

## ROLE OF CATALYST PREPARATIONS FOR THE REMOVAL OF ENVIRONMENTAL HAZARDS

E .M .Ezzo , S.A.Hassan , M.A.El – kherbawi and A.S.Hassan .

Department Of Chemistry, Weman Faculty For Science, Ain Shams University, Asmaa Fahmi Street , Heliopolis, Cairo (Postal Code)11757, Egypt.

**ABSTRACT:** *The kinetics of heterogeneous catalytic conversion of cyclohexane over Cu supported active carbon catalysts at 280-380 °C and time of contact 13.63-6.52 min were studied in flow system under normal pressure . The solids were prepared by impregnation of Cu and active carbon which was treated by phosphoric acid of percent ratio 5,10 and 15% producing CuACPI ,CuACPII and CuACPIII respectively . The prepared solids were characterized by TG A , DTA, X-ray diffraction pattern and BET surface area measurements. The catalytic activity of the prepared catalysts was studied for the conversion of cyclohexane at temperature ranging from 280 -380° C by using flow system techniques, the liquid and gaseous products were analyzed by gas liquid chromatography .The catalytic activity and selectivity toward toluene formation over the catalysts of Cu supported on an active carbon were investigated . Adsorption isotherm terms for the prepared solids and their application for the removal of different heavy metal ions were studied.*

**KEYWORDS:** Active Carbon, Dates Stones, Impregnation Method, Cyclohexane Conversion Adsorption Isotherms.

### INTRODUCTION

Catalytic hydrogenation and dehydrogenation reactions play a key role in the chemical industry particularly in the synthesis of various pharmaceuticals and fine chemicals apart from bulk chemicals . Although studied and utilized to a much lesser extent than hydrogenation reactions, dehydrogenation reactions involving organic compounds can also play an important role in the production of fine chemicals. Dehydrogenation reactions are typically endothermic<sup>1</sup> and conversions can be equilibrium controlled; in addition, low H<sub>2</sub> pressures may enhance deactivation due to coking, and a selectivity consideration of dehydrogenation versus dehydration as well as hydrogenolysis can become important when oxygenates are the reactants<sup>2</sup>. The dehydrogenation and alkylation of cyclohexane to benzene and toluene are a well-known industrial process<sup>3,4</sup> , as there are a very large number of petrochemicals produced from the toluene aromatics and these reactions are primarily carried out on copper catalysts because of their high selectivity to the dehydrogenation product<sup>5</sup>. The principal catalyst that has been used in these reactions is copper chromite; however, new EPA restrictions now prohibit the disposal of chromite in landfills. Thus, there is an incentive to develop new replacement of Cu catalysts which contain no chromium. The AC is promising adsorbent owing of its large surface area and high porosity<sup>6-9</sup> . In the present study AC was prepared cheapen from agricultural waste of date stone by chemical activation process using H<sub>3</sub>PO<sub>4</sub> of different concentration as activator . The selectivity and activity of the prepared solids were investigated through the heterogenous catalytic conversion of cyclohexane in flow system under normal pressure. The evaluation of the efficiency of the prepared solids for the removal of cadmium,

ferrous, nickel and cobalt ions from an aqueous solution was studied as environmental application and the physicochemical studied was carried for all prepared samples.

## EXPERIMENTAL DETAILS.

### Materials

cyclohexane  $C_6H_{12}$  (sigma- Aldrich b.p.  $80.7\text{ }^\circ\text{C}$ , chromatographically pure), copper (II) acetate  $Cu(CH_3COO)_2$  (Anhydrous pure, M Wt= 181.65, Koch –light laboratories), Hydrochloric acid HCl (d.1.18, p. 30-32%, BDH. laboratories), Phosphoric acid  $H_3PO_4$  (85%, M Wt = 98.00, ETWA 1,17), Ferric(III)nitrate  $Fe(NO_3)_3 \cdot 9 H_2O$  (Ex. Pure, M Wt = 404.00, Oxford laboratories), Cobalt acetate  $Co(CH_3COO)_2 \cdot 4 H_2O$ , (Ex. Pure, M Wt= 249.08, Koch –light laboratories), Nickel sulfate  $NiSO_4 \cdot 7H_2O$ , (Ex. Pure, M Wt= 280.88, Koch –light laboratories), Cadmium nitrate  $Cd(NO_3)_2 \cdot 4 H_2O$  (Ex. Pure, M Wt= 308.482, PRS-laboratories).

### Synthetic Method

#### An active carbon supports.

Date stones were received isolated from dates of palm trees that grow in Kom Hamada, Al Buhayrah, Egypt. The process of washing, agitation, and decantation was continued and the remaining hard stones were used in the experiments<sup>10</sup>. The clean stones were then dried at  $130^\circ\text{C}$  for about 24 h, then they were crushed using Pyrex mortar and sieved to the desired particle size. 85 grams of specified size particles was mixed with 300 ml solution of  $H_3PO_4$  of 85% concentration. Then it was left for 24 h at room temperature using impregnation ratios equal to 1:1. The solid particles were then washed with distilled water and filtered. The particles were then dried at  $85^\circ\text{C}$  for about 24 h followed by activation at temperature equal  $500\text{ }^\circ\text{C}$ . The pyrolysis products were grinded into fine powder. It was then thoroughly washed with 500 mL solution of 0.10 N HCl, and then rewashed thoroughly with distilled water. Finally, AC was dried at  $110^\circ\text{C}$  for 2 h and kept in tightly closed plastic bottles and carefully labeled.

#### Catalyst preparation.

All AC-supported Cu solids were prepared by a wet impregnation<sup>1</sup> technique. The AC (0.5 mm) was dried in an electric oven at  $140^\circ\text{C}$  for 2 h. A solution of copper acetate of known concentration (5, 10, and 15%) was allowed to pass drop wise over AC with constant stirring. The products obtained were dried in an electric oven at  $140^\circ\text{C}$  for 4 h. The solid was crushed in Pyrex mortar. The desired diameter of grain size (0.25-0.5 mm) by appropriate sieves was chosen for catalytic measurements.

#### Adsorbate aqueous solution.

The 10, 20 and 30 mg/l of  $Co(CH_3COO)_2$ ,  $NiSO_4 \cdot 7H_2O$ ,  $Fe(NO_3)_3 \cdot 9H_2O$  and  $Cd(NO_3)_2 \cdot 4H_2O$  aqueous solutions were used to prepare heavy metal ions stock.

#### Characterization Techniques

BET surface area, pore volume and average pore diameter for various samples were derived from nitrogen adsorption-desorption isotherms measured at  $-195\text{ }^\circ\text{C}$  (77K) (Micromeritics ASAP2020 USA). Before the measurement, each sample was degassed at  $550^\circ\text{C}$  for 3 h.

The X-ray diffraction patterns of the solid samples after calcinations for 4 h at  $500^\circ\text{C}$  were recorded on film at room temperature in a Philips model diffractometer type X Pert MPD at

$\lambda=1.54 \text{ \AA}$  with Cu-K $\alpha$  radiation and graphite monochromator, data collected over the range  $4 < 2\theta < 70$  with continuous scan mode TGA and DTA were measured for fresh samples of the prepared solids were measured using Shimadzu Japan 50H apparatus in temperature range 0 up to 900°C using thermo balance under a heating rate 10 °C/ min in air atmosphere.

