Thermodynamic and Kinetic studies for sorption 4,6- dihydroxy mercup-pyrimidine by granular Aluminum oxide

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Abstract

The Kinetic and thermodynamic practical parameter affected adsorption process such as initial compound concentration acidity.

Thermodynamic parameters, such as (ΔH^o, ΔG^o, ΔS^o) have been calculated by using the thermodynamic equilibrium coefficient obtained at different temperatures and concentrations were(13.164KJ.mol^{-1},7.295KJ.mol^{-1},0.019695KJ.mol^{-1} K^{-1}respectively).

The langmuir and freundlich adsorption model were applied to describe the equilib- rium isotherms.

The adsorption kinetics of organic compound (DHMP) on the surface(GAO) obeyed the pseudo -first order equation and show that the adsorption is complex due to different factors that control the rate of reaction. In this work , the adsorption average constant (K_{ad}) increase with the temperature increase when fixing concentration for the adsortion substance.
Activation energy was calculated using Arrhenius equation which depends on the nature of the adsorbent surface.

الخلاصة

يمكن فصل المواد الملوثة بطريقة سهلة من المحلول المائي وغير المائي . ففي هذا البحث تم امتزاز المادة (٤،٦- ثنائي هايدروكسي ميركب- برميدين) المذابة في الماء من قبل المادة المازة اوكسيد الألمنيوم الحبيبي. كما تم حساب القيم الثرموديناميكية مثل (ΔH^o, ΔG^o, ΔS^o) باختلاف درجات الحرارة والتركيز وكانت كالأتي(13.164KJ.mol^{-1}, 7.295KJ.mol^{-1}, 0.019695KJ.mol^{-1} K^{-1}).طبقت معادلتي لانكماير وفرندلش وذلك لوصف ايزوثيرم الامتزاز .

تم دراسة حركية الامتزاز للمركب العضوي (٦،٤- ثنائي هايدروكسي ميركب- برميدين) على سطح اوكسيد الألمنيوم الحبيبي وبينت النتائج إن الامتزاز يسير وفق حركية المرتبة الأولى الكاذبة وتم حساب ثابت معدل سرعة حركية الامتزاز حيث وجد انه يزداد بزيادة درجة الحرارة.كما تم قياس طاقة التنشيط.

Introduction

The removal of pollutants from aqueous solution plays an important role in west water treatment since it eliminates the need for huge sludge - handling process well - designed sorption processes have high efficiency resulting in a high- quality effluent after treatment which can be recycled(1). Furthermore , if low- cost sorbents or sorbent regeneration is feasible then the sorbent material cast can be kept low . It is therefore understandable that the study of sorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction path ways and into the mechanism of sorption reactions. In addition ,the kinetics describe the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid solution interface :Therefore, it is important to be able to predict .The rate to design appropriate sorption treatment plants. To develop sorption kinetics, aknowledge of the rate law describing the sorption system in required(2).

Organics are of great concern in water treatment due to their health and environmental hazard, small quantities of soluble organic and inorganic compounds such as sulfides, nitro and heavy metals remaining in the waste water(3).

There are different methods to purified the water from polluents -organig chemicals by using strong oxidizing agent such as the ozone(4), molecular oxygen(5), and hydrogen peroxide(6).

Adsorption process can be defined as the attachment of particles to a surface(7). The term adsorption isotherm refers to the relation between the extent of adsorption(Qe) or (X/M) with the equilibrium concentration of the adsobate in solution (Ce) at constant temperature. (X) is the amount of substance adsorbed in milligrams by (M) grams of the adsorbent(8).

Alumina and other metals oxides is considered to be a particularly competitive and effective process for the removal of organic compounds at trace quantities(9-11).

Stoichiometrically there is only one oxide of aluminum, alumina, Al_2O_3 .However, this simplicity is compensated by the occurrence of various polymorphs, hydrated species, etc., the formation of which depends on the conditions of preparation . There are two forms of anhydrous Al_2O_3,α–Al_2O_3 and γ- Al_2O_3 . In α–Al_2O_3 The oxide ions form a hexagonally close - packed array and the aluminum ions are distributed symmetrically among the octahedral interstices(12).

Experimental

Materials and Apparatus :

4,6-dihydroxy mercup- pyrimidine obtained from B. D. H, and granular aluminum oxide molecular weight (101.96), melting point (2015C°).

