Degradation of chlorobenzadehyde on (Bentonite , Kaolin and Attapulgite) surfaces

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Abstract

The present work study the adsorption and photolysis of chlorobenzaldehyde in solution on the surfaces of Bentonite , Kaolin and Attapulgite.
UV- visible spectrophotometer technique ,pH and conductivity have been used to follow the results,which showed a higher adsorption on kaolin surface than bentonite and Attapulgite.
Rate of degradation reaction is 10.5 , 2.55 and2.1(μ mol/l.min^{-1}) on kaolin,Bentonite and Attapulgite respectively.
While the value of conductivity and pH were increased through adsorption process when bentonite surface used.
Phtolysis processes for chlorobenzaldehyde showed higher rate of reaction in the absence of any and equal to 4.65 (μ mol/l.min^{-1}) .A kinetic study was carried out for the degradation of chlorobenzaldehyde different kind of clay .
The results showed first order reaction and a relatively high rate of reaction kaolin 4.5, 4.5 and 3.45 (μ mol/l.min^{-1}) on kaolin,Bentonite and Attapulgite respectively and a short half life time (23.1,23.1 and 30.13)min for the same surfaces .

الخلاصة

تم خلال البحث الحالي دراسة الامتزاز والتحلل الضوئي لكلوربنزالديهايد من محلولـه المـائي علـى سـطوح (البنتونايت ، الكاؤولين والاتبالكايت)
وتم استخدام تقنية مطيافية فوق البنفسجية لمعرفة كمية الامتزاز والاس الهيدروجيني والتوصـيلية .فـي عمليـة الامتزاز . اوضحت النتائج ان قابلية امتزاز الكاؤولين هي اكبر من البنتونايت والابتالكايت من خلال قيم سـرعة التفاعل والتي تساويμ mol/l.min^{-1} (2.1، 2.55، 10.5) الكاؤولين ، البنتونايت والابتالكايت على التـوالي .اما بالنسبة للتوصيلية والاس الهيدروجيني فان القيم تزداد بوجود البنتونايت مع الزمن خلال عملية الامتزاز .
اوضحت نتائج التحلل الضوئي ان سرعة التفاعل تكون الاكثر في حالة عدم وجود سطح او وجوده وتساوي μ= 4.65 mol/l.min^{-1} وقيم الاس الهيدروجيني تتناقص مع الزمن اما قيم التوصيلية تزداد مع الزمن في حالة البنتونايت . ووجد من خلال النتائج العملية ان التفاعل اقرب الى المرتبة الاولى.

Introduction

The presence of contaminates in aquatic enviroments may cause serious problem to human beings and other organisms (1-7) . It becomes necessary to remove the residues of this toxic compound from matrices such as water by devising an efficient and ecomoic purification method .Reports in literature reveal that are many methods used for removing metal ions from waste water such as : precipitation and membrane separation .

These methods have according to the source of wastewater and the concentration level of contaminants (8-9) The intermolecular interaction of organic pollutants with clay mineral surfaces can be expected to play a cruciale role in the subsequent chemical –biological transformations,transport and retention of these contaminants It has been well established that swellings clays such as montmorillonite adsorb organic molecules to their interlayer surfaces and that adsorption is strongly influenced by both the type of exchange able metal cation presenton the clay and the overall water content (10)

Bentonite is aclay that usually occurs as smectite crystals of colloidal size .Its parallel and stacked silicate layers are according to souzade santos.Bentonite is an absorbent aluminium physllosilicate in general, impure clay consisting mostly of montmorillonite .There are different types of bentonites , and their names depend on the dominant elements , such as potassium ,sodium, calcium and Aluminum.(11-13) Attapulgite is a kind of crystalloid hydrous magnesium-aluminum silicate mineral , having aspecial laminated chain structure in which there is a crystalline lattice displacement existed .Thus it makes the crystals contain uncertain quantities of Na^{+}, Ca^{+2}, Fe^{+3},Al^{+3} and present in the shape of needles, fibers or fibrous clasters . Attapulgite has very good colloidal properties such as: specific features indispersion , high temperature endurance salt and alkali resistance , and also high adsorbing and de-coloring capabilities.(14) Molecular formula Attapulgite : $Mg_5Si_8O_{20}(OH)_{24}(HO)_2.H_2O$ the stracture is some what between laminated and chain structure.