### Heterogeneous Catalytic Study:

The catalytic performance of the sample was evaluated by using flow system technique<sup>11,12</sup>. The analysis of the liquid and gases products was carried out chromatographically by gas – liquid chromatography (perkin Elmar 8600) double flame ionization detector on a DB-Wax column 30m x 0.53 mm id , 1 $\mu$ m(USA) . The temperature of injector and detector is 200 and 250 °C respectively which is recommended to apply for alcohols, using nitrogen as carrier gas

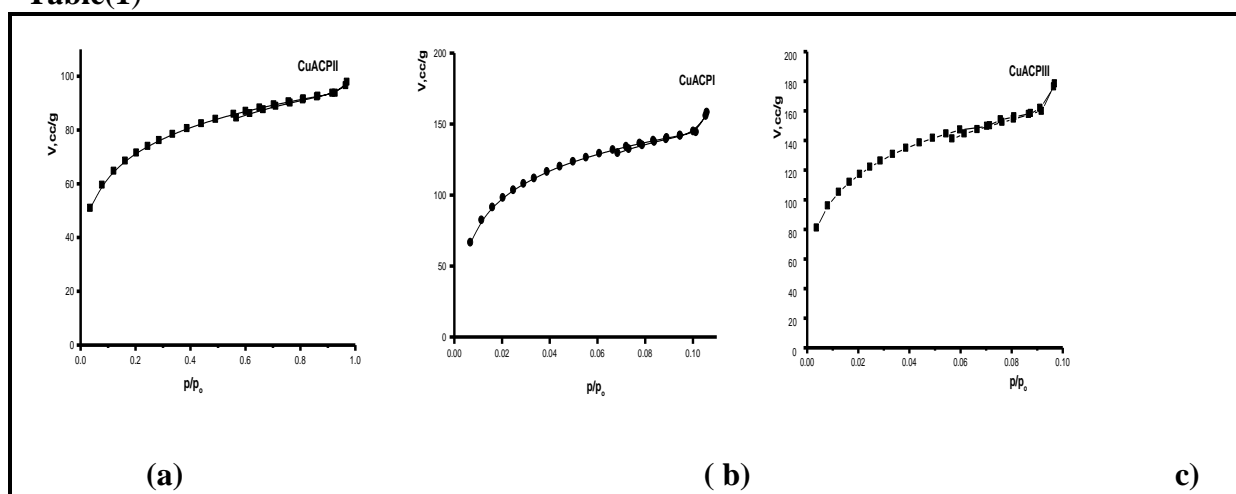
### Adsorption Isotherm for the Removal of Different Ions.

The prepared solids were tested for its efficiency in removing heavy metal ions such as (Co<sup>+2</sup>, Ni<sup>+2</sup>, Fe<sup>+3</sup> and Cd<sup>+2</sup>) using UV-Vis spectrometer in the range of (340-630nm) .The parameters studied include initial heavy metal ions concentration and contact time .Both Langmuir and Freundlich adsorption isotherm equilibrium models<sup>13</sup> were used for the analysis of equilibrium adsorption data.

## RESULTS AND DISCUSSION:

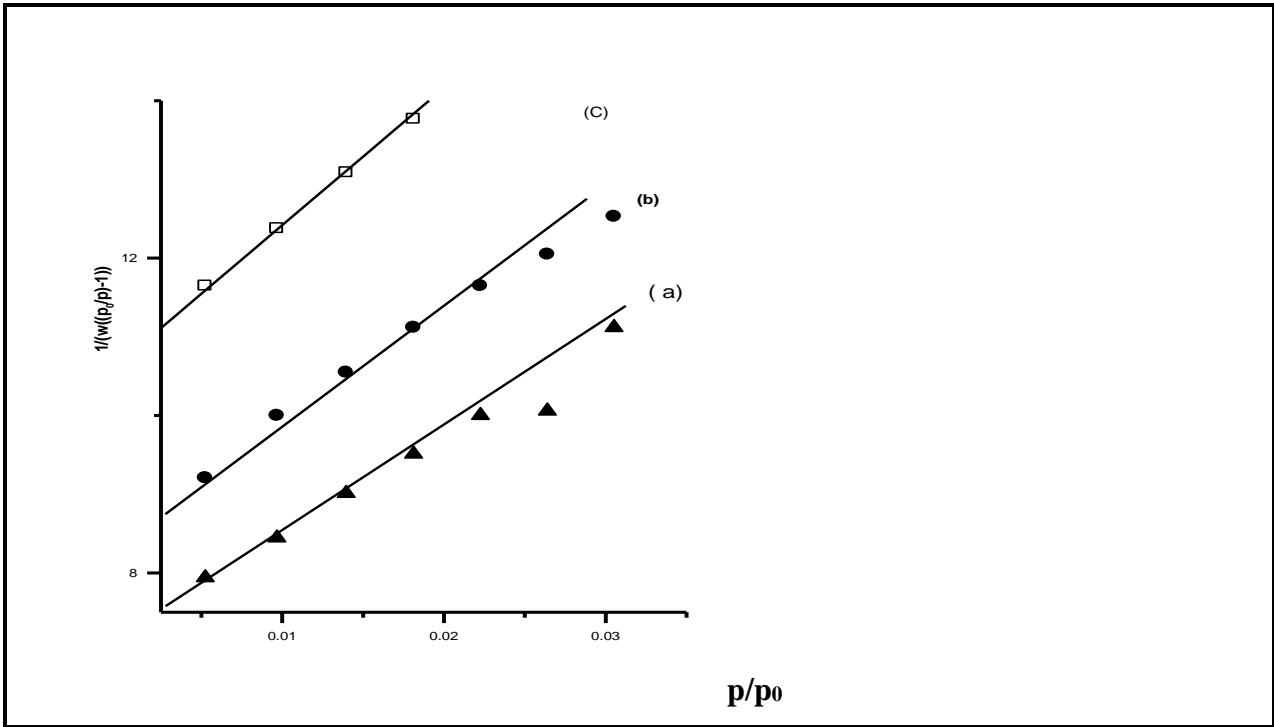
### Characterization of Catalysts.

