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CATALYTIC CRACKING OF HEPTANE USING PREPARED ZEOLITE

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ABSTRACT

This investigation was conducted to study the potential of type Y-zeolite prepared locally from Iraqi Rice Husk (IRH) (which considered as a type of agricultural waste that difficult to discard it in conventional methods in Iraq) on the removal of one heavy metals pollutant which was divalent zinc (Zn^{+2}) ions from industrial wastewater using different design parameters by adsorption process. The design parameters studied to remove (Zn^{+2}) ions using zeolite prepared locally from (IRH) as an adsorbent material were initial concentration of zinc ions (Zn^{+2}), height of absorbance material packing, pH, time of treatment, flow rate and temperature, these parameters were varied from (5-100) mg/l, (40-80) cm, (1-10), (1-60) min, (1-50) ml/min and (5-50°C) respectively. Results show that the removal efficiency of (Zn^{+2}) ions from aquatic solution decreased with increasing of initial concentration, flow rate and pH while the removal efficiency increased with increasing absorbance material bed height. A mathematical model is proposed for an adsorption packed bed column with porous adsorbent. The mathematical model takes account of both external and internal mass-transfer resistances as well as of non-ideal plug flow along the column. Statistical model is also achieved to find an expression relates the overall operating parameters used in this investigation in a general equation. The samples of type Y-zeolite remaining after using it in the removal of (Zn^{+2}) ions from aqueous solutions aforementioned were predestined to study the utilization of it as a promoted type Y-zeolite catalyst and compared this type with normally type Y-zeolite catalyst prepared from (IRH) alone in the process of n-heptane catalytic cracking under *different operating conditions. The results show that the promoted type Y-zeolite catalyst by (Zn^{+2}) ions gives higher conversion and better selectivity of n-heptane to light olefins than normally type Y-zeolite catalyst. By this way we can remove the toxic (Zn^{+2}) ions contaminated the water with adsorbent material prepared from agricultural waste (IRH) and in the same time, produce light and more benefit olefins hydrocarbons from n-heptane catalytic cracking using a type Y-zeolite catalyst (adsorbent material) synthesis from agricultural waste(IRH) and discarding it in a coast and eco-friendly method.*

Key Words: Adsorption, Zinc, Iraqi rice husk, Zeolite catalyst, Catalytic cracking

INTRODUCTION

Generally, the pollution of water is one of significant ecological problems. Among components of water pollution belong heavy metals. Heavy metals are generally considered to be those whose density exceeds 5 g/cm^3. Their presence in the environment has become a major threat for plant, animal and human life due to their bioaccumulating tendency, toxicity and carcinogenicity which may cause damage to various systems of the human body because they are neither been degraded nor destroyed by human body. The toxicity is mainly depending on form occurrence of appropriate metal. It stands to reason, that the essential higher toxicity belongs to ion form of metal than complex form (Barakat, 2010; Eva *et al.*, 2011). Nevertheless, utilization by human influences the potential for health effects in at least two major ways: first, by environmental transport, which is, by human or anthropogenic contributions to air, water, soil and food and second, by altering the speciation or the biochemical form of the element (Hamed *et al.*, 2006). Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater (Barakat, 2010). The main sources of heavy metals are mining, metallurgical, chemical manufacturing, tannery, battery manufacturing industries, fossil fuel, the modern chemical industry is based largely on catalysts, many of which are metals or metal compounds, production of plastics, such as polyvinyl chloride, involves the use of metal compounds, particularly as heat stabilizers etc. Therefore they must be removed from municipal and industrial wastewater effluents before discharge into the surface water because of their high solubility in the aquatic environments. Zinc is one of these heavy metals which consider as toxic materials if it exceeding the acceptable level. Zinc oxide is widely used as a white pigment in paints, and as a catalyst in the manufacture of rubber. Zinc waste causes environmental and public health problems. Although humans can handle proportionally large concentrations of zinc, excess zinc can be harmful. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish. Excess amount of zinc may cause zinc toxicity which zincs to a severe hemolytic anomie, liver and kidney damages; vomiting and diarrhea are possible symptoms. The consumption of fruit juices stored in galvanized cans has resulted in mass parrot poisonings with zinc (Muataz, 2011). Removal of heavy metals from wastewater effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal.