Kaolinite is aclay mineral ,part of the group of industrial mineral , with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral. Kaolinite has alow shring – swell capacity and alow cation exchange capacity (1-15 meg/100g).It is a soft ,earthy , usually white mineral (dioctahedral) phyllosilicate clay produced by the chemical weathering of aluminium silicate minerals like feldspar.

Experimental part

1-Materials and methods

A: -Materials

Absolute ethanol (99%) produced by B.D.H(L.D.T),4- chlorobenzaldehyde. (99%) produced by B.D.H(L.D.T).

B: Apparatus

The following apparatus were used in this study:

1-pH meter, type Kent EIL7045/46
2-Electronic Balance , Staton 46/AN
3-UV- visible spectrophotometer (100 conc./varian.USA)
4-Centrifuge(hitachi universal of Germany)
5- Thermostated shaker water bath (Hotter Mann,Germany)
6- Electrical sieve, KG Germany (200 mesh)

C- The Clays:

Bentonite , Kaolin and Attapulgite were supplied from the General company of Gedogical survey and Mining Iraq. The chemical analysis of there clays are listed in table (1)

Table(1) The chemical analysis of clays

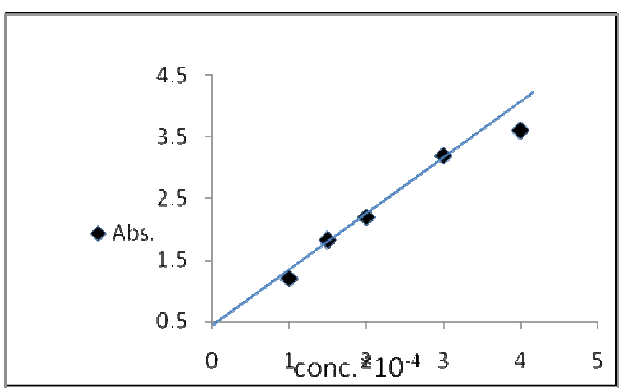
Compound	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	SO_3	TiO_2	Lossof ignition	Total
Bentonite	54.66	14.65	4.77	4.88	6.0	0.65	1.2	-	12.56	99.37
Kaolin	54.68	30.19	-	1.02	-	-	-	1.0	10.99	97.83
Attapulgite	44.66	13.36	13.71	4.20	3.20	-	0.23	-	17.97	97.33

2- Preparation of clay powders:

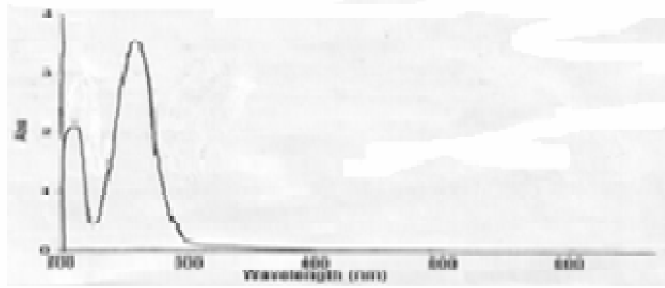
The clays were washed with distilled water, dried at 160^0C for three hours and then kept in airtight containers. The clays were sieved to a m by using an μparticles size of 75 Electrical sieve , KG Germany

3- Calibration curve.

The UV-Visible absorption spectra of chlorobenzaldehyde solutions were recorded in the wavelengths range between (200-800)nm using two quartz cells of (10mm)pathway.
A calibration curve for chlorobenzaldehyde was made by using the concentrations range $(1\text{-}5x10^{-4})$ M λ max (257 nm) for (fig(1)



fig(1) a calibration curve for chlorobenzaldehyde



Fig(2) The UV-visible spectra of chlorobenzaldehyde

4- Determination of Equilibrium time of adsorption

To a solution of ($1.5x10^{-4}$M) chlorobenzaldehyde in 25ml (1:1 ethanol and distilled water) , 0.3g of clay was added in a conical flask.The mixture was shaken in a thermostatic controlled water bath .The concentrations of the solution was followed using spectrophotometer at λ max (257 nm). The adsorption process was reached the equilibrium time for chlorobenzaldehyde .

5- Photolysis procedure:

Aknown amounts of clays (Bentonite , Kaolin and Attapulgite) were added to an aqueous solutions of chlorobenzaldehyde of initial concentration ($1.5x10^{-4}$M) The reaction mixture was magnetically stirred for (150 min) and the resulting suspention was irradiated using 125 watt medium pressure mercury lamp .2 ml of suspention were with drawn each 30 min of irradiation time intervals and immediately centrifuge to remove clay particles.The pH and conductivity changes of the mixture were measured during the irradiation process.

