

# Preparation and Characterization of Strong Polar Macro Porous Resin

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## Abstract

The macro porous adsorption resin produced in this experiment mainly uses dipole dichloride etc. as the material, a certain proportion of mixed solution composed of pyridine and 1, 4-dioxane as the composite oxidant. Then adding a certain proportion of mixed solution composed of cyclohexane and paraffin in the homogeneous solution of cellulose as the photogenic agent. As a result, these materials will polymerize, and generate the resin. Among these materials, the cellulose is polymeric monomer, dipole dichloride is cross linker, and they crosslink and polymerize each other, forming the porous skeletal structure of the macro porous adsorption resin, which is a kind of cross linked polymer consisting of ion exchange group. For the synthetic macro porous resin, using Fourier infrared spectrometer for pressed characterization, and scanning electron microscope (SEM) for resin pore-forming characterization, the result shows that the new macro porous resin has been synthesized. This paper taking ruin as adsorbate explores the adsorption property of the synthetic macro porous resin to glycoside material, including property of equilibrium adsorption, static adsorption and adsorption. Meanwhile the influence of different solvents on the resin adsorption property is testified. After a general comparison, we have found that the resin has the strongest adsorption property in ethanol solvent, while for adsorption, the best effect is reached when using water as the elegant. What's more, the adsorption data shows that the adsorption of ruin on the very resin conforms to the Freundlich isothermal adsorption equation.

**Keywords:** Cellulose, Photogenic agent, Macro porous resin

## 1. Introduction

The macro porous adsorption resin develops on the basis of ion exchange resin. In 1935, Adams and Holmes from British issued the Working Report on the Polycondensed Macromolecular Material made from Formaldehyde, Phenol and Aromatic Amine and Their Ion Exchange Property. This report stimulates a new line of ion exchange resin. In the 1950s, macro porous ion exchange resin was composed; this event is a landmark of the development of ion exchange resin. Besides, at the end of the 1950s, scientists synthesized macro porous adsorption exchange resin, which is a new type macro porous-structured organic nonionic macromolecular polymer without exchange group. It is also called macro lattice adsorption. With both adsorption and screening properties, this resin is a parting material with adsorption and screening properties. The macro porous adsorption resin has a stable physicochemical property, it is insoluble in acid, alkali and organic solvent, and has a good selectivity to organic matter; it is also characterized by immunity to mineral salt plasma and low molecular compound [Abrams, 1977].

In the end of the 1950s, Academician He Bungling in Nankeen University found macro porous resin when synthesizing porosity anion exchange resin. He found that in the process of suspension copolymerization of styrene and divinylbenzene, adding inert organic solvent or liner polymer photogenic agent in the co monomer, and then removing the photogenic agent after polyreaction, the porous polymer-- macro porous resin can be obtained. When the cross linking copolymerization is higher than 40%, the specific surface area of macro porous resin can be larger than 500-600m<sup>2</sup>/g, having good physical adsorption ability. Inspired by this, Pro. He found a new type adsorption parting material, which is macro porous adsorption resin. [Xijun, 1991; Rubaek, 1993; Galaffu, 2005; Dickert, 2000]

In 1962, Rohm & Hass of America announced that they have synthesized a macro porous reticulated adsorption resin with methyl methacrylate as the framework. After that, various kinds of synthetic adsorption resin of different properties sprinted out and came into wide use.

Early in the 1970s, the macro porous adsorption resin had been used in the extraction and separation of chemical

composition of Chinese medicinal herbs. Currently, macro porous adsorption resin is widely used in environmental protection, chemical engineering, medicine, food and other industrial fields; it has unique effect and prospect in the extraction of natural products and chemical composition of Chinese medicinal herbs, especially in water-soluble components.

However, there are many shortages to be improved in actual usage. For example: high organic residue, hard for pre-treatment, low strength, great disintegration in usage, short life, large scale of grain diameter, large differences in specific surface area and functional group among each batch within the same model produced in the same enterprise, and bad parting effect, bad reproducibility in traditional Chinese composition purification. At the same time, modern macromolecular functional material is synthesized from petrochemicals, leading to two difficulties: the first one is the predicament brought about by the exhaustion of raw materials day by day, and the second one is that all these materials are hard to degrade, which will do huge harm to human environment and production. To settle down the difficulties of raw material shortage and environment pollution, researchers diverted their attention to renewable resources. Cellulose is the most affluent renewable resources on earth, with favorable features of cheap price, supporting biodegradation, do no pollution to ecological environment, and easy to be converted to functional material through dramatization. Therefore, cellulose products have irreplaceable advantages of other macromolecular materials, and the fictionalization of cellulose has become a heat in research.

