Modeling, Synthesis and Application of Highly Performance Nano-Surface Catalysts towards Degradation of Some Organic Pollutants and Heavy Metals Capture from Industrial Water Drains

I- Modeling , Synthesis & of New Molecular Sieving for Organic Pollutants
II- Capture and Kinetics of Degradation of Some Selected Organic Pesticides

Khaled M. Elsabawy[a,b]* and Moamen S. Refat[a,c]

[a]Department of Chemistry, Faculty of Science, Taif University, Taif, Kingdom Saudi Arabia
[b]Materials Unit , Chemistry Department ,Faculty of Science ,Tanta University, Tanta, Egypt
[c]Department of Chemistry, Faculty of Science, Port Said University, Egypt

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ABSTRACT

New series of nano-molecular sieving were designated and visualized using computerized program DIAMOND IMPACT CRYSTAL version 3.2 and MERCURY version 2.3 Germany .The theoretical investigations was succeeded to design Hexa-Alumo-Silicates with chemical formula $Na_6Al_6Si_{10}O_{32}$ which has two different sizes of cavities to apply as nano-molecular sieving materials .The synthesized   molecular sieving was carefully characterized via XRD and SEM to prove the internal structure of the new molecular sieving material. A kinetic studies were investigated carefully of two types pesticides degradation . H_2O_2 loaded over molecular sieving materials ($Na_6Al_6Si_{10}O_{32}$) was applied as oxidative environmentally friend agent to decompose organic pollutant . The nano-synthesized   molecular sieving exhibited very good efficiency towards captures of organic pollutant from industrial water drains such as atrazine herbicides and carbaryl insecticides in presence of hydrogen peroxide . Many of the kinetic parameters were investigated in this article, results obtained indicated that, the rate of oxidative degradation of pesticides (atrazine herbicides and carbaryl insecticides) were found to be pH-dependent. The mechanism was proposed and the activation parameters were calculated.

Keywords : Organic Pollutant; Atrazine; Herbicides; Insecticides, Modeling.

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INTRODUCTION

Atrazine, 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, an organic compound [1] consisting of an s-triazine-ring is a widely used herbicide. Its use is controversial due to widespread contamination in drinking water and its associations with birth defects and menstrual problems when consumed by humans at concentrations below government standards. Although it has been excluded from a re-registration process in the European Union,[2] it is still one of the most widely used herbicides in the world. Atrazine is used to stop pre- and post-emergence broadleaf and grassy weeds in major crops.

Carbaryl herbicides   *Atrazine insecticides*

(1-naphthyl methylcarbamate)   *1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine*

Carbaryl (1-naphthyl methylcarbamate) is a chemical in the carbamate family used chiefly as an insecticide. It is a white crystalline solid commonly sold under the brand name Sevin, a trademark of the Bayer Company. Union Carbide discovered carbaryl and introduced it commercially in 1958. Bayer purchased Aventis CropScience in 2002, a company that included Union Carbide pesticide operations. It remains the third most-used insecticide in the United States for home gardens, commercial agriculture, and forestry and rangeland protection. Approximately 11 million kilograms were applied to U.S. farm crops in 1976 .

Beltran et al.[1] were investigated the oxidation of atrazine in water by means of direct photolysis at 254 mm and with hydrogen peroxide combined with a u.v radiation. The influence of bicarbonate/carbonate ions and a commercial humic substance on the oxidation rate has been observed. The oxidation rate is especially fast with the combination of hydrogen peroxide and u.v. radiation.

Technical atrazine and many other pesticides constitute one of the largest groups of organophpsphorous compounds that represent an increasing environmental danger[1, 2]. One of the novel technologies for treating polluted water and wastewater is the advanced oxidation processes (AOPs), by which hydroxyl radicals ($\cdot$OH) are generated to degrade organic pollutants [3].

Throughout the 20th century, the mechanisms, kinetics, and products of the AOPs using hydrogen peroxide (H_2O_2), ozone (O_3), UV or ultrasonic irradiation, titanium dioxide (TiO_2), and Fenton's reagent, which is a combination of ferrous ions and H_2O_2, were investigated extensively. These treatments were studied separately or in various combinations [4-7].

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Technical Carbaryl and their formulation types have a broad spectrum insecticidal control of sucking and chewing insects, including aphids, house flies, mosquitoes, scale insects and spider mites. Used in fruits, ornamentals, beans, vegetables, and stored products [8].

J.Wang et al. [9] confirm that nanometer rutile titanium oxide powder TiO_2 can be used as nano-catalytic degradation of organic pollutants for treating organic waste water.

