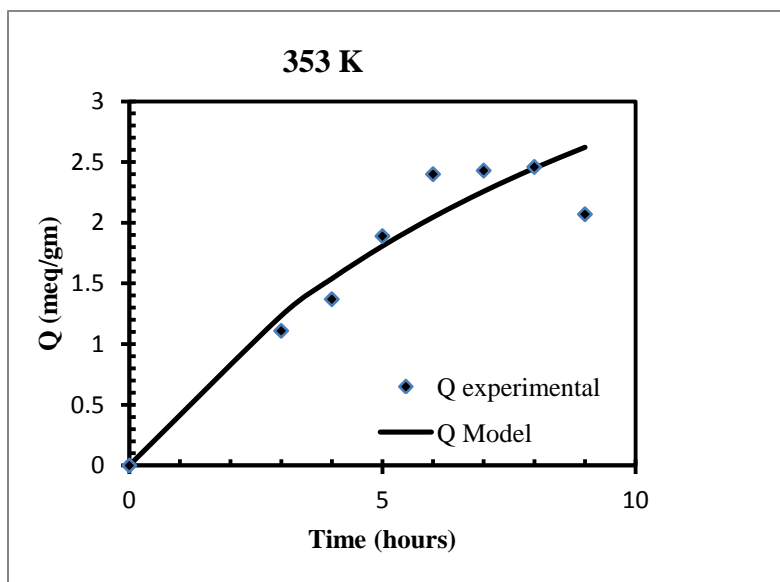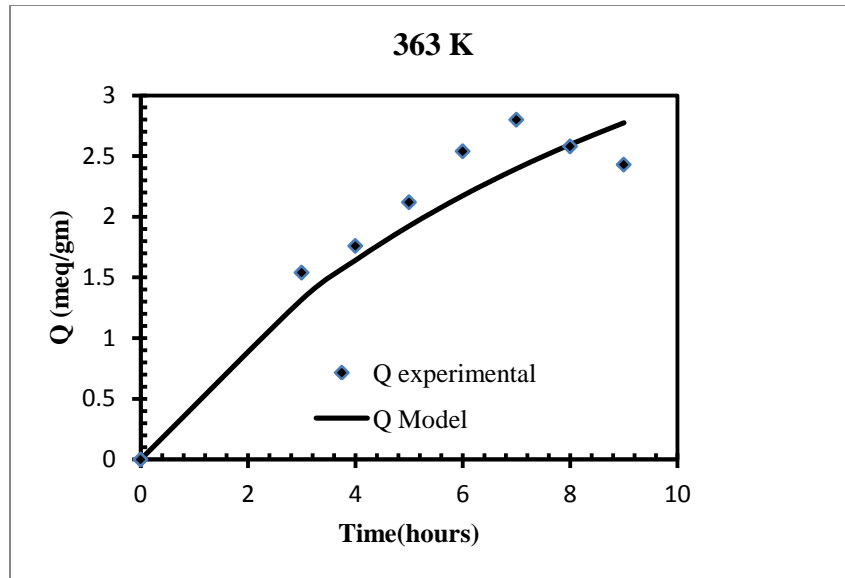**Figure 4.44 A curve between Q_{model} and $Q_{experimental}$ w.r.t Time at 333 K**