This experiment sets cellulose as the basic framework, making it has cross linking interact with dipole dichloride, and add a certain proportion of photogenic agent solvent at the same time. They crosslink and polymerize to cross linking polymer with macro porous framework structure, consisting exchange groups. Fourier infrared spectrometer for group characterization and SEM for resin pore forming characterization are used on the synthetic macro porous resin. With ruin as the adsorb ate, this paper is to explore the adsorption property of the produced macro porous resin, which includes property of equilibrium adsorption, static adsorption and adsorption, meanwhile exploring the influence of different solvents on the resin adsorption property.

## 2. Experimental section

### 2.1 Raw materials and equipments

#### 2.1.1 Raw materials

Microcrystal Cellulose (Queue Tamil Medical Supplements Co., Ltd); lithium chloride (LiCl) (Analytical reagent, Jinbei Fine Chemical Co., Ltd. Tannin); N,N-DMAc (AR, BASF Chemical Co., Ltd. Tannin); Adipic acid; thinly chloride; pyridine; liquid paraffin (AR, Tannin Gangue Science and Technology Development Co., Ltd.); Hexamethylene (AR, Tannin Kernel Chemical Reagent Co., Ltd.); Anhydrous sodium carbonate/anhydrous sodium bicarbonate (AR, Hanging Tannin Chemical Reagent Co., Ltd.); Sodium hydroxide (AR, Beijing Yale Fine Chemicals Co., Ltd.); Hydrochloric acid (AR, Harbin Minchin Chemical Products Co., Ltd.); Absolute ethanol; 1,4-dioxane (AR, Faye Fine Chemical Co., Ltd. Tannin); Ruin (Zhen Zhou Lingo Biotech Co., Ltd.).

#### 2.1.2 Equipments

Fourier infrared spectrometer (FT-R) (American E360 infrared spectrometric analyzer); SEM (American JMS-6700 SEM); T6 ultraviolet spectrophotometer (Beijing Pixy General Co., Ltd); RE-52A rotary evaporators (Shanghai Sarong Biochemical Instrument Co., Ltd.); SHZ-82 thermostat oscillators (Mingo Beano Co., Ltd).

### 2.2 Synthesis of Macro porous Resin

#### 2.2.1 The dissolution of cellulose

In the dry four-mouth bottle of 250ml volume, firstly put in a certain amount of DMAc, LiCl content of which is 5-10%; secondly add in a certain amount of microcrystal cellulose whose proportion is between 1-4%; thirdly install the reflux condenser, then pass into nitrogen gas, after that, heat up with heating jacket to 100°C, and keeping this temperature for 2 hours. Lastly, let it come to the room temperature until the cellulose dissolves completely, and the solvent become homogeneous solution.

#### 2.2.2 Preparation of dipole dichloride

Put 0.5mol hexanedioic acid in a three-mouth bottle of 500ml firstly, and secondly add 2.5mol thinly chloride into the constant pressure dropping funnel, controlling the reaction temperature lower than 30°C, and then heat the temperature slowly to 90°C when all the materials have been dropped completely. Conduct counterblow for 6 hours under this temperature, feeding nitrogen gas through the whole process for protection. After the reaction, distill at atmospheric pressure, and recycle thinly chloride by collecting 75-80°C distillates, and then distill under reduced pressure, collecting 126°C (1.6 Kappa) distillates with a collecting rate between 63-79.9%.

### 2.2.3 The preparation of Macro porous Resin

Put 10ml solution composed of pyridine and 1, 4-dioxane at a ratio of 1:1 into dissolved cellulose to function as catalyst, together with the solution composed of 40ml hexamethylene and liquid paraffin at a ratio of 1:4, making out the photogenic agent. Then evenly mix the dipole dichloride and, NN-DMAc at a ratio of 1:2, and hold the matter in the constant pressure dropping funnel, and then slowly drop it into the dissolved cellulose homogeneous solution. Rapidly mix the solution at a temperature between 40 -80°C, and make it react for 24 hours, making sure to feed nitrogen gas throughout the process for protection. After the reaction, let it cool down to the room temperature. Then pour the result into 500ml ice water mixture to wash and leach. Later, wash the product with ethanol, sodium bicarbonate solution, ethanol, water in sequence to neutrality, and then leach, and dry the reactants. [Zhou, 2002; Zhang, 1994; Yamaguchi, 1987]

## 3. Characterizations

### 3.1 Infrared characterization

Drying the treated macro porous resin sample at 60 °C under vacuum, then mixing it with Kerr at a mass ratio of 1:100, fully grinding and disc-forming the mixture. The wave number ranges from 400-4000cm<sup>-1</sup>, as shown in Figure 1.