All spectral and absorbance measurements were carried out on ashimadzu UV. Vis 1700 digital double beam recording spectrophotometer using(1cm) glass cells.

A digital pH- meter .720WTW 82362 was used .

1- Thermodynamic studies

Portions of (4,6- DHMP) solution (20ml) of known initial concentration(4,8, 12, 16,20 and 24)mg/L were shaken with (0.1g) of granular Aluminum oxide (GAO) Adsorbent at a certain temperature in thermostat shaker with a speed 90cycle/minute for 2hours which is measured experimentally as a time needed for reaching the equilibrium state .Acidity of the solutions were adjusted using few drops of (0.1N) HCl or (0.1N) NaOH solutions . Absorbances at the maximum wave length (λmax) of(4,6- DHMP) solutions were measured at different values of pH used in the experiment .

The maximum absorbance (λmax= 264n.m) at pH=7, (λmax=281n.m) at pH=4,

(λmax= 264n.m) at pH=10

The experiments were repeated at different temperatures (25,35,45,55 C°) in order to measure thermodynamic parameters (ΔH^o, ΔG^o, ΔS^o).

The amount of adsorbate substance was calculated from the relation(13):

$Qe= (C_\circ - Ce).V_{sol} / M$

Where :

$C_\circ$: is the initial concentration (mg/L).

Ce : is the equilibrium concentration (mg/L).

V_{sol} : is the volume of (4,6-DHMP)(L).

M : is the Wight of (GAO)(g).

Two main theories have been adopted to describe adsorption isotherms . the first, Langmuir isotherms which represented by the linear equation :

$Ce/Qe = 1/a + (b/a)\, Ce$……(2)

Where (a) represents aparetical limiting adsorption capacity when the surface is fully covered with a monolayer of adsorbate . The constant (b) is the equilibrium adsorption constant which related to the affinity of the binding sites(14).

The applicability of these equations on the adsorbent –adsobate (solute) system assume the formation of one layer of adsorbate molecules on the surface while the freundlich adsorption isotherm (equation) consider heterogeneity of the surface and the formation of move than one layer is probable .

The linear form of freundlich isotherm is :

$\log Qe = \log K_f + (1/n)\log Ce$……(3)

Where (K)and (n) are freundlich constants characteristics of the system, including the adsorption capacity and the adsorption intensity, respectively(15).

The equilibrium constant (K_{eq}) for the adsorption process at each temperature is calculated by using the relation ship as follow;

$K_{eq}= Qe\ (Wt_{suf})/Ce\ (V_{\mathbf{solu}})$..… (4)

Where (Wt_{suf} **)** is the weight of the used surface, (V_{solu}) is the volume of the used (4,6- DHMP) solutions. The change in free energy (ΔG°) could be determined form the equation:-

$$\Delta G^\circ = -RT \ln K \quad …………(5)$$

Where (R) is the gas constant (8.314 $J.mole^{-1}.K^{-1}$) and T is the absolute temperature.

The heat of adsorption (ΔH°) may be obtained from the vant Hoff's equation:-

$$\ln K = \frac{-\Delta H^\circ}{RT} + cons\tan t \quad …….(6)$$

Where K is the equilibrium constant when Ce approaches zero at certain temperature. It obtained from plotting (ln K) of each concentration against corresponding Ce. Plotting (In K) versus (1/T) should produce a straight line with a slope = (-ΔH°/R) from which the enthalpy (ΔH°) of the adsorption process is obtained.

The change in entropy (ΔS°) was calculated from Gibbs equation :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad …… (7)$$

Adsorption Kinetics studies :

In order to investigate the mechanism of sorption, characteristic constants of sorption were determined,using pseudo-first order equation of lagergren(16) based on solid capacity, a first order equation of Bhattacharya and Venkobachar(17) based on solution concentration .

A kinetic model for sorption analysis is the pseudo- first order rat expression of lagergren(16) in the form :

$dq_t/dt = K_{ad}\ (q_e-q_t)$ ……(8)

Integrating this for the boundary conditions t=0 to t=t and q_t=0 to q_e=q_t , Eq (8) may be rearranged for linearized data potting as shown by Eq (9) :

$\ln (q_e-q_t) = \ln q_e – K_{ad} * t$ … (9)

Where K_{ad} is the rate constant of first order sorption$(min)^{-1}$, q_e is the amount of solute sorbed at equilibrium (mg/g), q_t is the amount of solute sorbed on the surface at the sorbent at any time t(mg/g).