These processes have significant disadvantages, which are, for instance, incomplete removal, high-energy requirements, and production of toxic sludge. Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Adsorption has become one of the alternative treatments, in recent years; the search for low-cost adsorbents that have metal-binding capacities has intensified. The adsorbents may be of mineral, organic or biological origin, polymeric materials, industrial byproducts, biomass, agricultural wastes, and zeolites (Barakat, 2010). Rice husk, which is often considered as a solid waste from rice milling, contains approximately 70% of organic compounds and 30% of hydrate silica (SiO_2). In general, the rice husk can be used as a cheap energy source through combustion, generate heat or electric power or for other purposes as low value material such as adsorption of heavy metals, synthesis of different types of zeolites and also to produce metallurgical silicon. Previously, the content of rice husk ash at different combustion temperatures has been studied. The white ash that was obtained from combustion is generally 10-15% of the total dry weight of rice husk. The water content may affect the combustion temperature and the rice husk that has been treated with hot-water and some steam-explosion processes give a lower level of metallic impurities. When the rice husk is leached with mineral acid and calcined in air, white powder rice husk silica (RHS) is obtained. The RHS with high silica purity is suitable as a silica source for the production of inorganic materials such as silicon carbide and silicon nitride. In a research field related to catalysis, RHS was used as a silica source for the synthesis of micro-porous materials such as zeolites and meso-porous silica such as MCM- 41 (Hasliza, 2005; Jatuporn *et al.*, 2008). RHS was successfully used as a silica source for the synthesis of type Y-zeolite in sodium form (NaY) (Jatuporn *et al.*, 2008) . For a catalyst where the metal function and the acid function are well balanced like a zeolites, isomerization and hydrocracking are consecutive reactions and the rate limiting step is the skeletal rearrangement of the alkenes obtained via dehydrogenation over the metal sites, which takes place on the Brønsted acid sites (Akhmedov *et al.*, 1999).

Light olefins, such as ethylene, propylene and butenes, are produced mainly by the thermal cracking of naphtha to supply these important raw materials for petrochemical industry. In this process, a large amount of energy is consumed because the process is usually operated at high temperatures around 1100 K. Moreover, it is difficult to control the selectivity to obtain propylene in a high yield because the thermal cracking favors the ethylene formation. The catalytic cracking, however, would require less energy and could produce propylene with higher selectivity. The catalytic cracking of light paraffin's, such as pentane, hexane, heptane and octane, has been studied on various zeolite catalysts as a test reaction of naphtha cracking to clarify the performance of catalysts and the reaction mechanism. Type Y-zeolite catalyst is the most extensively studied zeolite because it has been used commercially for Fluid Catalytic Cracking FCC process. Though the dealumination of type Y-zeolite gives Ultra Stable Y-zeolite (USY) catalyst with higher activity and stability and varies the selectivity significantly, the large space inside supercages would not be favorable to obtain small molecules such as propylene. In addition, the large space will accelerate the hydride transfer, one of the undesirable side reactions to produce paraffin's and hydrogen deficient species, a coke precursor, resulting in the decrease in olefin selectivity and catalyst life (Takayuki, 2010).

In this study, a low coast agricultural waste, which is Iraqi Rice Husk was used as a raw material to synthesis type Y-zeolite and the using of this prepared zeolite in the removal of zinc ion (Zn^{+2}) from industrial wastewater in a semi continuous packed bed was investigated. The remaining samples of type Y-zeolite after treating with aqueous solutions containing zinc ion (Zn^{+2})was tested as a zinc promoted type Y-zeolite catalyst and compared this catalyst with normally type Y-zeolite catalyst prepared from Iraqi rice husk only (without treatment with zinc ion (Zn^{+2})) in n-heptane catalytic cracking process to produce the main hydrocarbon which was propylene.

EXPRIMENTAL WORK

Catalyst Preparation

Iraqi rice husk

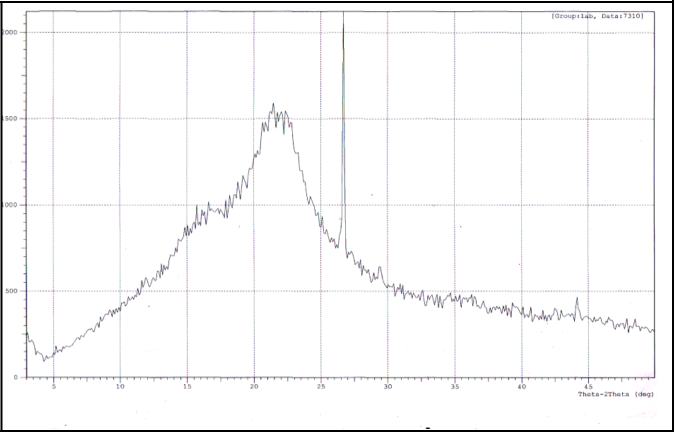
Iraqi rice husk was collected from Al-Shanafia fields for rice in the Southern of Iraq. The (IRH) was washed three times with doubled distilled water. Excess distilled water was used to remove the soluble materials present in the (IRH) bringing from the field, boiled to remove color and other fine impurities may be found in the (IRH), and then dried at 105°C for 24 hours. The surface area of (IRH) was measured by BET (**B**runauer – **E**mmett – **T**eller) nitrogen adsorption technique. When the (IRH) was heated at 105°C in an oven, most of the water had been removed from the (IRH) while the second major mass loss of about 45-65% was attributed to the breakdown of cellulose constituent char, which is a carbonaceous residue. The (IRH) was treated with 10% sulfuric acid (H_2SO_4) for 24 hours for preliminary removing all impurities. Dry (IRH) were sieved to eliminate residual rice and clay particles. They were well washed with double distilled water, filtered, dried in air, and calcined at 750°C for 6 h. 12 g of (IRH) calcined were then subjected for dissolution in sodium hydroxide NaOH (4 M) followed by refluxing at 90°C for 12 h. Concentrated hydrochloric acid (HCl (37%)) was then added to the aforementioned base dissolved (IRH) for complete precipitation. (IRH) were filtered, washed with excess distilled water to be freeing from chloride ions and finally dried in an oven at 120°C for 6 h. The chemical composition and X-ray diffraction of (IRH) is showed in **Table1**, all numbers in wt% basis (Mohammed *et al.*, 2008; Rahman *et al.*, 2009) .