From the spectrum of a graph, we can see that there is an obviously sharp adsorption peak, which can be judged as the feature absorption peak of ester carbonyl group in stretching vibration. This peak implies the esterification of cellulose. The absorption peaks appear around the 1652.44cm<sup>-1</sup> is deduced to be the amide-type carbonyl compound, because the association between acid amide and hydrogen bond can result to the change of spectrum belt to 1650-1640cm<sup>-1</sup>.

### 3.2 SEM

Take some hexane diced cellulose after treatment for SEM test, as shown in Figure 2.

Macrospore cross linked between dendrite cellulose skeleton and dipole dichloride appears on the surface of cellulose ester through the figure. But the macrospores distributes are in no uniform distribution, probably because in the dissolve process of cellulose, the amorphous region of cellulose swells firstly, and crystalline region transform into amorphous region and swell, following that in the cross-linking reaction, certain dissolved parts of amorphous regions react with dipole dichloride, and then the parts of amorphous regions not dissolved or undeveloped crystalline region react with dipole dichloride; differences between the extent and time of reactions leads to no uniform macrospores diameter, so as to form macro porous resin with macrospores of no uniform distribution.

## 4. Dipole dichloride cross-linked cellulose macro porous resin

### 4.1 Standard curve plotting and content determination of ruin

Accurately weigh 0.1500g of ruin, and add 80% ethanol with to dissolve the ruin, and then fix the volume to 50 mL; accurately draw ruin standard solution of 0.00, 0.50, 1.00, 2.00, and 4.00 respectively, and place the ruin standard solution into 50 mL volumetric flasks, then add ethanol-water to the mark, and then shake up, and finally determine the absorbance at 365 nm level.

According to data linear regression-figure 3, we can reach a regression equation:  $y = 12.498 x - 0.0071$ ,  $R^2=0.9996$ . Ruin content then can be calculated according to absorbance value of waiting samples.

### 4.2 Static adsorption and adsorption of macro porous resin

#### 4.2.1 Static adsorption of macro porous resin

In the static adsorption test, accurately weigh 0.0100 g of ruin, 0.4000 g of resin, and put the two into 80% ethanol following by vibration at room temperature. Determine concentration of ruin in the supernatant at different time period, and, choosing the adsorption time as abscissa and adsorption capacity as ordinate, plot adsorption dynamics curve-Figure 4.

$$Q=(C_0-C_1)\times V/M$$

In the formula, Q refers to adsorption capacity;  $C_0$  refers to concentration of ruin before adsorption; V refers to volume of test solution; M refers to weight of resin. [Chao, 2010; Babić, 2008]

According to Figure 4, the curve rises rapidly in the beginning, showing the rate of adsorption is rapid in this time period; the curve shows a tendency of gentle change, showing that when adsorption capacity reaches to certain extent, increment of rate of adsorption and adsorption capacity decrease rapidly as time period grows,

and that small quantity of macro porous adsorption occurs. So this test chooses “11h” as the adsorption time of column-loading buffer. [Zhang, Y., 2007; Zhang, L.-p., 2006]

#### 4.2.2 Static adsorption of macro porous resin

Adsorption rate of macro porous resin- concentration curve of fluent. According to static adsorption test: prepare ruin solution with initial concentration of 0.0100 g/L, add 0.5000 g of macro porous resin for 24 h of adsorption at a constant temperature of 25°C; measure the concentration to ruin and record as  $C_1$ ; dry the macro porous resin which reaches adsorption equilibrium under vacuum; put 1g of macro porous resin which reaches adsorption equilibrium to 0%, 20%, 40%, 60%, 80% ethanol solution separately, and keep them for 10 h at constant temperature of 35°C; Fetch the processed solution, and measure the concentration to ruin and record as  $C_1$  with ultraviolet spectrophotometer. The calculation formula for adsorption rate  $d$  (%):

$$W(\%) = C_2 / (C_0 - C_1) \times 100$$

In this formula,  $d$  refers to adsorption rate;  $C_1$  refers to ruin concentration at adsorption equilibration,  $C_2$  refers to ruin concentration after adsorption. According to Figure 5, the adsorption property decreases along with the increasing of fluent (ethanol) concentration. The explanation root in molecular structure of ruin, that is, ruin belongs to spooning material, the glycols of which are strides and triterpenoids, which two connects to be glycols and glycoside and gains strong polarity; the polarity of fluent decreases along with the increasing of fluent (ethanol) concentration, leading to decline of eluting effect. Polarity of water is the strongest, so eluting effect of water is the best [ Du, 2008; Fu, 2007].