The essential goals of present article are modeling and application of new Hexa-Alumo-Silicates with chemical formula $Na_6Al_6Si_{10}O_{32}$ which has two different sizes of cavities to apply as nano-molecular sieving materials for oxidative degradation of technical atrazine and carbaryl pesticide.

MATERIALS AND METHODS

II.I.A.Materials Modeling :
New series of nano-molecular sieving were designated and visualized using computerized program DIAMOND IMPACT CRYSTAL version 3.2 and MERCURY version 2.3 Germany . The theoretical investigations was succeeded to design Hexa-Alumo-Silicates with chemical formula $Na_6Al_6Si_{10}O_{32}$ which has two different sizes of cavities to apply as nano-molecular sieving materials .

II.I.B.Catalyst synthesis:
The sample with general formula $Na_6Al_6Si_{10}O_{32}$ was prepared by conventional solid state reaction route and sintering procedure using appropriate amount of Na_2CO_3, and $(Al)_2Si_2O_5$ each purity >99%. The mixture was ground in an agate mortar for one hour. Then the finely ground powder was subject to firing at 1050 ^oC for 10 hours and reground and finally pressed into pellets with thickness 0.15 cm and diameter 1.2 cm. Sintering process was carried out at 950 ^oC for 12 hours. Then the furnace is cooled slowly down to room temperature. Finally the materials are kept in vacuum desiccator .

II.II. Carbaryl and Atrazine solutions synthesis :
Technical Carbaryl and Atrazine insecticides were supplied from Kafr Elzayat for Pesticides and Chemicals Co., all investigations were performed spectrophotometrically at λ_{Max} of Atrzine 220 nm / 378 nm and maximum absorption λ_{Max} of Carbaryl was 280 nm / 412 nm respectively .

II.III. Molecular Siever Characterization:
II.III.I. X-Ray diffraction (XRD):
The X-ray diffraction measurements (XRD) were carried out at room temperature on the fine ground $Na_6Al_6Si_{10}O_{32}$ systems on the range (2θ =5-70°) using Cu-Kα radiation source and a computerized [Bruker Axs-D8 advance] X-ray diffractometer with two theta scan technique. Analysis of the corresponding 2θ values and the interplanar spacing d (A^o) by using computerized program proved that the compound is mainly typical to the visualized one which confirm the quality of preparations .

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II.III.II. Scaning Electron – Microscope:
Scaning electron microscope (SEM) measurements were carried out using small pieces of prepared samples on different sectors to be the actual molar ratios by using "TXA-840,JEOL-Japan" attached to XL30 apparatus with EDX unit, accelerant voltage 30kv, magnification 10x up to 500.000x and resolution 5. nm. The samples were coated with gold.. The average grain size was calculated and found to be 3.19 µm.
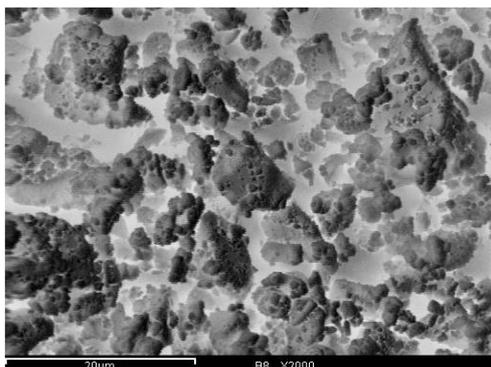
SE-micrograph recorded for $Na_6Al_6Si_{10}O_{32}$ with estimated grain size 3.19 µm which is completely matched with literature specially for silicates type structure .

II.IV. Kinetic measurements:
The kinetic measurements of the reaction were carried out using UV-VIS spectronic 6021 spectrophotometer at $\lambda_{max.}$ 378 and 412 nm for technical carbaryl and atrazine insecticides respectively . Deionized water was used in preparations of all solutions.

RESULTS AND DISCUSSION

III.I.Modeling of Molecular Catalyst For Sieving Process :
New series of nano-molecular sieving were designated and visualized using computerized program DIAMOND IMPACT CRYSTAL version 3.2 and MERCURY version 2.3 Germany . The theoretical investigations was succeeded to design Hexa-Alumo-Silicates with chemical formula $Na_6Al_6Si_{10}O_{32}$ which has two different sizes of cavities to apply as nano-molecular sieving materials.

From Figure 1 one can notify that the unit cell of molecular formula $Na_6Al_6Si_{10}O_{32}$ crystalize as hexagonal crystals and aluminum ,silicon occupy the sama crystal sites . Sodium ions located in between silicons atoms perpendicularly to the plan of oxygen atoms .