Result and Discussion

Figures (1) shows the adsorption isotherms of the (4,6- DHMP) at 25C^{o} using(GAO). The equilibrium adsorption density Qe increased with the increase in (4,6- DHMP) concentration .

The adsorption curve were fitted to both Langmuir and Freundlich equation. Are shown in Table(1) figures (2) and (3) .

Parameters of the Langmuir and Freundlich isotherms were computed and listed in table(1). The isotherm fits quite well with the experimental data (correlation coefficient R^2 =0.986) where as the low correlation coefficients R^2 = 0.919 show the less agreements of the Langmuir isotherm with the experimental data(18).

In order to study of the effect of hydrogen ion concentration (pH) on (4,6-DHMP) by adsorbent(GAO). Different concentration of (4,6-DHMP) were prepared based on the researches concentrations(19) in the range (4-24)ppm and adjusted to different pH values of (4,7and10) . The results are displayed in figures(4).It is clear that the amount of (4,6- DHMP) removed varies pH= 4, pH value produces a large adsorbed quantity. The higher adsorption capacity(0.24) was recorded in aqueous solution of (4,6-DHMP) by (GAO). May be related to the surface properties of (GAO) are depended on pH of the solution .

Adsorption isotherms were taken for the (4,6-DHMP) in the temperature range (298-328K). The result are shown in figure(5). Endothermic process for the adsorption of (4,6-DHMP) on (GAO)is consistent with other adsorption processes(21).

The thermo dynamical parameters values are :

ΔH^o = 13.164 KJ.mol^{-1}, ΔG^o = 7.295 KJ.mol^{-1}, ΔS^o = 0.019695KJ.mol^{-1} K^{-1}

Free energy change and entropy values were measured at 298K .

The positive value of free energy change indicates a non spontaneous adsorption process(20).

In order to investigate the mechanism of sorption kinetic models have been used to test experimental data. The kinetic model in this study includes the pseudo-first order equation .

The value of rate constant for the pseudo- first order reaction is calculated experimentally by plotting log(q_e-q_t) against time of the adsorption of(4,6-DHMP) on to(GAO) according to equation(9), results are shown in figure(6) and values of rate constant are illustrated in table (2) .

The value of rate constant K_{ad} , are calculated experimentally from figure(7), were found to be increased when temperature increased from 298K to 328K and the values of rate constant are illustrated in table (3).

The sorption rate constant may be expressed as a function of temperature by following the relation ship$^{(7)}$.

$\log K_{ad} = \log A - (E_a / 2.303RT)$ …….(10)

Where K_{ad} is the rate constant of sorption(min)$^{-1}$, E_a is the activation energy of sorption(KJ/mol), R is the gas constant (8.314 J.mole^{-1}. K^{-1}), T is solution temperature(K).

The log K_{ad} values for the pseudo-first order were plotted as a function of recipro- -cal of the Kelvin temperature. Linear variation were observed as shown in figure (8). The value of activation energy of adsorption obtained is (1.74Kcal. mole^{-1}).since sorption is an endothermic process, it would be expected that an increase in solution temperature would result in a increase in adsorption capacities.

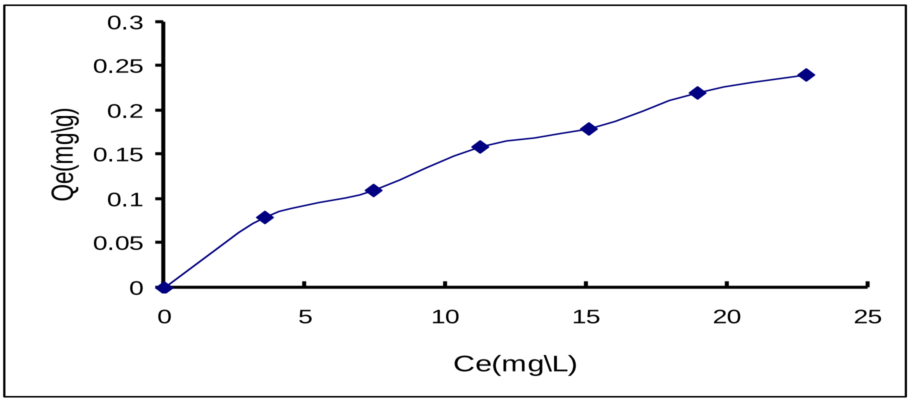

Figure (1): Adsorption isotherms of (4,6-DHMP) on (GAO) surface at 298K and PH=7.