#### 4.3 Equilibrium adsorption of macro porous resin upon ethanol-water solution

Commonly used adsorption isotherm models are Longmuir and Freundlich adsorption equation. Longmuir formula indicates the ideal surface adsorption. In fact, adsorption in very close limit can be seen as adsorption on well-distributed surface, and so can be described with Longmuir formula. Fitting by Freundlich adsorption equation, adsorption isotherm can be described as: Figure 6 serves as adsorption isotherm of macro porous resin upon ethanol-water solution, and shows that adsorption isotherms are I type isotherm, which can be fitted by Freundlich isothermal adsorption equation:

In this formula,  $1/n$  refers to measurement of adsorption strength;  $K_F$  refers to measurement of adsorbent adsorptive capacity.

Conclusions can be made through multiplication tests: adsorption is easy when  $1/n$  goes between 0.1 and 0.5; adsorption is unlikely to occur when  $1/n$  reaches no less than 2. Absorbance of the adsorbent increases as the  $K_F$  value rises. After the fitting, regression equation of ruin upon macro porous shall be:  $y = 1.4835 x_s + 0.0502$ ,  $R^2 = 0.9917$ . Apparently, adsorption of ruin in macro porous resin conforms to Freundlich adsorption equation.

#### 4.4 The influence of time on static adsorption

Weigh 5g produced macro porous resin and put it in a conical flask, then add 0.1g ruin and 80% ethanol-water solution in the conical flask. Lastly, shake up the flask under a constant temperature of 30°C, and extract supernatant fluid from the flask at the react time of 2 hours, 4hours, 6hours, 8hours, 10hours, 12hours, 14hours, and 16hours to determine their ultraviolet absorbency. Concluding the ultraviolet absorbency values, we can obtain the adsorption quantity of each flask: 0.005033 g/l, 0.006545 g/l, 0.008158 g/l, 0.008362 g/l, 0.008362 g/l, 0.009033 g/l, 0.009033 g/l, and 0.009033 g/l, so that we can protract the Figure 7. [ Zhang, F., 2009; Zhang, C., 2009; Slomkiewicz, 1997]

From Figure 7, we can observe that the adsorption quantity of the produced macro porous resin to ruin increases with the pretension of time, and brief adsorption equilibrium appears between 8-10 hours. With time continues to extend, the adsorption quantity increases continually, and the climax appears at “12h”. After “12h”, the adsorption quantity keeps stay with the time pretension showing that at “12h”, the adsorption quantity to ruin reaches the highest level for the macro porous resin made in this experiment.

#### 4.5 The influence of temperature on static adsorption

Weigh 5g produced macro porous resin and put it in 5 conical flasks respectively, then add 0.1g ruin and 80% ethanol-water solution in every conical flask. Lastly, shake up the flasks for 24 hours at a constant temperature of 20°C, 25°C, 30°C, 35°C and 40°C respectively. After that, extract supernatant fluid from every flask to determine their ultraviolet absorbency. Concluding the ultraviolet absorbency values, we can obtain the adsorption quantity of each flask: 0.002440g/l, 0.005998 g/l, 0.008158 g/l, 0.005341 g/l, and 0.003440 g/l, so that we can protract the Figure 8.

From Figure 8, we can draw that the adsorption of resin to ruin increases gradually with the increase of the

temperature. When the temperature reaches 30°C, the adsorption capability arrives its climax. However, in the condition that the temperature continues to rise, the adsorption capability shows a trend to decline. Therefore, this experiment concludes 30°C as the best adsorption temperature. [Umar, 2009; Tejero, 1988]

## 5. Conclusions

(1) This test adopts polymerization reaction between dipole dichloride and cellulose, adding certain proportional pyridine and 1, 4-dioxane as composite oxidant and cyclohexane & paraffin as progeny, and obtains macro porous absorption resin with porous skeletal structure through cross linking reaction.