Figure 4.45 A curve between Q_model and Q_experimental w.r.t Time at 343 K

Figure 4.46 A curve between Q_model and Q_experimental w.r.t Time at 353 K

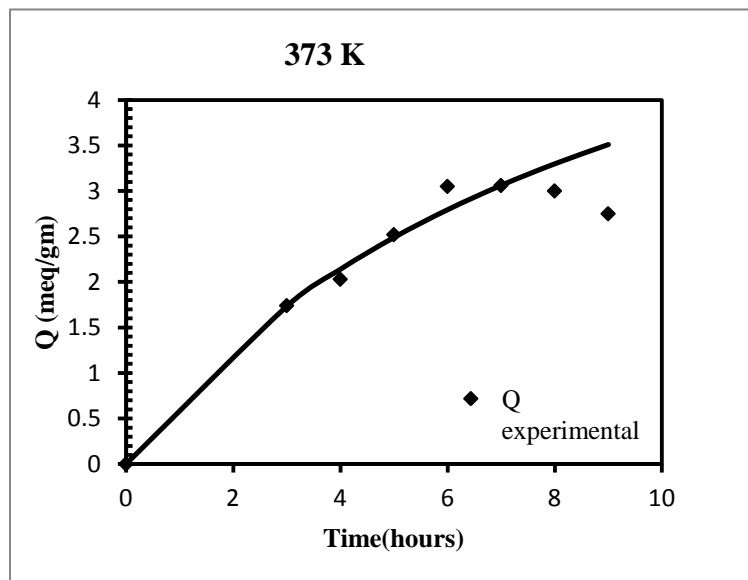**Figure 4.47 A curve between Q$_{model}$ and Q$_{experimental}$ w.r.t Time at 363 K**

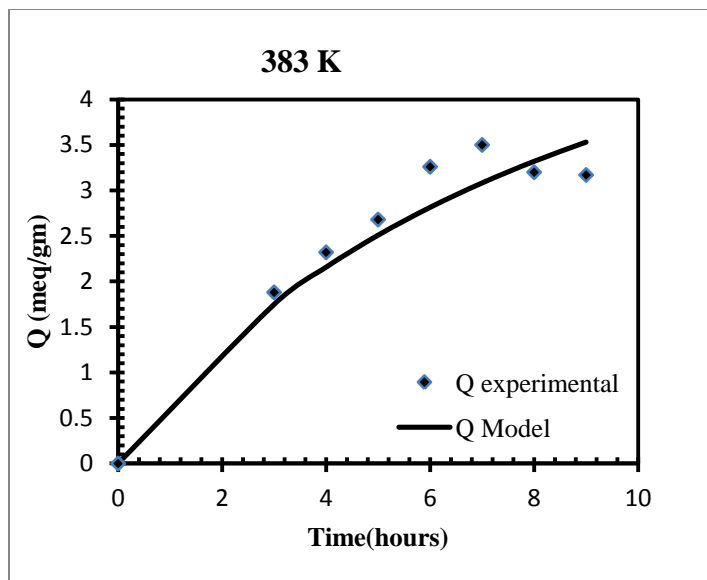**Figure 4.48 A curve between Q$_{model}$ and Q$_{experimental}$ w.r.t Time at 373 K**

Figure 4.49 A curve between Q$_{model}$ and Q$_{experimental}$ w.r.t Time at 383 K

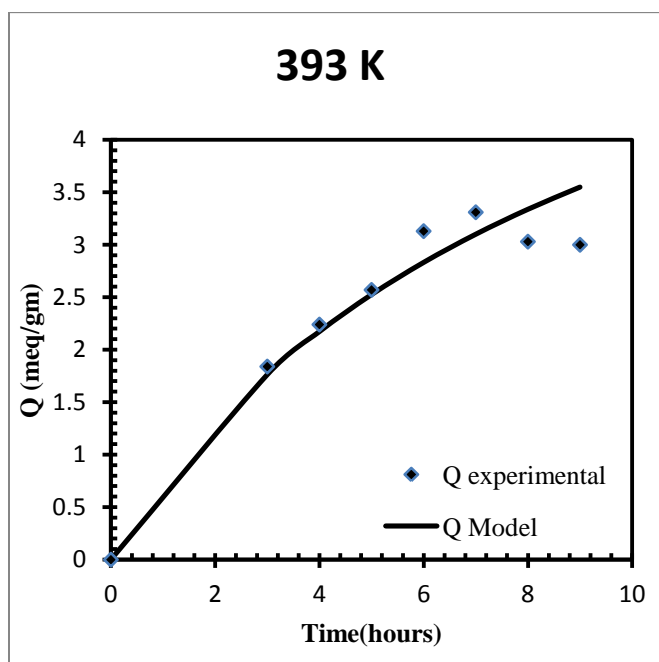**Figure 4.50 A curve between Q$_{model}$ and Q$_{experimental}$ w.r.t Time at 393 K**