The photolysis experiments were carried out in apyrex cell 35ml in volume .

6- Effect of pH and conductivity .

The change in pH and conductivity of the mixture due to adsorption and photolysis were studied through time of reaction and the results are listed in table(2)

Table (2) measurements of pH and conductivity for adsorption and photolysis process for different clays at 120 min.

Chlorobenzaldehyde With	Adsorption			Photolysis		
	pH	Conductivity(μS/cm)	Q%	pH	conductivity(μS/cm)	Q%
-	5.8	0.8	-	4.68	0.8	90.67
Bentonite	7.6	15.5	27.27	6.62	7.2	72.47
Kaolin	6.78	1.6	61.54	6.17	1.3	58.79
Attapulgite	6.91	9.6	8.24	6.92	2.2	56.05

Results and Discussion

Adsorption of Chlorobenzaldehyde on Bentonite , Kaolin and Attapulgite.

The results of the adsorption processes of Chlorobenzaldehyde on different clays surface showed that the kaolin surface adsorped ahigher quantity of Chlorobenzaldehyde relative to other clays surface.

The following equation (1) was applied to calculated the adsorped quantity .

$Qe = V(C_o - C_e)/m$…………………(1)

C_o= solution concentration before adsorption in (mg/l)

C_e= equilibrium concentration in (mg/l), m= the weight of the adsorbed (g)

V= the volume of solution used in adsorption

Qe= the quantity adsorbed in mg/g

Table (3) Adsorption of chlorobenzaldehyde on clays

chlorobenzaldehyde	Bentonite		Kaolin		Attapulgite	
C_o(mg/L)	C_e(mg/l)	Q_e(mg/g)	C_e(mg/l)	Q_e(mg/g)	C_e(mg/l)	Q_e(mg/g)
21.075	14.05	0.585	12.85	0.685	17.04	0.34

That result due to a higher surface area of the kaolin (around 11 m^2/g) relation to both Bentonite and Attapulgite surface area (around 7,5 m^2/g)

Table (4) Adsorption processes of chlorobenzaldehyde with time .

t(min)	Bentonite			Kaolin			Attapulgite		
	Abs.	(A_t-A_∞)	$Ln(A_t-A_\infty)$	Abs.	(A_t-A_∞)	$Ln(A_t-A_\infty)$	Abs.	(A_t-A_∞)	$Ln(A_t-A_\infty)$
0	1.82	0.39	-0.94	1.82	1.12	0.113	1.82	0.15	-1.89
30	1.54	0.11	-2.21	0.93	0.23	-1.47	1.73	0.06	-2.81
60	1.51	0.08	-2.54	0.81	0.11	-2.21	1.72	0.05	-2.99
90	1.49	0.06	-2.81	0.77	0.07	-2.66	1.72	0.05	-2.99
120	1.47	0.04	-3.22	0.72	0.02	-3.91	1.69	0.02	-3.91
150	1.43			0.70			1.67		

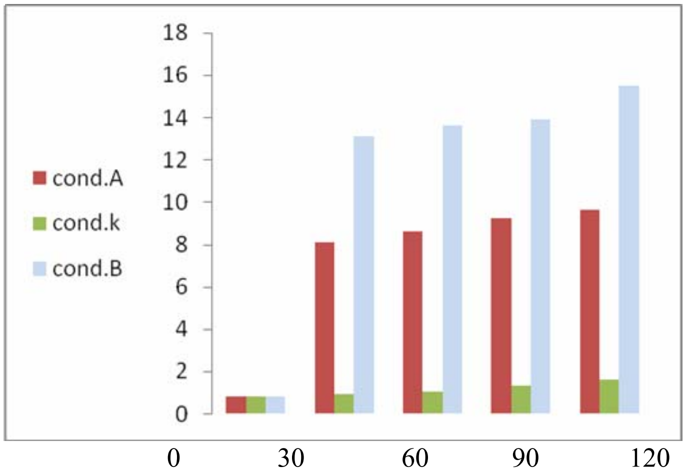
The results adsorption shown in fig (4b,5b and 6b)

Study of conductivity and pH of chlorobenzaldehyde through the adsorption .