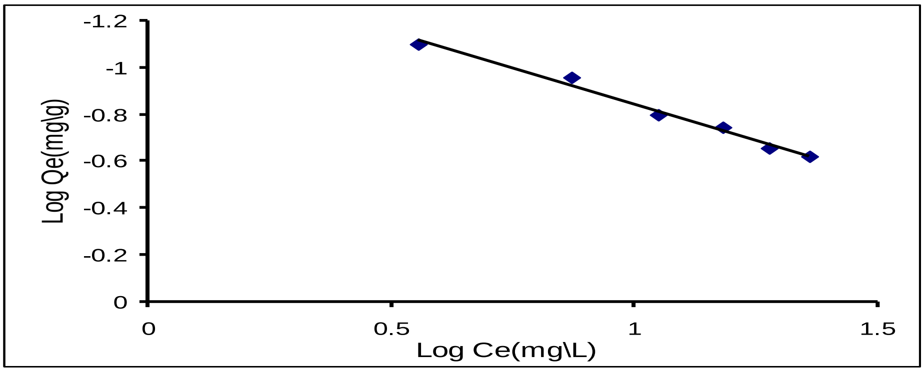

Figure (2): Linear form of Freundlich equation for the adsorption of (4,6-DHMP) on (GAO) surface at 298K and PH=7.

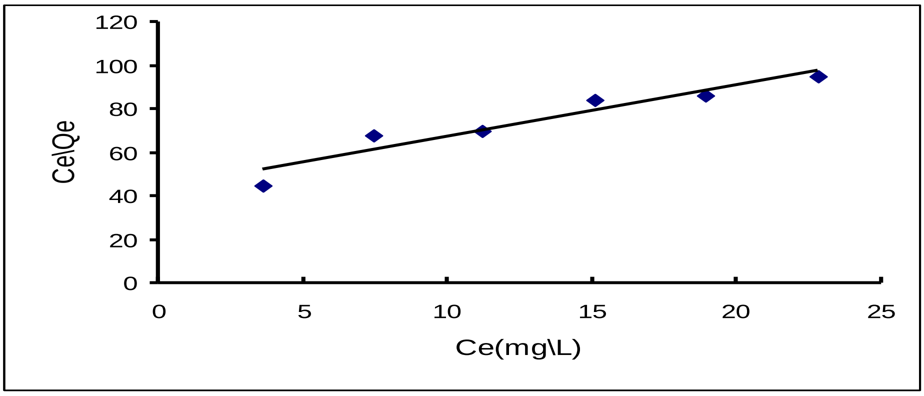

Figure (3): Linear form of Langmuir equation for the adsorption of (4,6-DHMP) on (GAO) surface at 298K and PH=7.

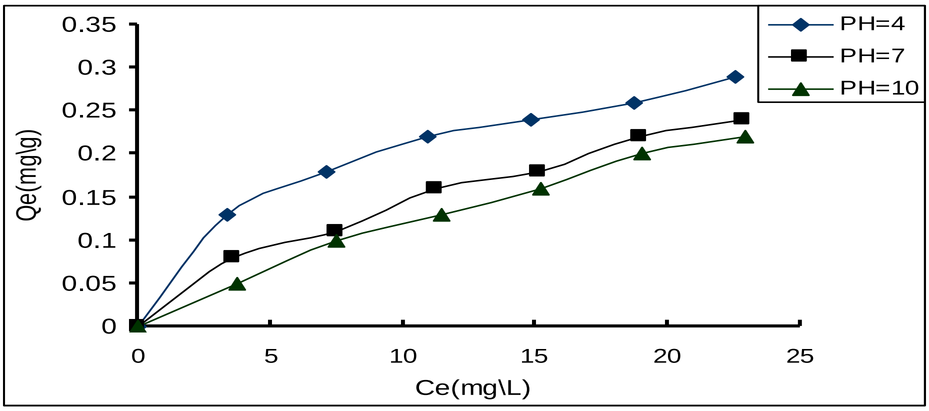

Figure (4): Freundlich isotherms of adsorption of (4,6-DHMP) on (GAO) surface at different pH (4, 7, 10).