The Fig 1(a,b and c) represents the nitrogen physisorption measurement of three samples of type II isotherm of the Brunauer-Deming –Teller classification of mesoporous solids<sup>14</sup>. The Fig 2 (a,b and c) shows the linear plot for nitrogen adsorption according to the BET equation . The specific surface area  $S_{BET}$  estimated for CuACPI, CuACPII and CuACPIII catalysts are given in Table(1) using the conventional BET equation . The pore volume distribution analysis was performed using the modeless method<sup>14</sup> for three samples calcinated at 500°C, for the solids, are shown in Fig 3(a,b and c).. The method adopt the calculation depending on the hydraulic radius of pores of any shape which is the half the radius of acylinder and half the distance between the walls of the parallel plate pore . Two important sets of values are calculated which are the cumulative surfaces  $S_{cum}$  and  $V_{cum}$  as represented in Table(1)

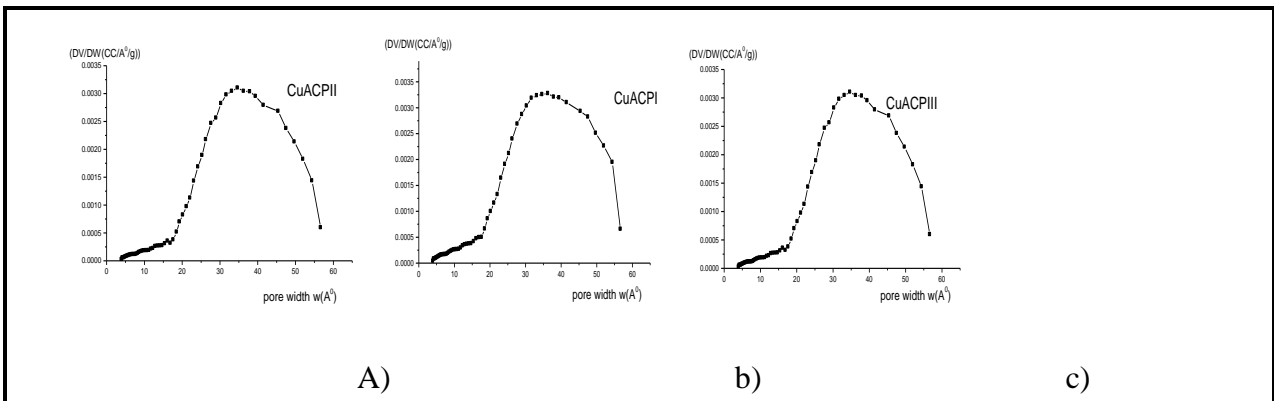


**Fig (1): Adsorption -desorption isotherm of nitrogen**

(a - CuACPI, b- CuACP II and c- CuACP III.)



**Fig (2):** The linear plots for nitrogen adsorption for (a - CuACPI, b- CuACP II and c- CuACP III.)



**Figure(3)** Pore volume distribution curves for (a - CuACPI, b- CuACP II and c- CuACP III.)

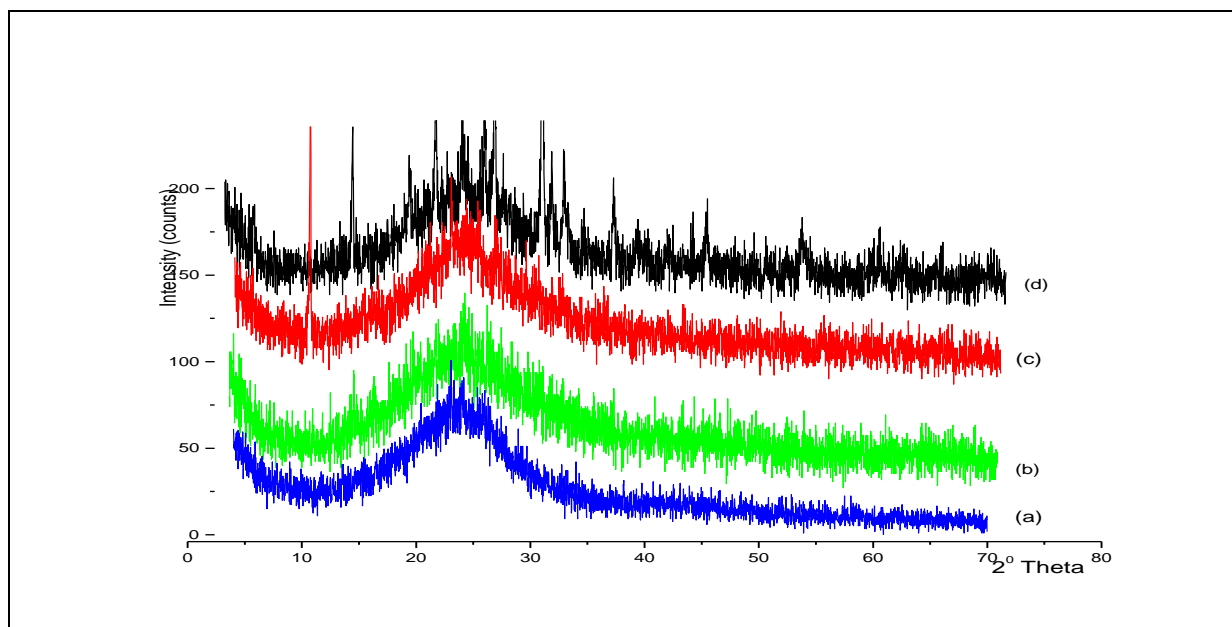
**Table (1) .The texture and catalytic properties of the investigated solids .**

Catalysts	$\Delta E$ , kcal.mol	$K_o$ , $10^5 s^{-1}$	$S_{BET}$ , $m^2.g^{-1}$	$S_{cum}$ , $m^2.g^{-1}$	$V_{cum}$ , $cc.g^{-1}.e^{-2}$	Mean pore radius, $\text{Å}^0$
CuACPI	12.51	10.36	174.50	221.40	4.83	11.08
CuACPII	11.55	4.58	159.50	196.70	4.29	10.78
CuACPIII	11.05	2.42	123.70	152.60	3.33	10.79

As follows from these results, that  $S_{BET}$  value of the prepared solids from Cu supported on an active carbon treated by phosphoric acid of 5, 10 and 15% for CuACPI, CuACPII and CuACPIII respectively depending on copper content, the V-t plots of all the prepared solids exhibit a downward deviation which was characteristics of micropores and the pore size distribution curves which also indicate the presence of very small different size of micropores

The X-ray diffraction patterns of prepared solids were represented in **figure 4 (a,b,c, and d)** where in **figure (4)** a- represent the X-ray diffraction of AC after activator by  $H_3PO_4$  (ACP), b-,c- and d- of CuACPI, CuACPII and CuACPIII respectively. From XRD pattern of ACP showing the amorphous nature of the active carbon