Visualizing the crystallographic data of molecular formula $Na_6Al_6Si_{10}O_{32}$ using computerized program DIAMOND IMPACT CRYSTAL version 3.2 and MERCURY version 2.3 Germany gave us the opportunity to judge the success of theses formula as molecular sieving materials see Fig.2 and Table.1 . Fig.2 displays the visualized XRD of $Na_6Al_6Si_{10}O_{32}$ formulated to apply as molecular sieving materials with characteristics peak lies at ~ two theta = 28 as clear in Fig.2.
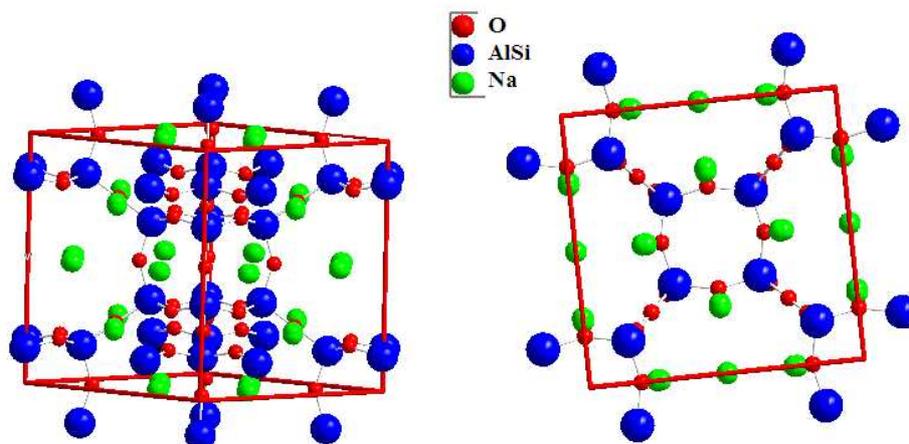
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Fig.1 : Hexagonal crystal form of proposed Sodium -Alumino-Silicates with P6₃ Space Group
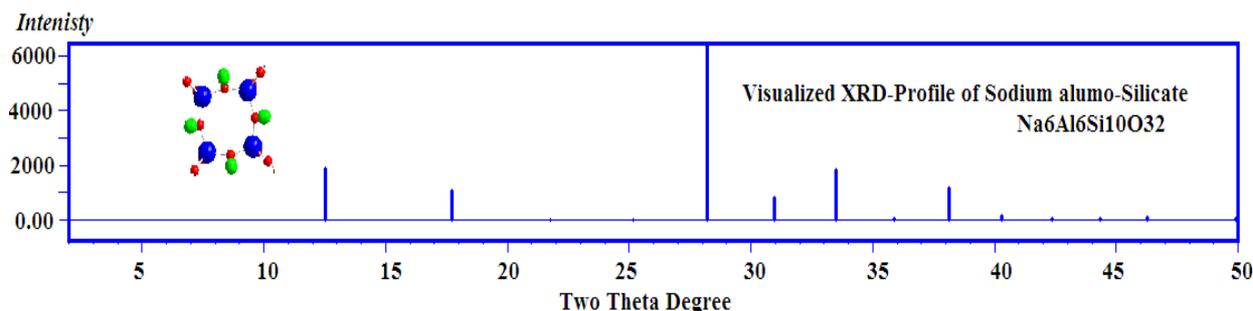

Fig.2: Visualized XRD-profile for modeled formula $Na_6Al_6Si_{10}O_{32}$

Table.1 Selected bond distances and angles inside unit cell of hexagonal $Na_6Al_6Si_{10}O_{32}$

Atom1	Atom2	D1-2	Atom3	D1-3	Angle213
O1	Al1|Si1	1.6243	Al1|Si1	1.6243	147.646
O2	Al1|Si1	1.6281	Al1|Si1	1.6281	180.000
Al1|Si1	O1	1.6243	O1	1.6243	109.852
	O1	1.6243	O1	1.6243	109.852
	O1	1.6243	O2	1.6281	109.087
	O1	1.6243	O1	1.6243	109.852
	O1	1.6243	O2	1.6281	109.087
	O1	1.6243	O2	1.6281	109.087

From table .1 it is clear that there is two different types of oxygen atom symbolized as O_1 and O_2 respectively while aluminum and silicons atoms are located on the same sites inside the unit cell of $Na_6Al_6Si_{10}O_{32}$ which is hexagonal with P6₃ *space group* .As clear there are two types of bond distances nominated as O_1-$AlSi_1$ and O_2-$AlSi_1$ which found 1.6243 and 1.6281 Å respectively . The elongation occurred on the O_2-$AlSi_1$ bond length is due to shielding effect caused by oxygen atoms that surround the silicones atoms sties.