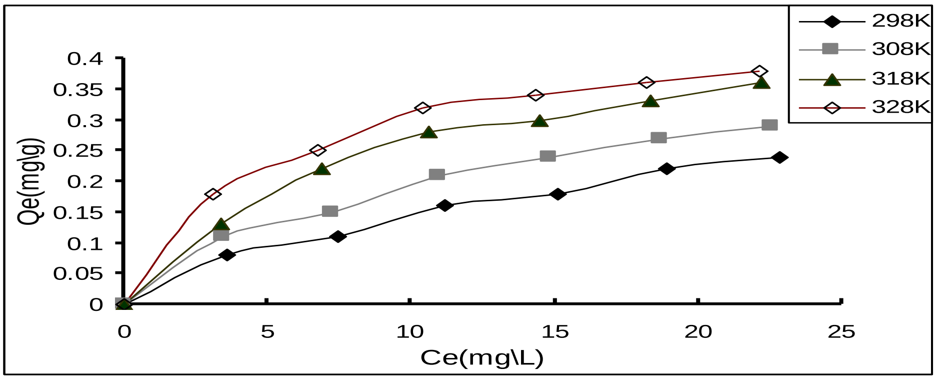

Figure (5): Adsorption isotherm of (4,6-DHMP) on (GAO) surface at (25, 35, 45, and 55°C).

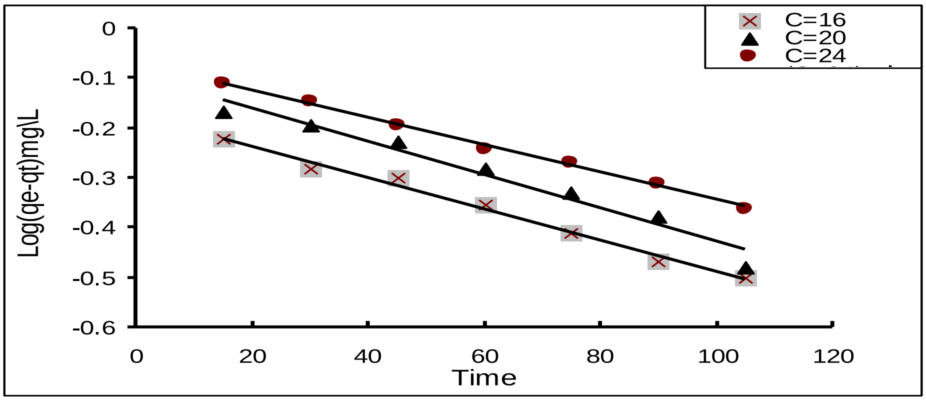

Figure (6):The effect of initial compound concentration on the adsorption kinetic of(4,6-DHMP)on (GAO)at PH 7, 25C°

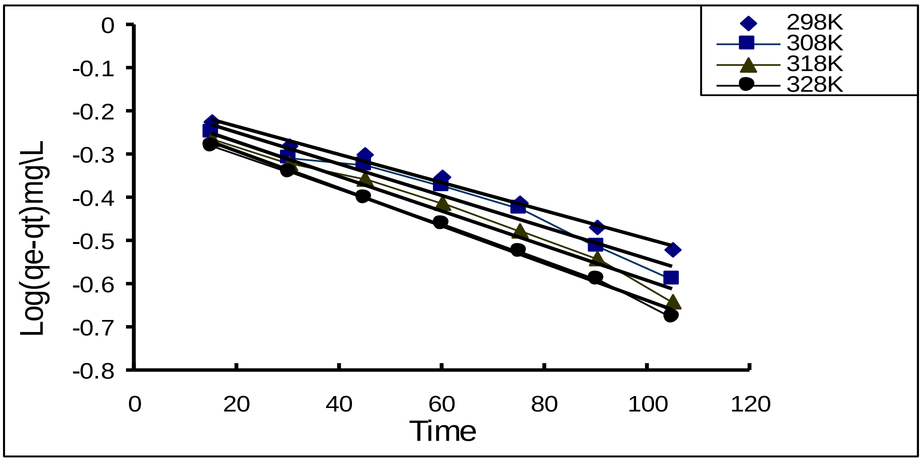

Figure (7):Pseudo- first order adsorption kinetic of (4,6-DHMP) on the(GAO) surface at different temperature and PH 7.