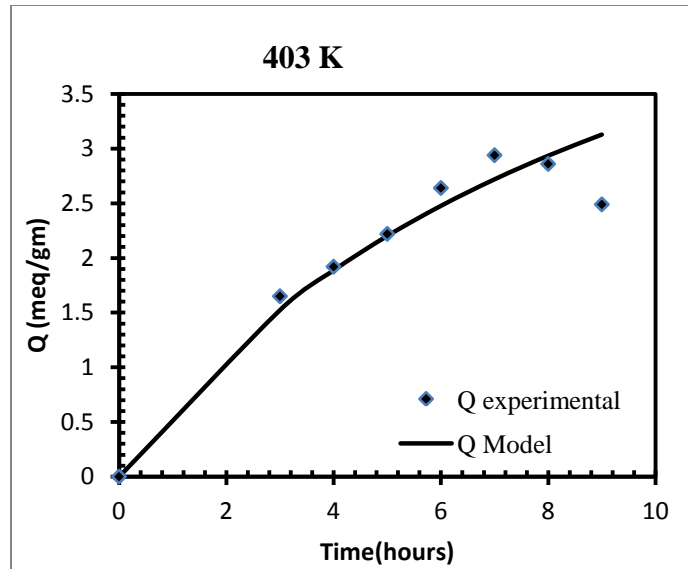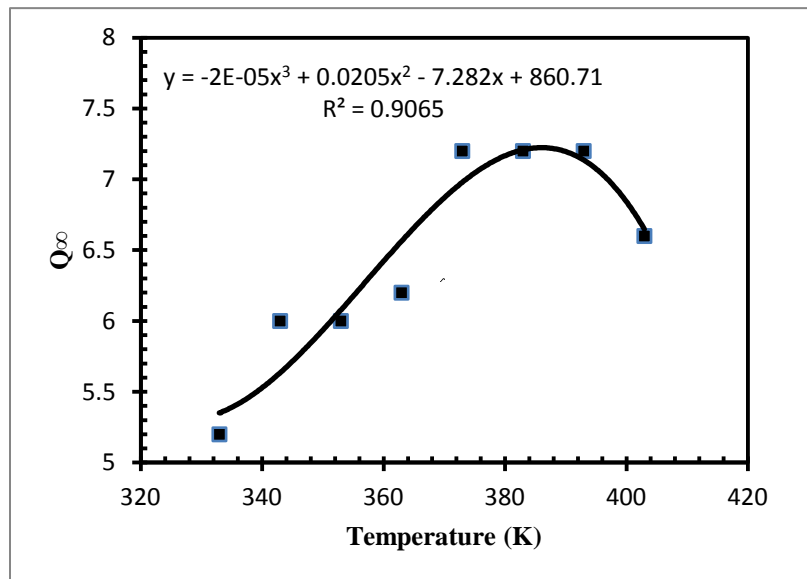**Figure 4.51 A curve between Q$_{model}$ and Q$_{experimental}$ w.r.t Time at 403 K**

Figure 4.52 A curve between Q$_{asymptotic}$ and Temperature (K)

For Solid Model (n=2)

$$Q = \frac{k_2 Q_\infty^2 t}{1 + k_2 Q_\infty t}$$

Best fit rate Constant:

k_2=0.00984exp(0.0011/T)

where Q_∞ = -2E-05*T^3 + 0.020*T^2 - 7.282*T + 860.7

CONCLUSION

In the present work effect of the temperature and time on the exchange capacity is studied from the research and a solid phase model for the determination of the rate constant is developed and through the model data and the experimental data is compared and this comparison between the given experimental and model data give the following conclusions:

- In the development of the model equation for the PMMA-EGDM resin and the first order of the reaction the model developed give the close result to the experimental data at the higher temperature , at the temperature near about 363 K the model give the better correlation factor than the lower temperature below 363 K.

- At the second order of the reaction of the PMMA-EGDM data the model developed give the better and close result to the temperature above 353 K and the curve developed through the model give the slight variation at the higher reaction time.

- For the developed model for PS-EGDM resin the first order model give the vary good or near result to the experimental data at the temperature above the 363 K and for the second order model PS-EGDM resin give the better result with respect to experimental data at the temperature above the 373 K.

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