(2) By assaying the surface features of pressed in the macro porous resin obtained in this test with FFT spectroscopy apparatus, infrared spectrum reveals hydroxyl and ester group in reactant, indicating that hydroxyl of cellulose did not completely react and that the reaction generated ester group. By assaying surface features of macropore-forming by scanning electron microscope, the image shows macropore in no uniform distribution and inconsistent layers, indicating that macro porous resin was generated in the reaction.

(3) This paper probes into adsorption property of macro porous resin through synthetic reaction by adopting ruin as adsorbents, and discussed the influence of different monstros on adsorption property of the resin. The adsorption data shows that Freundlich isothermal adsorption equation is applicable to the adsorption of ruin by the resin, that is, the new type macro porous resin is able to adsorb glycoside. This paper also observe that adsorption property of the macro porous resin reaches the highest when using ethanol as menstrual and that adsorption property reaches the highest when using water as fluent.

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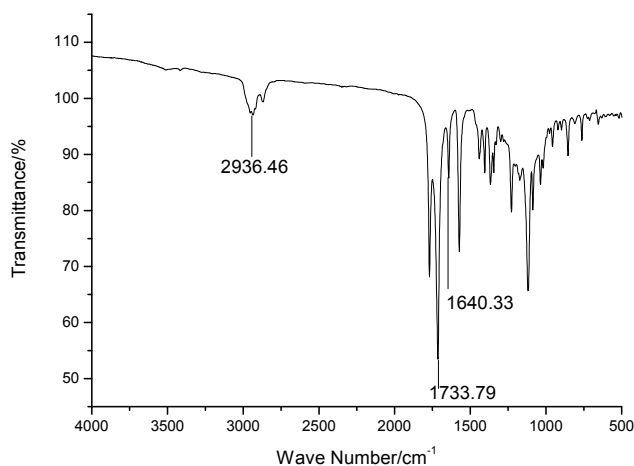


Figure 1. The FTIR figure of dipole dichloride-cellulose cross linking macro porous resin

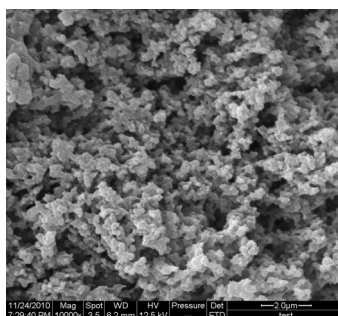


Figure 2. Election microscope image of Dipole dichloride cross-linked cellulose macro porous resin

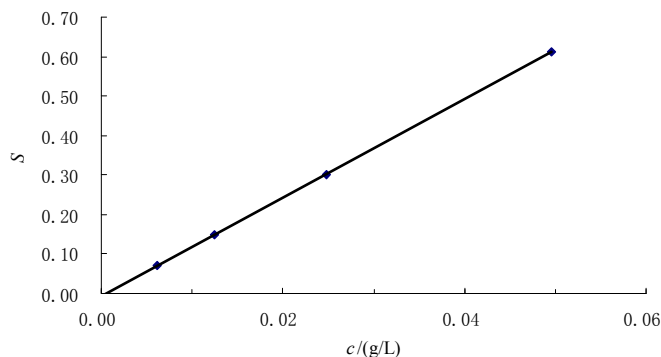


Figure 3. Ruin standard curve

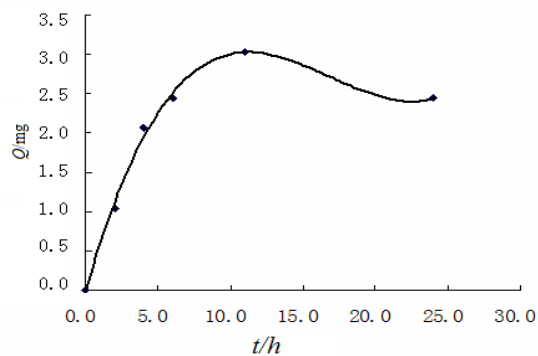


Figure 4. Static adsorption dynamics curve

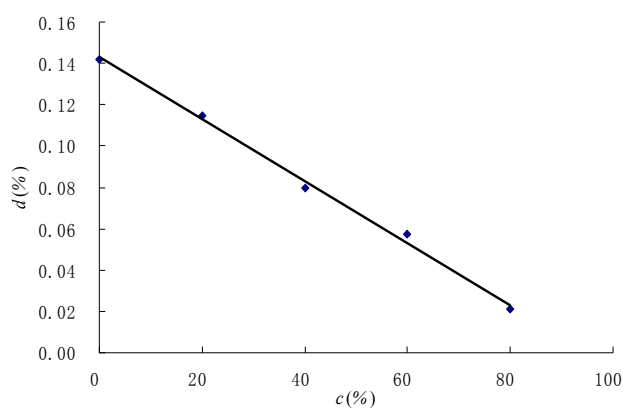


Figure 5. The effect of fluent concentration on adsorption property at the temperature of 25 °C