The conductivity changes of chlorobenzaldehyde solution on bentonite through the adsorption time was increased ,Its found that bentonite was more efficient than other clays in ion exchange .The clays can also bind a large number of organic pollutants because of their large surface area.The active site with their participate is in diverse with molecular interactions exclusive of ion-exchange .This process left a long normally of free ions .Table (5) and fig(2,3) show the results of conductivity and pH of chlorobenzaldehyde through the adsorption.The result indicating the dechlorination of chlorobenzaldehyde for formation of alkali products .

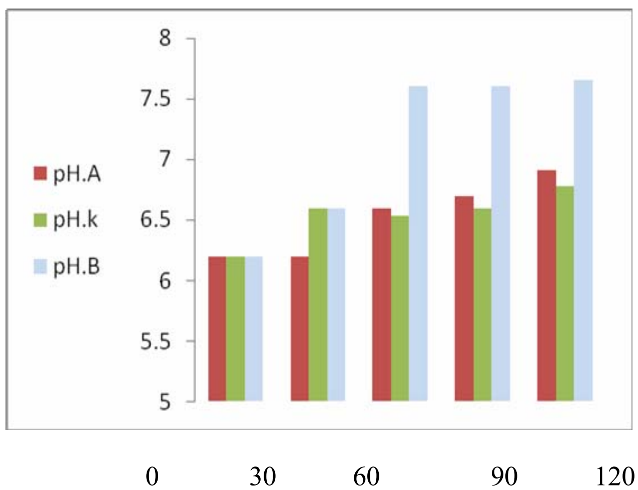
Table (5)The conductivity and pH of chlorobenzaldehyde through the adsorption

t(min)	Conductivity (µS/cm)Bentonite	Conductivity (µS/cm) Kaolin	Conductivity (µS/cm) attapulgite	pH Bentonite	pH Kaolin	pH Attapulgite
0	0.8	0.8	0.8	6.2	6.2	6.2
30	13.1	0.9	8.1	6.6	6.6	6.2
60	13.6	1.0	8.6	7.6	6.5	6.6
90	13.9	1.3	9.2	7.6	6.6	6.7
120	15.5	1.6	9.6	7.65	6.78	6.91



Time(min)

Fig(2) the conductivity of chlorobenzaldehyde of adsorption on clay with time



Time(min)

Fig(3) change of pH with time of adsorption on clays

Bentonite(B),kaolin(k),Attapulgite (A)

Photolysis of chlorobenzaldehyde on Bentonite , Kaolin and Attapulgite.

The irradiation results of chlorobenzaldehyde photolysis without and with clays shown in table (6) and fig(4a,5a,6a,7) .

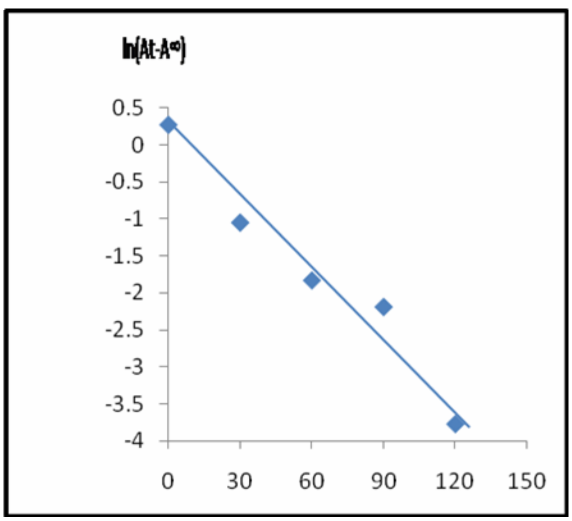
The reaction mixture was magnetically stirred and the resulting suspension mixture was irradiated with a medium – pressure mercury lamp.

Sevral samples were withdrawn at different irradiation time intervals and immediately centrifuged to remove clays particles.There samples were analyzed for chlorobenzaldehyde concentration .