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The angles inside unit cell have no violation only O1-Si1-Si1 and O2-Si1-Si1 angles are different in attitude due to environmental atoms effects recording values 147.64° and 180° respectively. The rest of angles are ranged between two values 109.85° and 109.08° respectively.
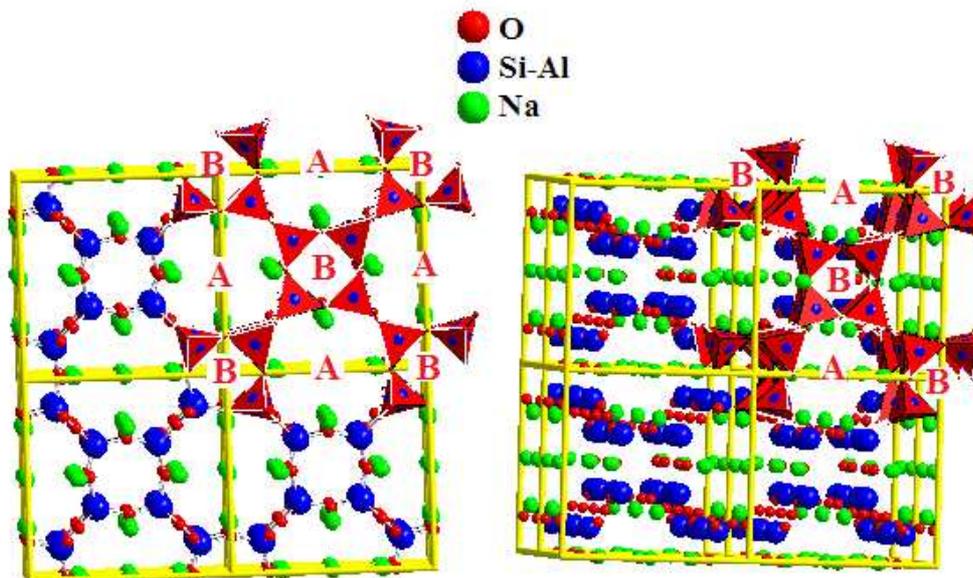

Fig.3   2x2x2 superunit cell of Hexagonal $Na_6Al_6Si_{10}O_{32}$ showing the two different sizes of cavity symbolized as cavity A and B respectively

Fig.3 displays the 2x2x2 super-unit cell of the synthesized hexagonal $Na_6Al_6Si_{10}O_{32}$ .It is clear that the synthesized compound are having two different kinds of cavities the first one is hexagonal in shape and large in size in contrast with second one which is squares as clear in fig.3.
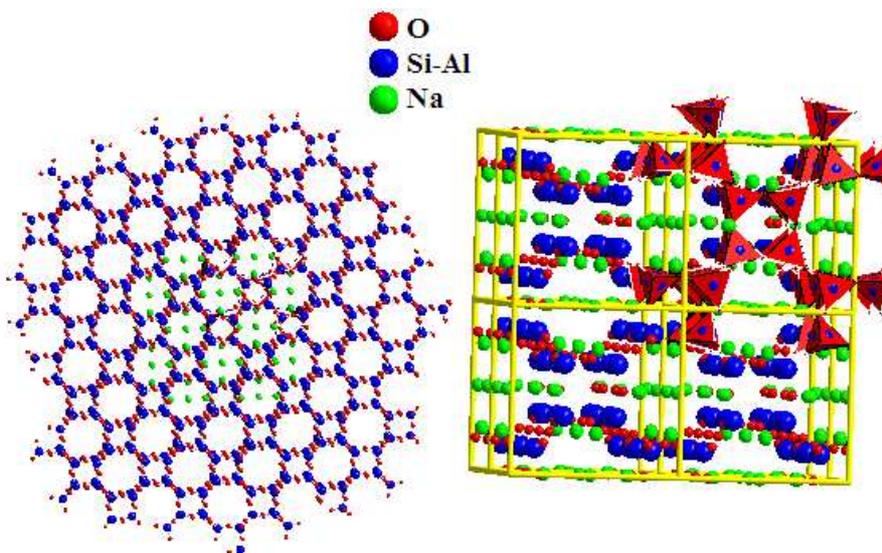

Fig.4   3D-framenet of proposed Sodium alumino-silicates molecular sieving compounds .