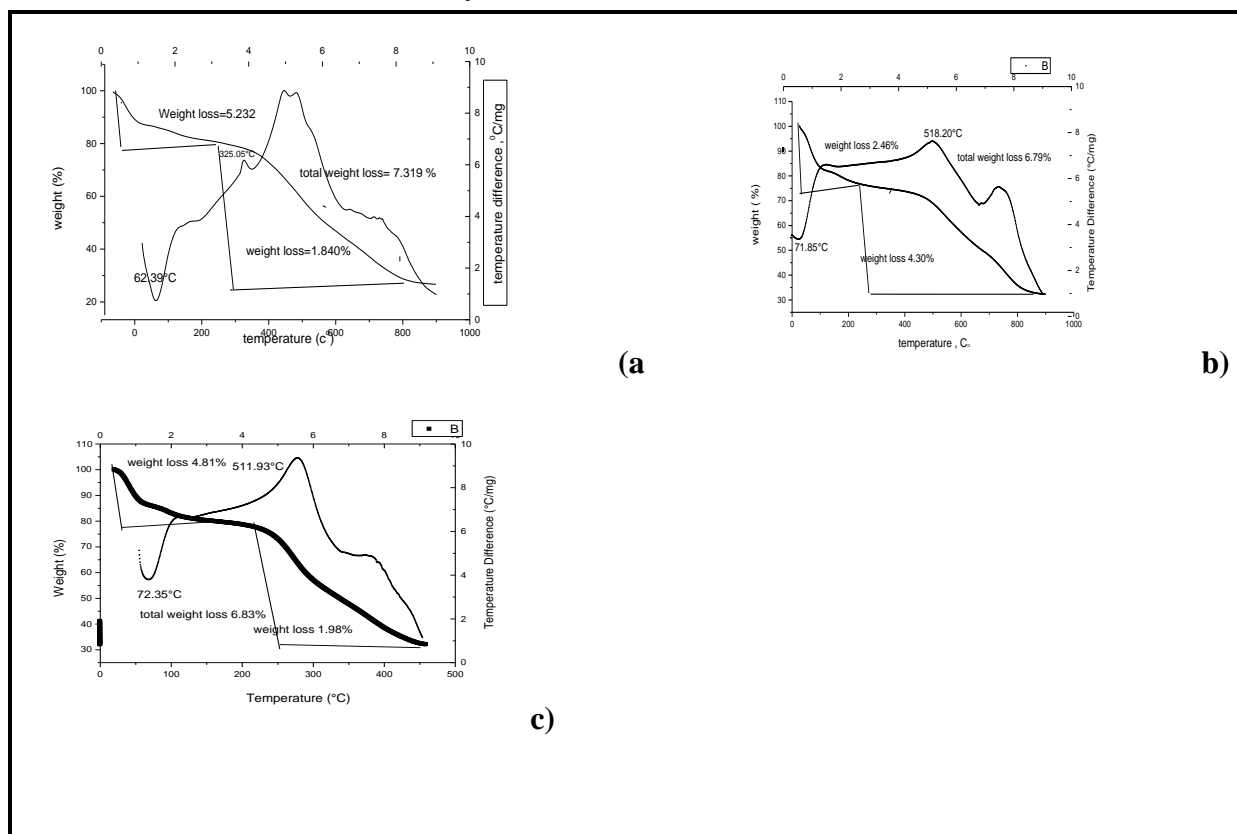
**Fig 4 (b,c,d)** shows peaks indicating that the information of  $Cu_3(PO_4)_2$  on the surface of the active carbon treated by  $H_3PO_4$ . And also, showing by addition of Cu / ACP enhancement its structure.

**Fig.4.XRD pattern of (a - ACP, b - CuACPI, c - CuACPII, and d - CuACPIII.)**

The TGA and DTA curves of the prepared solids from CuACP are shown in **Fig 5(a,b and c)**. According to data in **Fig5(a,b and c)** the TGA curves of CuACPI, CuACPII and CuACPIII shows two main steps of thermal decomposition. The first step at 255 °C. for three catalysts

corresponds to the loss of (18.4,24.5 and 19.8%) of the weight of CuACPI, CuACP II and CuACP III catalysts respectively as water of hydration . The second step at 850 °C for three catalysts corresponds to the loss of(54.8,43.3and 48.1%) of the weight of CuACPI, CuACP II and CuACP III catalysts respectively as combined water or phase transfer , while the weight of three catalysts remains constant up to 900 °C. The total weight loss of three catalysts were (( 73.5, 67.9 and 68.0 %) of the weight of CuACPI, CuACP II and CuACP III catalysts respectively . from results , the prepared solids from Cu supported on an active carbon treated by phosphoric acid by percent ratio 5 % for CuACPI , 10 % for CuACP II and 15 % for CuACP III show the stability over temperature range 25<sup>0</sup>C to above 900<sup>0</sup>C.

The thermodynamic activation parameters of the decomposition process for CuACPI, CuACP II and CuACP III solids were calculated using Coats-Redfern equation<sup>15,16</sup> in **Table (2)**. From thermodynamic parameters values give information about thermal stability of the system<sup>17</sup>. The DTA curves for three catalysts displays two endothermic peaks at (62.39 and 325.05 °C) for CuACPI catalyst and (71.85 and 518.20 °C) for CuACP II catalyst and (72.35 and 511.93°C) for CuACP III catalyst.



**Fig (5) The TGA and DTA curves of**  
**(a - CuACPI , b- CuACP II and c- CuACP III .)**

**Table(2) The thermodynamic parameters of the decomposition process.**

Solids	Decomp. Temp.,K	$\Delta E$ , ,kJmole <sup>-1</sup>	$\Delta S$ , ,kJmole <sup>-1</sup> k <sup>-1</sup>	$\Delta H$ , ,kJmole <sup>-1</sup>	$\Delta G$ , ,kJmole <sup>-1</sup>
<b>CuACPI</b>	298-528	27.29	-221.75	24.81	90.89
	528-1123	6.78	271.79-	2.39	117.38
<b>CuACPII</b>	301-573	20.94	-201.91	18.44	79.19
	573-1173	5.79	276.03-	1.02	159.18
<b>CuACPIII</b>	295-531	26.72	-230.92	24.27	92.39
	531.1173	5.66	-280.05	1.25	149.95

### The Kinetic of Heterogeneous Catalytic Conversion of Cyclohexane .

The kinetic of decomposition of cyclohexane on the prepared catalysts , different series of experiments were done at different times of contact and at a specific temperature<sup>18</sup> . This were repeated at 280 , 300 , 330 , 350and 380 °C. The corresponding data for the dependence of the rate of heterogeneous catalytic of cyclohexane on the space of velocity and on the time of contact are given in **Tables 3(a, b and c)** as representative tables for CuACPI, CuACPII, and CuACPIII catalysts respectively. The gaseous and the liquid products of the reaction studied were analyzed chromatographically . The gaseous products were methane, ethane and hydrogen. The liquid products were cyclohexane , toluene , xylene and naphthalene<sup>19</sup> .

**Fig 7. (a, b and c).** for CuACPI, CuACPII and CuACPIII catalysts respectively represent the effect of variation of time contact  $\tau$  on the rate of conversion cyclohexane and variation of the rate  $v^0$ , ml.min<sup>-1</sup> . of the gaseous products. It follows from these **Figures** and **Tables** that :