Table (6) Absorption of chlorobenzaldehyde through photolysis with time .

t(min)	Bentonite			Kaolin		
	Abs.	A_t-A_∞	$Ln(A_t-A_\infty)$	Abs.	A_t-A_∞	$Ln(A_t-A_\infty)$
0	1.82	1.32	0.27	1.82	1.06	0.06
30	0.85	0.35	-1.05	0.82	0.07	-2.56
60	0.66	0.16	-1.83	0.79	0.04	-3.05
90	0.61	0.11	-2.19	0.78	0.03	-3.35
120	0.52	0.02	-3.77	0.77	0.02	-3.65
150	0.50			0.75		
t(min)	Attapulgite			Without surface		
	Abs.	A_t-A_∞	$Ln(A_t-A_\infty)$	Abs.	A_t-A_∞	$Ln(A_t-A_\infty)$
0	1.82	1.02	0.02	1.82	1.65	0.50
30	0.85	0.05	-2.97	0.53	0.36	-1.02
60	0.85	0.05	-2.99	0.41	0.24	-1.41
90	0.84	0.04	-3.10	0.22	0.05	-2.99
120	0.83	0.03	-3.50	0.21	0.04	-3.21
150	0.80			0.17		

Table (6) shows the results of photolysis with using clays gave aclose results ,on other hand the photolysis without a clay surface gave a better result and that because the particles of clays made a light shielding to chlorobenzaldehyde molecules



T(min)