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These two different sizes of cavities inside the same compound allow us to apply such these compound to sieve to different kinds of ionic radius in molecular sieving process .The hexagonal cavity consists from eight octahedron units and squ*a*res one forms from only four units of silicon-octahedra.
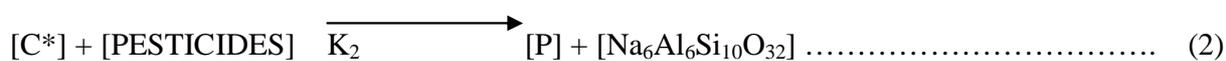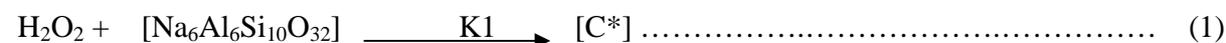
It is well known that the molecular sieving process is ambient conditions dependent which means all selective process by using $Na_6Al_6Si_{10}O_{32}$ must be controlled to be efficient in selectivity of organic moieties such as carbaryl or atrazine pesticides.

As clear in Fig.4 the regular shape of the meshes confirm the success of sodium alumino silicates as molecular sieving materials with huge surface area in the nano-range that enhances the capability of ions selective due to two factors 1st is the huge of surface area and 2nd is the two cavity sizes in the 3D-framenet structure of modeled $Na_6Al_6Si_{10}O_{32}$ nano-structure .

III.II Mechanism and order of reaction:

The mechanism of oxidative degradation of technical Atrazine and Carbaryl were proposed in our investigations as two step process. The first step, is the fast one which includes the reaction between hydrogen peroxide and Hexa-Alumino-Silicates $Na_6Al_6Si_{10}O_{32}$ solid surface irreversibly with a rate constant K_1 (Eq. 1) to form intermediate activated complex C*, but this step is the fast one and irreversible.

The second step is the rate-determining step (slow step) includes the reaction between activated complex C* with the technical Atrazine or/and Carbaryl with a rate constant K_2 (Eq.2).

$$H_2O_2 + [Na_6Al_6Si_{10}O_{32}] \xrightarrow{\quad K1 \quad} [C^*] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (1)$$

$$[C^*] + [PESTICIDES] \xrightarrow{K_2} [P] + [Na_6Al_6Si_{10}O_{32}] \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (2)$$

Where [P] is decoloured oxidative PESTICIDES , [PESTICIDES] = [Atrazine] or [Carbaryl] .

The mechanistic sequences may describes as follow: the addition of H_2O_2 to the catalyst $[Na_6Al_6Si_{10}O_{32}]$ surface which includes different oxidation states of different ions but generally we will use symbol M^{+n} which indicate to all positive cations on the catalyst surface (Al^{3+}, Na^{1+} and Si^{4+}) which reacts with H_2O_2 forming μ^2 bound peroxide, which stabilized by hydrogen bonding [10-11] forming activated complex [C*] that finally reacts rapidly reversibly with substrate malathion oxidizing it as described in equation (2).
Robbins *et al*. [10] studied the activation of hydrogen peroxide for oxidation of quinaldine blue indicator by using copper II complexes and they reported that, using of metal redox mechanisms [12] for activation of H_2O_2 decomposition but, in their mechanism of activation H_2O_2 coordinates fastly with copper II without any change in its oxidation state.

III.II. Order of the reaction:

The order of reaction is evaluated by application the conditions of pseudo-first order reaction by keeping H_2O_2 in large excess and consequently, the overall reaction can be expressed as shows in

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Eq.(3). $[H_2O_2] + [Na_6Al_6Si_{10}O_{32}] + [PESTICIDES] \xrightarrow{\;K_{true}\;} [PESTICIDES]$…………... (3)

Hence the rate of oxidation depends only on the concentration of

[PESTICIDES] = carbaryl /atrazine and can be expressed as follows :

Rate = $K_{true} [H_2O_2] [Na_6Al_6Si_{10}O_{32}] [PESTICIDES]$…………………………………………(4)

Where K_{true} is the true rate constant but, $[Na_6Al_6Si_{10}O_{32}]$ and $[H_2O_2]$ >>> [PESTICIDES]

Thus, rate = $K_{obs.}$ [PESTICIDES], where $K_{obs.} = K_{true} [H_2O_2] [Na_6Al_6Si_{10}O_{32}]$ (5)

According to the first order reaction condition a plot between $\ln(A_t - A_0)$ and time was constructed giving straight lines (Fig.5$_{a,b}$) with slop equal to observed rate constant $K_{obs.}$ and hence, the true rate constant K_{true} can be easily evaluated by knowing [catalyst] and $[H_2O_2]$.In this respect, A_t and A_0 are the absorbance of the [PESTICIDES] at time t and infinity, respectively.