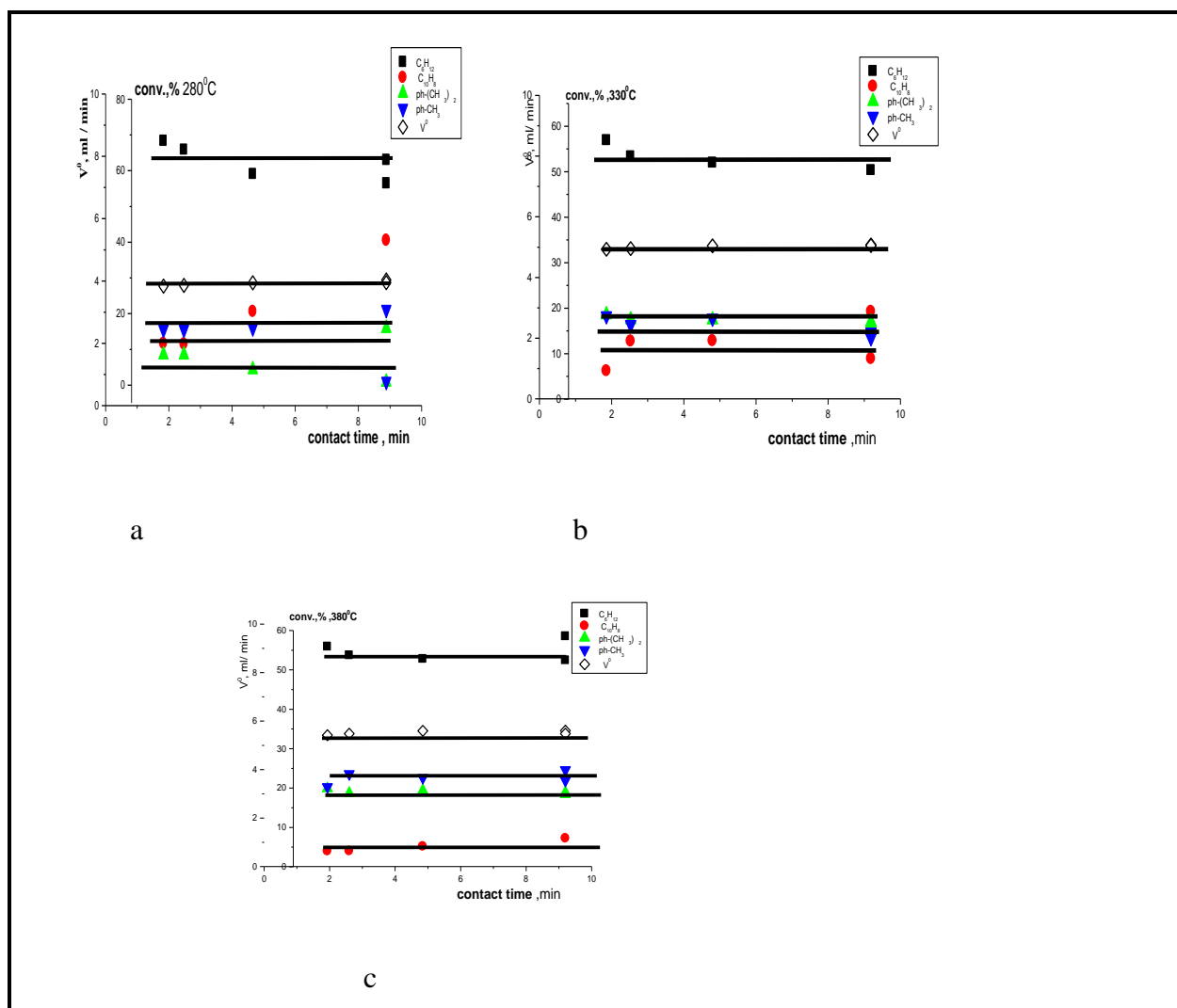
**i)** The rate of formation of gases products and % of conversion of cyclohexane are independent on the flow rate of cyclohexane over CuACPI , CuACPII and CuACPIII catalysts at 280 ,300, 330 ,350 and 380 °C and was depended on the nature of the solids and kinetic conditions. Generally , it was found that the rate of gaseous products was increased with experimental temperature for CuACPI , CuACPII, and CuACPIII catalysts respectively .

**ii)** The percent of conversion calculated from the analysis of liquid products was independent of the  $\tau$  , of cyclohexane and was increased by increasing experimental temperature .

**iii)** The catalytic conversion of cyclohexane is taken place on a surface completely covered with the adsorbed molecules of cyclohexane , which is quite different from Henry' s region characterized by incomplete coverage , i.e. the reaction of zero order .

**iv)** The weight of theses catalysts were determined before and after experiment. The increase in the weight was calculated taking into consideration the loss in weight due to calcination .

The apparent weight gain was found to be depend on the chemical nature of the solids pretreatment conditions , experimental temperature and kinetic conditions . The formation of different products and gain in the mass of the catalyst after precipitation in the process of catalytic conversion of the cyclohexane are explained in the terms of the condensation products on the surface which may decompose in different ways giving reaction products. The apparent activation energy for the catalytic conversion of cyclohexane over (CuACPI , CuACPII or CuACPIII) catalysts following Arrhenius equation was determined at space velocity of 7.20 ,10.66 ,14.00 , 15.30 and  $7.20 \times 10^{-2}$  ml.min<sup>-1</sup> and temperature range from 280 °C to 380 °C. **Fig 8 (a,b, and c )** represents the effect of temperature on the conversion of cyclohexane over the prepared solids . The apperant activation energy was calculated and was found to be 12.51,11.51 and 11.05 K.cal.mol<sup>-1</sup>for CuACPI, CuACPII and CuACPIII respectively . Cleary , all possible ways of conversion of cyclohexane , under the studied conditions may take place through the poly molecular mechanism<sup>18</sup> . According to this mechanism , the intermediate poly molecular complex may decompose in different ways giving different products and the decomposition of desorption is one kinetic step

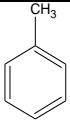
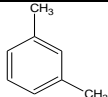
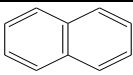



**Fig.(7) . Effect of variation of time of contact on the catalytic conversion of cyclohexane over CuACP catalysts .**





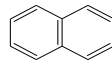

( a- CuACPI at 280 °C, b-CuACPII at 330 °C and c- CuACPIII at 380°C. )

**Table 3(a) .The effect of temperature on the catalytic dehydrogenation of cyclohexane on CuACPI catalyst pretreated by air at 500 °C in flow system under normal pressure on catalyst sample half an hour in cyclohexane vapour .**

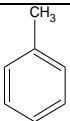
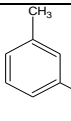
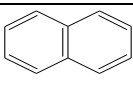

Te mp., °C	f . 10 <sup>-2</sup> , ml min <sup>-1</sup>	V <sup>o</sup> , ml. min <sup>-1</sup>	Con v., %	ΔS, cal.K <sup>-1</sup>	Wt gain , %	Analysis of products			
									
280	7.30	4.45	43.5	-19.49	17.3	0.99	0.86	40.52	56.47
	10.66	3.70	3			15.96	4.35	20.62	59.03
	14.00	3.02	40.9			15.52	8.49	11.52	65.87
	15.30	2.833	7			15.52	8.50	11.64	68.37
	7.30	3.75	34.1			21.08	15.89	Traces	63.02
			3						
		31.6							
		3							
		36.9							
		7							
300	7.30	4.7	46.3	-20.16	17.2	15.16	8.55	22.57	53.70
	10.66	3.76	0			15.15	10.55	20.50	55.70
	14.00	3.19	44.3			19.23	15.38	2.49	62.87
	15.30	2.91	0			20.23	11.08	0.81	67.83
	7.30	3.55	37.1			23.49	10.48	Traces	66.018
			3						
		32.1							
		7							
		33.9							
		8							
330	7.30	5.70	48.1	-23.61	15.8	10.47	28.18	9.46	51.86
	10.66	4.00	4			14.08	15.35	15.59	54.97
	14.00	3.57	45.0			18.70	14.51	9.39	57.41
	15.30	3.32	3			20.19	27.10	1.01	61.70
	7.30	3.80	42.5			34.22	11.01	Trace	54.76
			9						
		38.3							
		0							
		45.2							
		4							
350	7.30	5.62	55.9	-23.75	11.3	23.57	23.57	9.73	44.10
	10.66	4.87	0			30.21	11.57	10.60	47.60
	14.00	3.84	52.4			29.82	13.94	8.40	47.82
	15.30	3.83	0			25.19	22.09	Traces	52.77
	7.30	4.75	52.1			38.414	9.44	2.66	51.47
			8						