Fig (4a)The photolysis of chlorobenzaldehyde with bentonite through time

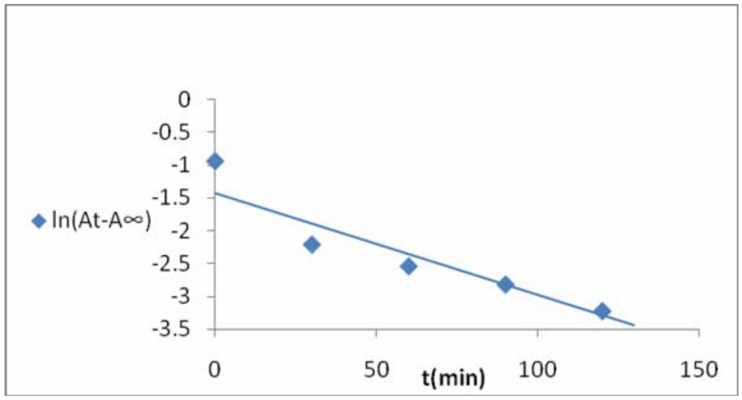


Fig (4b)The Adsorption of chlorobenzaldehyde with bentonite through time

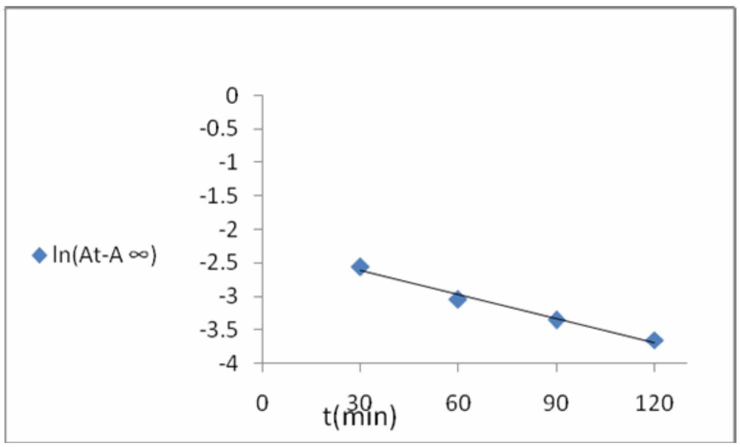


Fig (5a)The photolysis of chlorobenzaldehyde with Kaolin through time

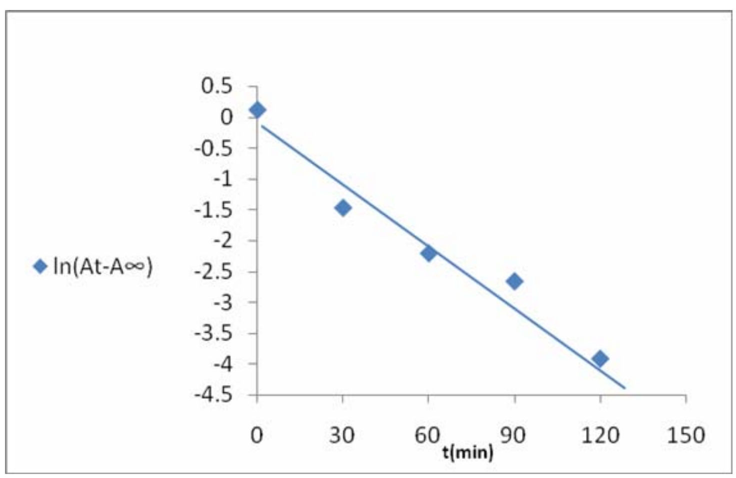


Fig (5b)The Adsorption of chlorobenzaldehyde with Kaolin through time

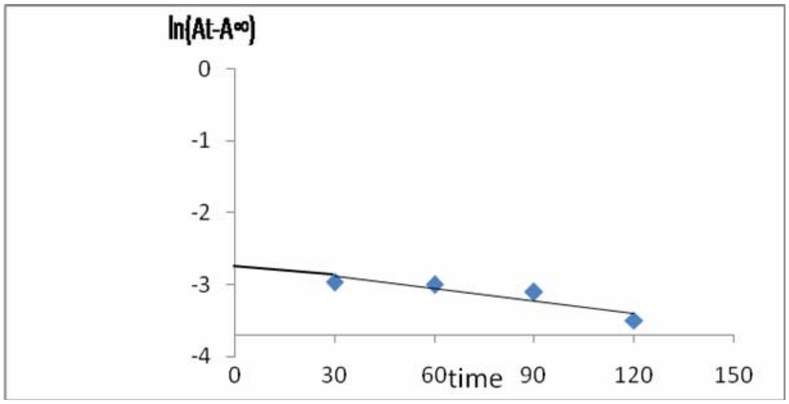


Fig (6a)The Photolysis of chlorobenzaldehyde with Attapulgite through time

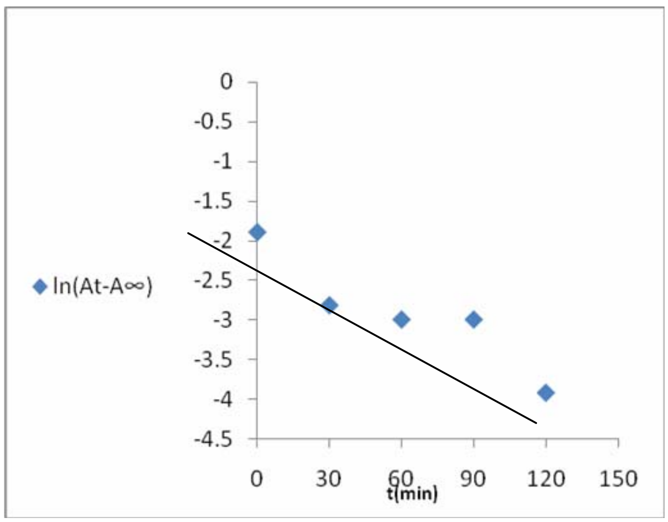


Fig (6b)The Adsorption of chlorobenzaldehyde with Attapulgite through time

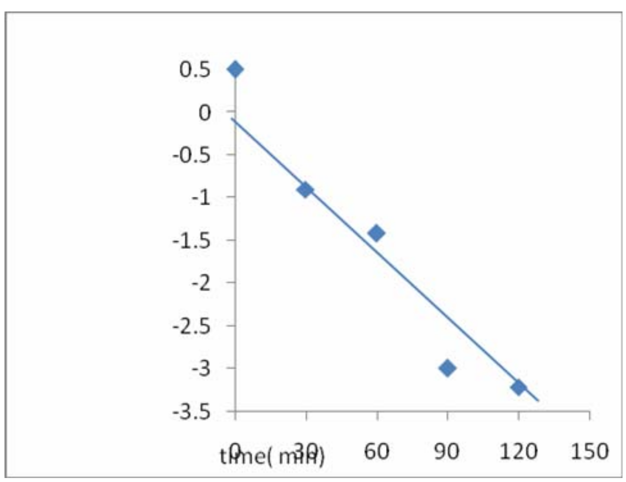


Fig (7)The photolysis of chlorobenzaldehyde without surface through time

Study of rate constant and rate of reaction for chlorobenzaldehyde with Bentonite , Kaolin and Attapulgite through adsorption and photolysis.

Table (7) shows the results of rate constant (k) and rate of reaction for chlorobenzaldehyde.The results shown that kaolin is more efficient than other clays in adsorption processes .While the photolysis process for chlorobenzaldehyde without any clays is more efficient through the values of rate constant (k). Clays possess-extensive sorption capacity because they have a high surface areas and lattices energy that release charges which are balanced by exchangeable cations.hence ,clays play an important role in pollution problems because they can retain large amounts of pollutants in soil.