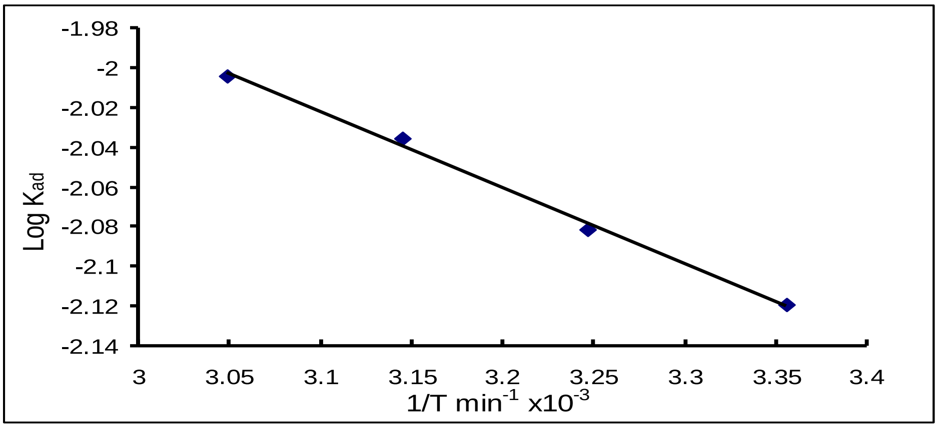

Figure (8):Relationship for Arrhenius equation to calculate the activation energy for pseudo- first order reaction by effect of temperature.

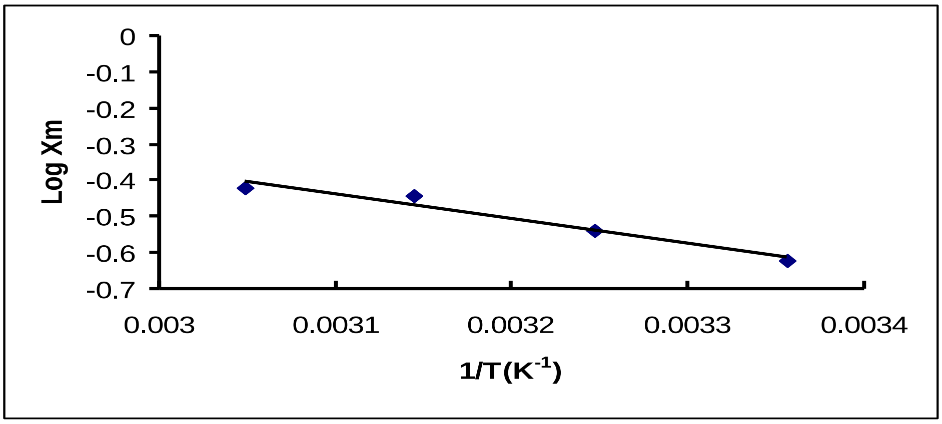

Figure (9):Graphic representation of the modified vantHoff's equation for the adsorption of (4,6-DHMP) on (GAO) at different temperatures.

Table(1): Langmuir and Freundlich isotherm constant.

Compound	Freundlich constant			Langmuir constant		
	K_f	n	R^2	a	b	R^2
4,6-DHMP	0.035	1.627	0.9857	0.023	0.055	0.919

Table(2):Rate constants for effect of different concentration on the adsorption of (4,6-DHMP) at 298K and PH=7.

C_0 ppm	K_{ad} min^{-1}
16	X10^{-3}7.5999
20	X10^{-3}7.830
24	X10^{-3}6.4484

Table(3):Rate constants for effect of different Temperature on the adsorption of (4,6-DHMP)(16mg/L) at PH=7.

Temperature K	K_{ad} min^{-1}
298	X10^{-3}7.5999
308	X10^{-3}8.291
318	X10^{-3}9.212
328	X10^{-3}9.903

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