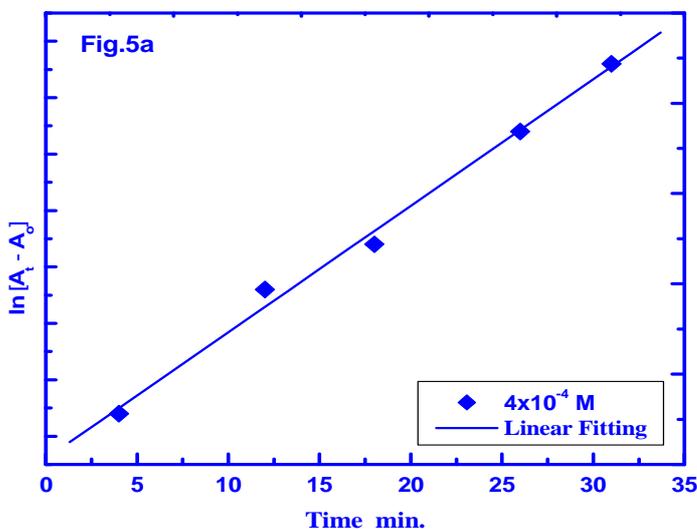**Fig.(5a): The first oxidative reaction of [Atrazine]=4x10^{-4}M with wt.of catalysis = 0.02 g, in the presence of H_2O_2 = 0.05 M, Temp. 30°C and pH = 7.**
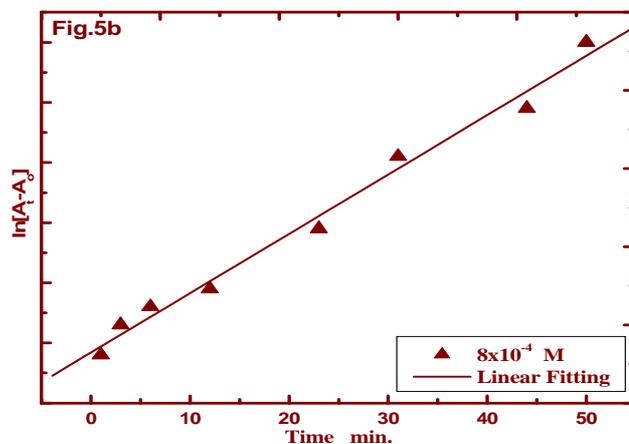
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Fig.(5b): The first oxidative reaction of [Carbaryl]=8x10⁻⁴M with wt.of catalysis = 0.02 g, in the presence of H₂O₂ = 0.05 M, Temp. 30°C and pH = 7.

III.III. Pesticides concentration effect:

Fig. ($6_{a,b}$) show the relation between the concentration of Atrazine and H_2O_2 respectively with the evaluated rate constant ($K_{obs.}$) and it is found that, the values of rate constant increase with increasing both of atrazine concentration and hydrogen peroxide confirming that the oxidative degradation of atrazine is a first order reaction under these conditions and hydrogen peroxide dependent .

According to Eq.1 and Eq.2, both of H_2O_2 and pesticides play an important role in the reaction sequence since the hydrogen peroxide initially attacks the active centers on the catalyst surface forming μ^2 bound peroxide, which stabilized by hydrogen bonding [10-11] forming activated complex [C*] that finally reacts rapidly and reversibly with substrate pesticides oxidizing it as described in equation (2). And by the same the increasing in the substrate pesticides concentration must leads to correspondence increase in the reaction rates.

III.IV. Temperature effect:

Fig.(7) display the effect of temperature on the reaction rate of degradation of the pesticide. The reaction between [pesticide] = 6x10⁻⁴ M with 0.02 g of the catalyst at pH = 7 and H_2O_2 = 0.05 M was carried out at different temperatures.