The decrease in concentration of chlorobenzaldehyde was monitored with different irradiation time and different adsorption time fig(4a,4b.5a,5b,6a,6b) shows a straight line obtained from the plot of $\ln(A_t-A_\infty)$ versus irradiation (adsorption) time .From the slope of straight line the value of k .In order to see whether the adsorption process of chlorobenzaldehyde on surfaces will contribute to the decomposition . The equation(2) was applied to calculated reaction order (n) from the value of slope which was found a first order of reaction responsibility .

$\ln R = \ln K + n \ln C$ ……………(2)

Table (7) The value of rate constant and rate of reaction for chlorobenzaldehyde in adsorption and photolysis process.

	Adsorption			Photolysis		
Chlorobenzaldehyde With clays	k(min^{-1})	R (μmol/l)min^{-1}	$t_{1/2}$(min)	k(min^{-1})	R (μmol/l)min^{-1}	$t_{1/2}$(min)
Bentonite	0.017	2.55	40.76	0.03	4.5	23.10
Kaolin	0.027	10.5	25.66	0.03	4.5	23.10
Attapulgite	0.014	2.10	49.50	0.023	3.45	30.13
Without surface				0.031	4.65	22.35

Study of conductivity and pH of chlorobenzaldehyde through the photolysis.

The results of conductivity and pH of chlorobenzaldehyde through the photolysis processes are listed in table (8) and plotted in fig(4,5)

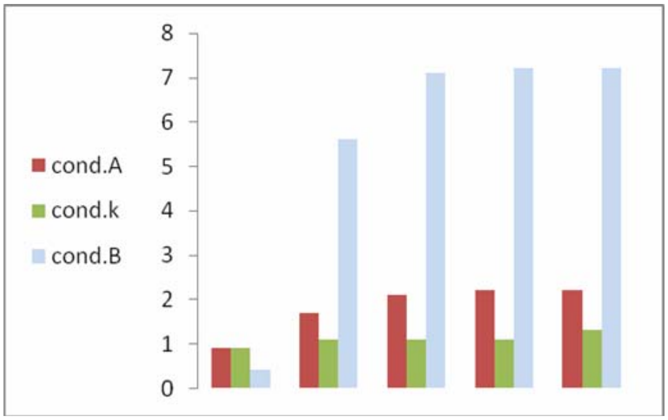
Table (8) The value of conductivity and pH for chlorobenzaldehyde solution through the photolysis.

Time (min)	Conductivity (μS/cm)	Conductivity (μS/cm)	Conductivity (μS/cm)	pH	pH	pH	Conductivity (μS/cm)	pH
	Bentonite	Kaolin	attapulgite	Bentonite	Kaolin	Attapulgite	Without surface	
0	0.4	0.9	0.9	5.2	5.2	5.2	0.5	5.1
30	5.6	1.1	1.7	5.9	6.7	6.2	0.6	4.9
60	7.1	1.1	2.1	6.1	6.6	6.8	0.7	4.8
90	7.2	1.1	2.2	6.2	6.4	6.8	0.8	4.4
120	7.2	1.3	2.2	6.6	6.2	6.9	0.8	4.6

The results of the conductivity during irradiation processes showed a high values for bentonite surface which indicating that bentonite is more efficient 10

than the other clays. In addition the dechlorination of chlorobenzaldehyde help for formation of conductive products.

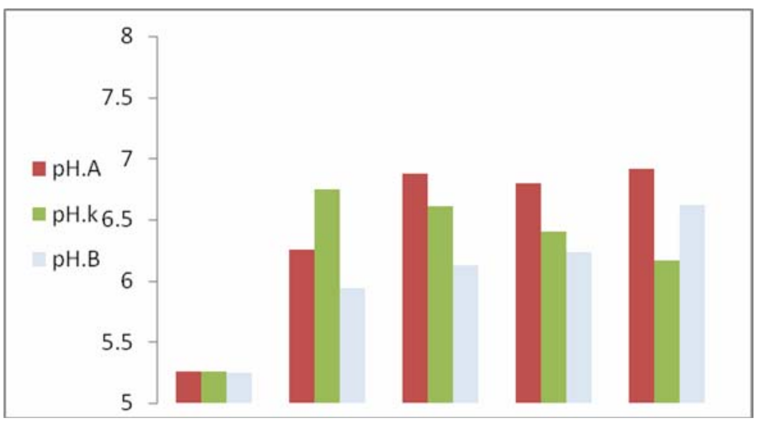
Table (8) showes an decreasing in acidity which indicating that the surface particales produced an acidic products in the mixture and on other hand the increasing in conductivity indicated that the surface help removing of an ions that the value pH of any solution less acidic the solution shows that the protons dissociated from the solvent spread by the surface in the form of a compound OH- or ion,leaving the remaining ions from water or alcohol solution ,which leads to increased conductivity and the lack of acidic. which rase the conductivity of the mixture.