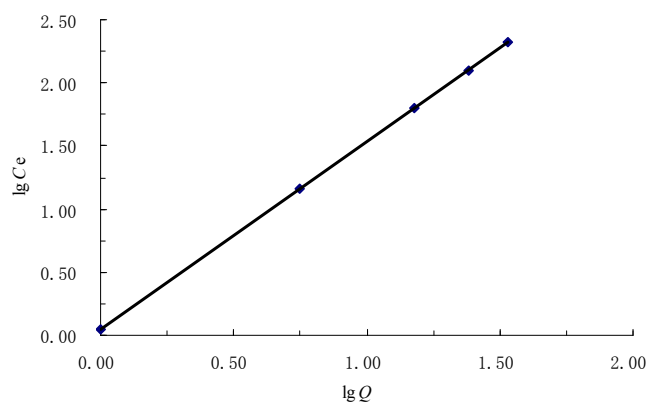


Figure 6. Freundlich isothermal adsorption equations

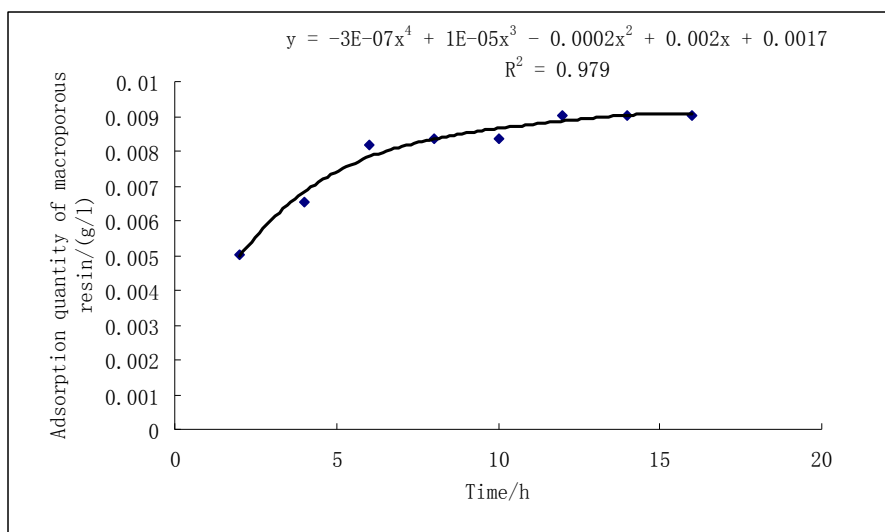


Figure 7. The influence of time on the adsorption quantity of macro porous resin under constant temperature

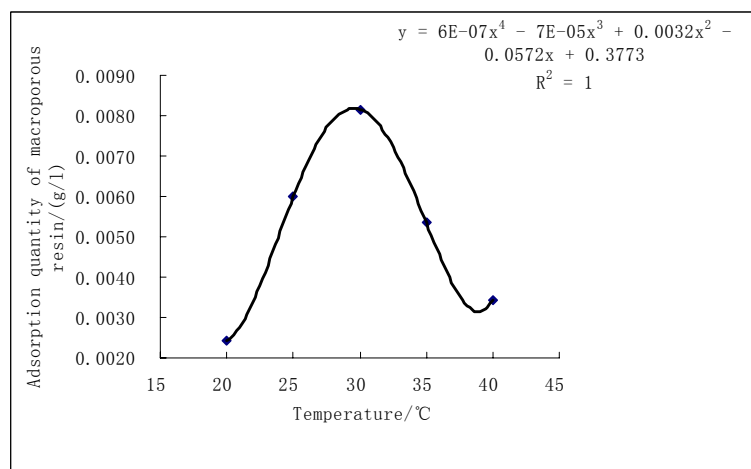


Figure 8. Adsorption quantity of macro porous resin to ruin under different temperatures