It is found that, the rate of oxidative degradation of carbaryl with $Na_6Al_6Si_{10}O_{32}$ silicates catalyst increases with increasing the temperature. It clear that the increasing of temperature causes an activation to the surface area of the $Na_6Al_6Si_{10}O_{32}$ silicates catalyst that already reacted to reform new one and consequently the numbers of active centers will be raised yielding to correspondence increase on the reaction rate degradation process.
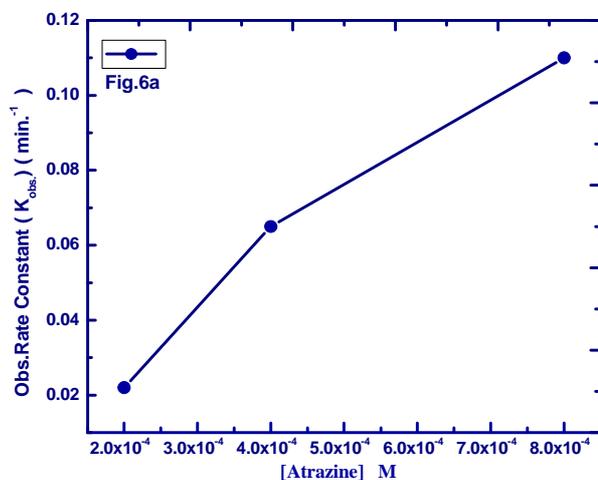
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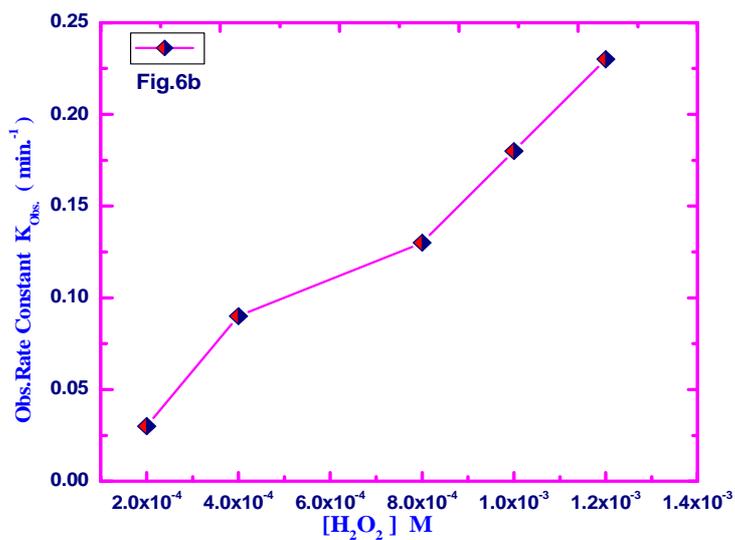**Fig.(6_a): The variation of observed rate constant ($K_{obs.}$) versus Atrazine concentrations.**

Fig.6_b: The variation of observed rate constant ($K_{obs.}$) versus H_2O_2 concentrations.
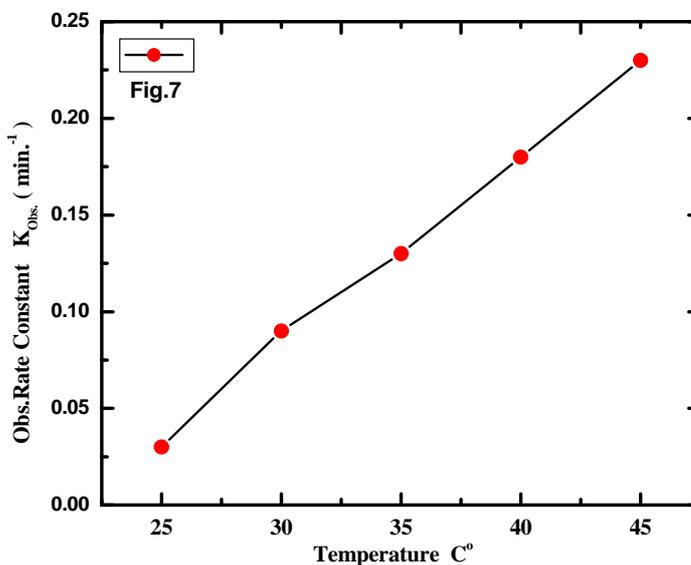
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Fig.(7): The variation of observed rate constant (K$_{Obs.}$) versus temperatures.

III.VI. Determination of the activation parameters:

Fig.(8) displays the Arrhenius plot of ln K versus 1/T, where T is the absolute temperature K is the observed reaction rate constant at this temperature in accordance with the Eyring- equation [13].

$$K = k_bT/h.e^{\Delta G*/RT}$$ …………………………………………….. ……………..……………….(6)

Where k_b and h are the Boltzmann's and Plank's constants, respectively.

From this plot, the activation enthalpy was found to be $\Delta H* = -234.6$ KJ/mol & $\Delta G* = 47.8$ KJ/mol and $\Delta S* = 67.8$ J/mol K. These thermodynamic activation parameters help to understand and support the proposed catalytic oxidative mechanism enhancing us to estimate how much the ease of such these reaction to occur spontaneously.
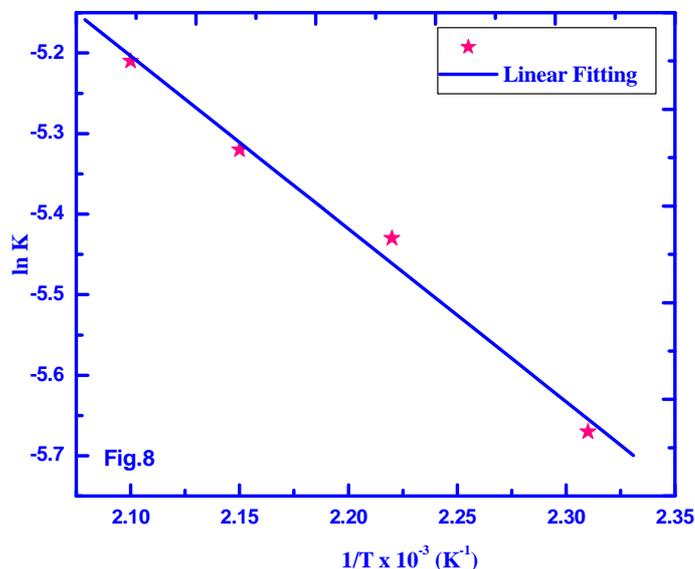
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Fig.(8): Arrhenius plot for degradation of atrazine with $Na_6Al_6Si_{10}O_{32}$ silicates catalyst .