0 30 60 90 120

Time(min)

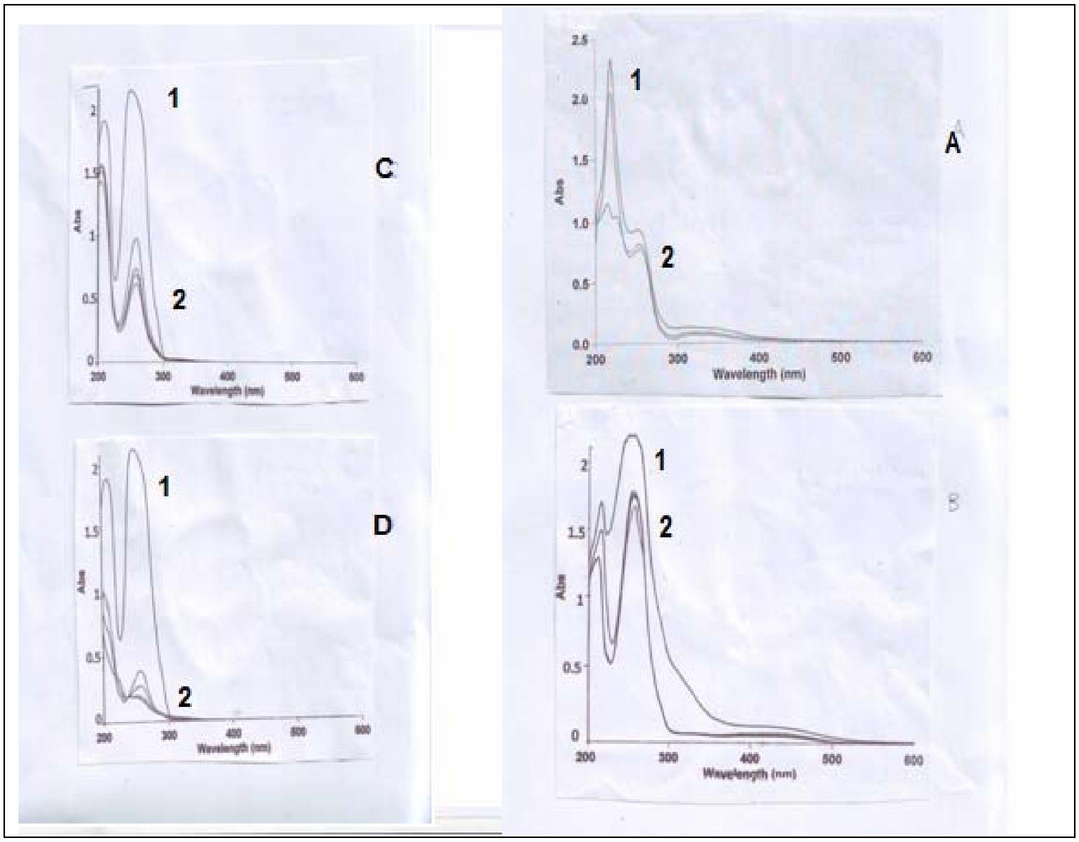
Fig(4) The change of conductivity of chlorobenzaldehydethrough photolysis with time



0 30 60 90 120

Time(min)

Fig(5) Change of pH with time of photolysis on clays



Fig(6) Different degradation spectra of chlorobenzaldehyde

A= Adsorption chlorobenzaldehyde with kaolin,(1)before Adsorption process ,(2) after Adsorption process
B= Adsorption chlorobenzaldehyde with Attapulgite ,(1)before Adsorption process ,(2) after Adsorption process
C=photolysis chlorobenzaldehyde with Bentonite ,(1)before photolysis process ,(2) After photolysis process
D= photolysis chlorobenzaldehyde without surface ,(1)before photolysis process ,(2) After photolysis process

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