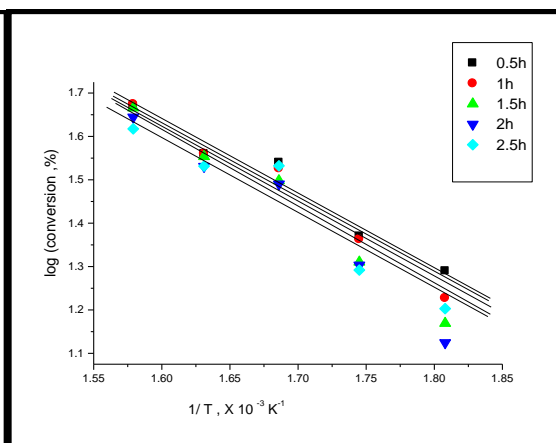
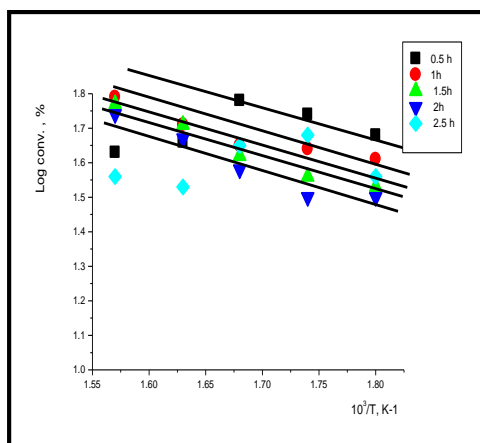
			47.2 3 48.5 3						
380	7.30 10.66 14.00 15.30 7.30	6.75 4.97 4.22 3.83 6.56	61.0 7 61.6 7 60.0 9 55.9 0 45.2 4	-24.18	8.57	33.74 37.84 39.11 46.15 34.22	13.74 15.83 15.33 5.73 11.22	13.88 7.98 5.65 Traces Traces	38.93 38.33 39.91 44.10 54.76

**Table 3( b ) .The effect of temperature on the catalytic dehydrogenation of cyclohexane on CuACPII catalyst pretreated by air at 500 °C in flow system under normal pressure on catalyst sample half an hour in cyclohexane vapour .**

Temp ., °C	f . 10 <sup>-2</sup> , ml min <sup>-1</sup>	V <sup>o</sup> , ml.min <sup>-1</sup>	Conv ., %	ΔS cal.K <sup>-1</sup>	Weight gain , %	Analysis of products			
									
280	7.30	4.29 36.32		-19.61	17.20	2.72	9.96	23.62	63.68
	10.66	3.75 35.77				11.04	13.61	11.10	64.23
	14.00	3.06 34.05				13.08	13.49	4.74	65.95
	15.30	3.03 33.93				16.57	15.82	3.19	66.07
	7.30	3.77 35.91				15.03	14.90	5.96	64.09
300	7.30	4.20 42.03		-20.13	17.17	8.87	12.87	20.27	57.97
	10.66	4.00 44.09				17.11	14.06	12.90	55.91
	14.00	3.94 39.63				9.73	14.31	15.59	60.37
	15.30	3.19 34.63				13.60	15.03	5.98	65.37
	7.30	3.78 34.84				15.49	13.70	5.63	65.16
330	7.30	4.07 49.69		-20.82	16.87	13.44	16.96	19.27	50.31
	10.66	3.99 48.04				17.76	17.43	12.83	51.96
	14.00	3.38 46.63				16.38	17.50	12.75	53.37
	15.30	3.25 43.09				18.27	18.57	6.23	56.91
	7.30	4.08 40.32				14.67	16.73	8.90	59.68
350	7.30	5.57 50.63		-21.40	15.80	13.86	17.51	19.24	49.37
	10.66	4.83 49.63				17.77	18.87	12.97	50.37
	14.00	3.80 47.23				15.76	18.98	12.47	52.77
	15.30	3.47 45.39				15.71	17.69	11.97	54.61
	7.30	4.17 38.35				13.68	16.68	7.97	61.65
380	7.30	5.49 54.09		-22.18	14.98	17.46	18.34	18.27	45.91
	10.66	4.92 51.44				21.26	19.23	10.93	48.56
	14.00	4.17 47.6				18.27	19.56	9.75	52.4
	15.30	3.88 44.73				16.48	20.27	7.96	55.27
	7.30	5.18 41.44				12.86	22.02	6.54	58.56

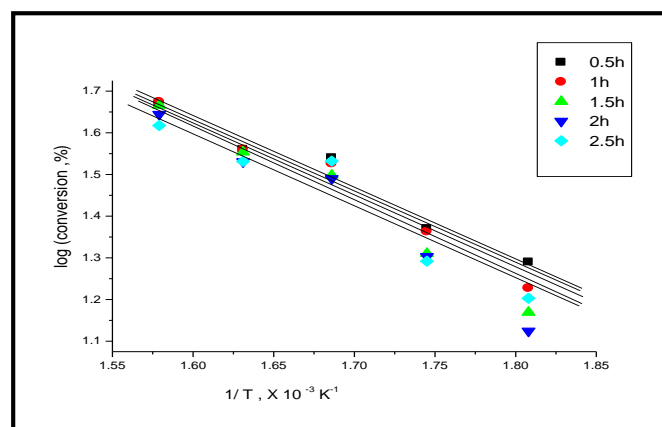
**Table 3 (c) .The effect of temperature on the catalytic dehydrogenation of cyclohexane on CuACPIII catalyst pretreated by air at 500 °C in flow system under normal pressure on catalyst sample half an hour in cyclohexane vapour.**

Temp., °C	f . 10 <sup>-2</sup> , ml.min <sup>-1</sup>	V <sup>o</sup> , ml.min <sup>-1</sup>	Conv., %	ΔS, cal.k <sup>-1</sup>	Weight gain, %	Analysis of products			
									