III.VII. Salt effect:

Fig.(9$_{a,b}$) show the effect of the [KCl] and [KBr] on the oxidation reaction rate of both atrazine /carbaryl. It is clear that, the increasing of salt concentration leads to an increase in the total ionic strength in the reaction medium and consequently increasing the adsorption of the substrate on the catalyst surface. These results are in agreement with number of articles like [15-19] in which the kinetics investigations on the degradation of hazardous materials organic substrates were performed in presence of hydrogen peroxide and metal oxide surface catalyst [20,21].
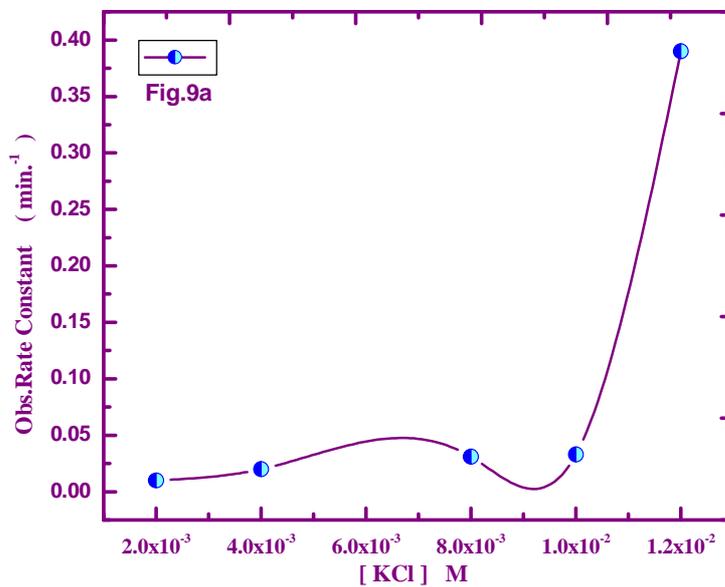
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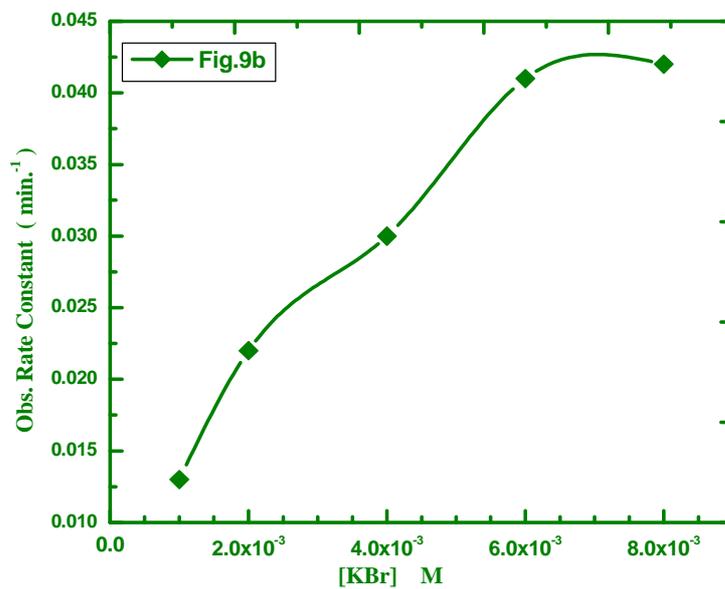**Fig.(9_a): The variation of observed rate constant ($K_{obs.}$) versus conc. of KCl.**

Fig.(9_b): The variation of observed rate constant ($K_{obs.}$) versus conc. of KBr.

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CONCLUSIONS

The conclusive remarks can be summarized in the following points :

1- Modeled Hexa-Alumo-Silicates succeeded as molecular siever and environmental catalyst .

2- Degradation of atrazine and carabaryl pesticides over Hexa-Alumo-Silicates are succeeded and proved that the degradation is first order reaction and concentration dependent .

3- The modeled $Na_6Al_6Si_{10}O_{32}$ silicates have two different kinds of cavities capable to capture two different sizes of atomic radius .

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