280	7.30	3.89	19.59	-21.19	17.24	Traces	4.81	14.74	80.41
	10.66	3.65	16.88			Traces	5.70	11.16	83.12
	14.00	3.00	16.88			1.02	3.78	9.97	85.24
	15.30	2.34	14.76			1.00	2.05	9.99	86.68
	7.30	3.09	13.32			3.02	2.74	9.71	84.04
300	7.30	3.16	23.68	-21.33	16.01	Traces	12.25	9.98	76.32
	10.66	4.00	23.05			1.31	13.73	8.71	76.95
	14.00	2.95	20.43			1.14	13.40	5.87	79.57
	15.30	2.66	20.1			0.88	14.01	5.19	79.90
	7.30	3.08	19.59			1.69	14.44	3.44	80.41
330	7.30	4.07	35.3	-21.46	15.09	10.04	13.61	11.10	64.70
	10.66	2.99	33.58			24.33	5.45	2.83	66.42
	14.00	2.37	31.47			23.34	5.10	2.33	68.53
	15.30	3.011	30.9			19.83	11.05	Traces	69.10
	7.30	2.07	34.05			13.08	13.49	4.74	65.95
350	7.30	5.50	36.63	-21.95	14.89	9.68	17.57	9.09	63.37
	10.66	4.83	36.32			23.62	5.75	6.93	63.68
	14.00	3.807	33.93			23.49	8.24	4.02	64.23
	15.30	3.44	33.99			12.37	11.82	3.19	66.07
	7.30	4.178	35.77			23.49	10.48	Traces	66.01
380	7.30	4.97	47.57	-22.29	9.56	21.90	18.40	7.25	52.43
	10.66	4.92	47.23			22.62	19.40	5.19	52.77
	14.00	4.19	46.3			23.57	18.71	4.00	53.70
	15.30	3.83	44.09			20.27	19.87	3.98	55.91
	7.30	4.18	41.44			24.57	18.86	Traces	58.56



a

b



C

**Fig(8) The effect of temperature on the catalytic conversion of cyclohexane on**

**(a - CuACPI , b- CuACPII and c- CuACPIII . ) Catalysts preactivated in dry air CO<sub>2</sub> free for 0.5-2.5 h .**

#### ADSORPTION ISOTHERMS .

The adsorption capacity of the prepared solids (biosorbents )towards the treatment of the aqueous solution of heavy metal ions such as Co<sup>+2</sup> , Ni<sup>+2</sup> , Fe<sup>+3</sup> and Cd<sup>+2</sup> ions were studied (table (6)) .

The experimental data were analyzed according to Langmuir and Freundlich isotherm models<sup>20</sup> .Table 7 (a,b andc).The lineared form of Langmuir isotherm<sup>21</sup> was used to characteristic adsorption process of heavy metals ions onto prepared solids and their maximum adsorption capacity<sup>22</sup> :

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}}$$

Where  $q_e$  = amount of metal absorbed (mg/g) at equilibrium , $q_{max}$  = maximum of langmuir monolayer adsorption capacity , $C_e$  = equilibrium concentration of the metal ions in the solution , $b$ = Langmuir constant .

$b$  and  $q_{max}$  constants related to adsorption efficiency and energy of adsorption. The freundlich isotherm model is the earliest known relation describing the sorption equation :

$$\text{Log } q_e = \text{log } K_f + (1/n)\text{log}C_e$$

Where  $K_f$ = freundlich adsorption constant,  $n$  = adsorption intensity constant.

$K_f$  is an indication of the adsorbents ,  $n$ , indicates the effect of concentration on the adsorption capacity and represents adsorption intensity<sup>19</sup>.  $K_f$  measure adsorbent capacity which calculated from linear plote of  $\text{Log } q_e$  against  $\text{log}C_e$ .also calculated separation factor according to the equation :

$$R=1/1+ K_f C$$

From the results , it is clear that the value of adsorption efficiency  $q_m$  of ACP increased by addition of Cu for adsorption of Co<sup>+2</sup> and Ni<sup>+2</sup> ions and was decrease for adsorption of Fe<sup>+3</sup> and Cd<sup>+2</sup> ions . The observed  $b$  value show that the endothermic nature of the process involved

in the system . For separation factor  $R_L$  were found to be between 0-1 confirm that the adsorption process is favorable and values of  $n$  are greater than one , indicating also the adsorption is much more favorable .

Biosorbent	Initial ions conc, g/l	Co <sup>+2</sup> ions			Ni <sup>+2</sup> ions		
		Q <sub>e</sub> mg/g	C <sub>e</sub> mg/g	Removal %	Q <sub>e</sub> mg/g	C <sub>e</sub> mg/g	Removal %
CuAC PI	0.03	15.75	14.25	52.50	13.72	16.27	45.75
	0.02	14.28	5.71	71.42	15.11	4.89	75.55
	0.01	8.33	1.66	83.33	8.88	1.11	88.88
CuAC PII	0.03	17.10	12.89	57.03	12.99	17.00	43.33
	0.02	12.00	8.00	60.00	9.00	11.00	45.00
	0.01	6.30	3.70	63.00	5.76	4.234	57.66
CuAC PIII	0.03	22.23	7.76	74.11	19.28	10.71	64.28
	0.02	15.55	4.44	77.77	15.54	4.44	77.77
	0.01	8.66	1.33	86.66	8.57	1.43	85.71

**Table .(6)1. Equilibrium adsorbents and percent of removal of heavy metal ions(Co+2 ,Ni+2 ions )**

Biosorbent	Initial ions conc, g/l	Fe <sup>+3</sup> ions			Cd <sup>+2</sup> ions		
		Q <sub>e</sub> mg/g	C <sub>e</sub> mg/g	Removal %	Q <sub>e</sub> mg/g	C <sub>e</sub> mg/g	Removal %
CuACPI	0.03	17.64	12.35	58.82	19.99	10.00	66.66
	0.02	14.23	5.71	71.42	14.64	5.35	73.21
	0.01	9.49	0.51	94.90	8.03	1.96	80.35
CuACPI I	0.03	25.99	4.00	86.66	20.48	9.51	68.29
	0.02	17.50	2.50	87.50	16.00	4.00	80.00
	0.01	8.82	1.17	88.23	9.44	0.56	94.44
CuACPI II	0.03	21.33	8.66	71.11	27.12	2.86	90.44
	0.02	15.68	4.31	78.43	18.46	1.54	92.30
	0.01	8.23	1.77	82.35	9.60	0.40	96.05

**Table .(6 ,)2. Equilibrium absorbents and percent of removal of heavy metal ions(Cd+2 ,Fe+3 ions )****Langmuir constants and statistical parameters**

Co <sup>+2</sup> ions			Ni <sup>+2</sup> ions			Fe <sup>+3</sup> ions			Cd <sup>+2</sup> ions		
q <sub>m</sub>	b	R <sup>2</sup>	q <sub>m</sub>	b	R <sup>2</sup>	q <sub>m</sub>	b	R <sup>2</sup>	q <sub>m</sub>	b	R <sup>2</sup>
17.6	0.60	0.99	14.0	0.71	0.99	18.46	0.98	0.99	31.5	0.16	0.9
9			2						8		9

**Freundlich constants and statistical parameters**

q <sub>m</sub>	b	R <sup>2</sup>	k <sub>f</sub>	n	R <sup>2</sup>	k <sub>f</sub>	n	R <sup>2</sup>	k <sub>f</sub>	N	R <sup>2</sup>
7.94	3.2	0.95	8.70	5.54	0.80	9.12	5.65	0.99	7.24	1.7	0.99
	6									9	

**Table (7a). Parameters of Langmuir and Freundlich isotherm models for the adsorption of HMI'S onto CuACPI****Langmuir constants and statistical parameters**

Co <sup>+2</sup> ions			Ni <sup>+2</sup> ions			Fe <sup>+3</sup> ions			Cd <sup>+2</sup> ions		
q <sub>m</sub>	b	R <sup>2</sup>	q <sub>m</sub>	b	R <sup>2</sup>	q <sub>m</sub>	b	R <sup>2</sup>	q <sub>m</sub>	b	R <sup>2</sup>
33.33	0.23	0.97	21.9 7	0.07	0.95	20.00	0.30	0.99	11. 01	3.6 7	0.99

**Freundlich constants and statistical parameters**

q <sub>m</sub>	b	R <sup>2</sup>	k <sub>f</sub>	n	R <sup>2</sup>	k <sub>f</sub>	n	R <sup>2</sup>	k <sub>f</sub>	N	R <sup>2</sup>
2.21	1.2 4	0.99	2.48	1.76	0.98	7.70	1.1 3	0.99	11.0 1	3.6 7	0.99

**Table (7B). Parameters of Langmuir and Freundlich isotherm models for the adsorption of HMI'S onto CuACP II.**



**Langmuir constants and statistical parameters**

Co <sup>+2</sup> ions			Ni <sup>+2</sup> ions			Fe <sup>+3</sup> ions			Cd <sup>+2</sup> ions		
q <sub>m</sub>	b	R <sup>2</sup>	q <sub>m</sub>	b	R <sup>2</sup>	q <sub>m</sub>	b	R <sup>2</sup>	q <sub>m</sub>	b	R <sup>2</sup>
33.33	0.05	0.99	14.2	0.16	0.93	7.45	0.70	0.99	11.0	3.67	0.99
			8						1		

**Freundlich constants and statistical parameters**

q <sub>m</sub>	b	R <sup>2</sup>	k <sub>f</sub>	n	R <sup>2</sup>	k <sub>f</sub>	n	R <sup>2</sup>	k <sub>f</sub>	N	R <sup>2</sup>
2.21	1.2	0.99	2.48	1.76	0.98	7.70	1.1	0.99	11.0	3.6	0.99
	4						3		1	7	

**Table (7C). Parameters of Langmuir and Freundlich isotherm models for the adsorption of HMI'S onto CuACPIII.**

**CONCLUSION.**

The Cu supported on an active carbon treated by phosphoric acid of 5, 10 and 15% for CuACPI, CuACPII and CuACPIII respectively catalysts were prepared by impregnation method and characterized by mean of TG A, DTA, X-ray and BET surface area measurements. The CuACPI, CuACPII and CuACPIII catalysts are mesoporous with  $S_{BET}=174.50, 159.50$  and  $123.70 \text{ m}^2 \cdot \text{g}^{-1}$  respectively, the decreasing in  $S_{BET}$  values due to  $\text{Cu}_3(\text{PO}_4)_2$  formation (planner structure, high M.Wt and less amorphously structure of ACP) on the surface of the active carbon treated by  $\text{H}_3\text{PO}_4$ . The catalytic activity of the prepared catalysts was studied for the conversion of cyclohexane at temperature ranging from 280-380°C by using flow system techniques, the liquid and gaseous products were analyzed by gas liquid chromatography and The kinetics of cyclohexane conversion were determined and a reaction model was proposed which provides a rate expression consistent over the catalysts was studied and the reaction was zero order. Comparatively, much lower catalytic activities are exhibited by CuACPIII catalyst on the catalytic conversion of cyclohexane: a maximum conversion of cyclohexane of 47.57% at 350°C While CuACPII catalyst a maximum conversion of cyclohexane of 54.09% at 350°C and CuACPIII catalyst a maximum conversion of

cyclohexane of 61.07% at 350°C at space velocity  $7.30 \times 10^{-2} \text{ min}^{-1}$  under normal pressure. The order of catalytic activities of the prepared catalysts from Cu supported on an active carbon treated by phosphoric acid of percent ratio 5, 10 and 15% for CuACPI, CuACPII and CuACPIII respectively for toluene formation (cyclohexane aromatization):  $5\% \text{ CuACPI} > 15\% \text{ CuACPIII} > 10\% \text{ CuACPII}$ . Whereas for Cyclohexane condensation (poly aromatic formation):

$10\% \text{ CuACPII} > 15\% \text{ CuACPIII} > 5\% \text{ CuACPI}$

Adsorption isotherm parameter were calculated. The amount of heavy metal ions adsorbed increase with decreasing its concentration. Removal, % of  $\text{Cd}^{+2}$  ions from aqueous solution increase by addition of Cu to ACP catalyst while other metal ions no.  $R_L$  and  $n$  values showed that the prepared adsorbents more effective for the removal of  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Fe}^{+3}$  and  $\text{Cd}^{+2}$  ions from an aqueous solutions.

## REFERENCES

- R.M. Rioux and M.A. Vannice, *Journal of Catalysis* 216 (2003) 362–376.
- G.C. Bond, *Catalysis by Metals*, Academic Press, New York, (1962).
- G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Environmental Catalysis*, Wiley–VCH, Weinheim, (1999).
- J. Armor (Ed.), *Environmental Catalysis*, in: ACS Symposium Series, Vol. 552, Am. Chem. Society, Washington, DC (1994), p. 372
- M. Kraus, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, Vol. 4, Wiley–VCH, Weinheim (1997), p. 2159.
- Hashem, A. et al., Adsorption based on agricultural wastes for heavy metal and dye removal: a review, *Energy Education Science and Technology*, 19(2007), pp.69-86.
- Lin, S. and Juang, R., Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review. *Journal of Environmental Management*, 90(3)(2009), pp.1336-1349.
- Demirbas, E., Kobya, M. and Konukman, A.E.S., Error analysis of equilibrium studies for the almond shell active carbon adsorption of Cr(VI) from aqueous solutions. *Journal of hazardous Materials*, 154(1-3)(2008), pp.787-794
- N.M. Haimour, S. Emeish, *Waste Manage.* 26 (2006) 651–660.
- S.E. Samra, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 163 (2000) 199 – 208
- Hala G.El-Shobaky, Suzan A.H.Ali, Neven A.Hassan, *Materials Science and Engineering B*(2007)143.
- E.M.Ezzo, M.A.Elkharpawi, M.A.Elaishy, Mans. *Sci. Bull. (A Chem)* (2004), 31, 13.
- Langmuir, I., *S. Am. Chem. Soc.*, (1918) 40.361-403.
- Brunaure, S., Emmett, P.H and Teller, E., Adsorption of gases in multimolecular layers. *Journal of American Chemical Society*, 60(1939), pp.309-319.
- A.W.Coats, J.P.Redfern, *Nature* 201(1964)68-69
- Arshed Adam salema, Muhammad T.Afzel, Farough Motasemi, *Analytical and Applied Pyrolysis* 105(2014)217-226.
- Morsi M. Abou-Sekkina, Raafat M.Issa, Alam El-Deen M. Basawisy and Wael A. El-Helece, *International Journal Of Chemistry* 2 No.1 (2010)81-88.
- E.M.Ezzo, A.A. Balandin, and A.P.Rundenk, *Kenet. Katal*, 9 (1968), 1101
- Silvia Granata, Tiziano Faravelli, Eliseo Ranzi\*, *Combustion and Flame* 132 (2003) 533–544
- Jia, Y.F.: Thomas, K.K. *Labguir*, (2002), 18-470.

Namasivayam , C:Muniasamy , N:Gayathri ,k: Rani, M:Renganthan ,K.Biores .Technol  
.,(1996),57-37.

Reichert , H., .Some theory.In: Sorption software ADP 5 Users manual . 1<sup>st</sup> Edition .Rodano ,  
Milan :Thermo Electron Technical Publications , (2005)pp. 39-60.