Table-1. Characterization Properties of (IRH)

Chemical Composition

Compound	Composition wt %
SiO_2	90.70
Al_2O_3	0.13
Fe_2O_3	0.06
TiO_2	0.015
CaO	0.61
MgO	0.25
Na_2O	0.09
K_2O	2.64
P_2O_5	0.73
LOI	4.71
S.A (m^2/g)	17.5

XRD of Iraqi Rice Husk (IRH)



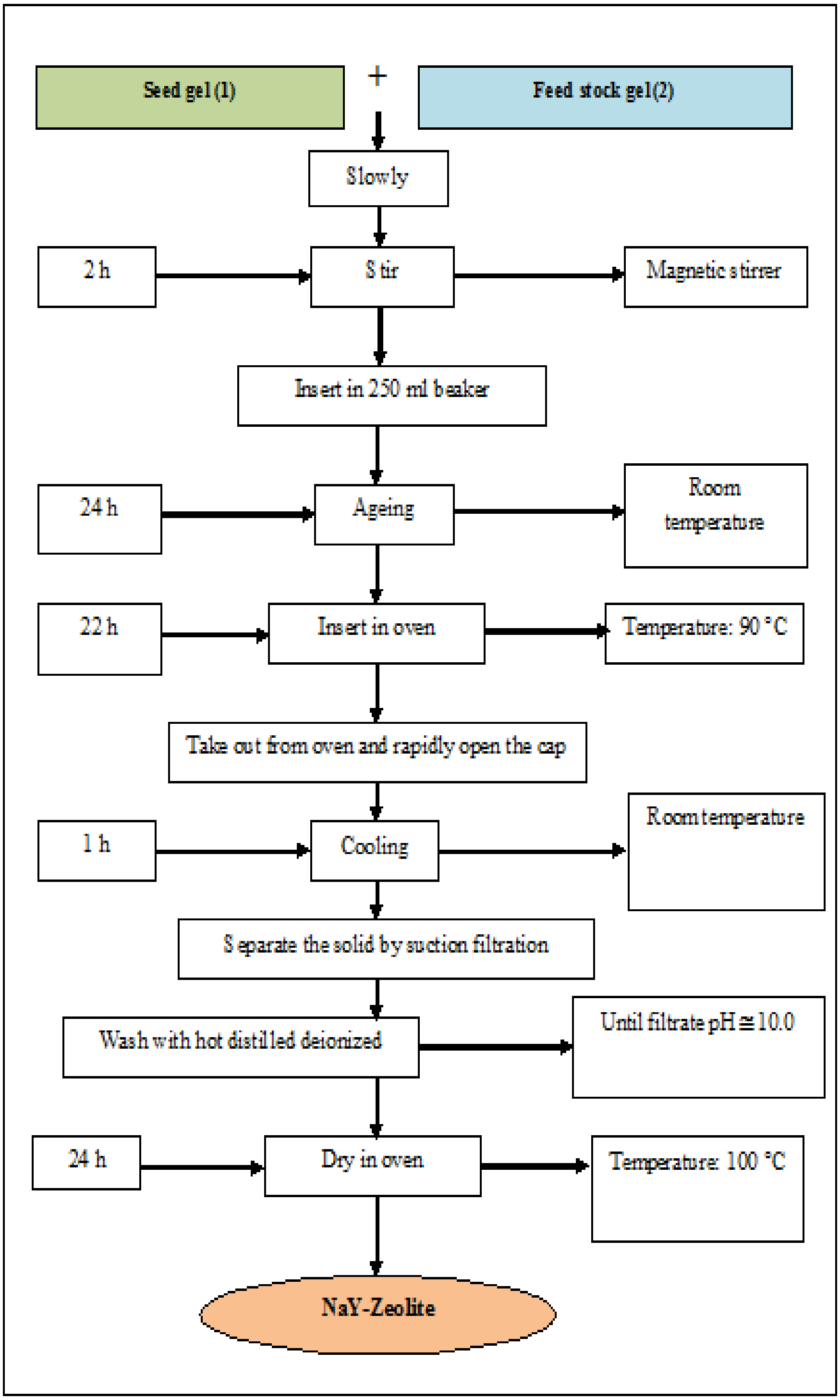
Preparation of Faujasite Type Y–Zeolite from Iraqi Rice Husk

Faujasite type Y–zeolite could be synthesized (Rahman *et al.*, 2009) using (IRH) as a silica source. A 500 ml Teflon beaker containing a magnetic stirrer was washed with deionized water. Sodium hydroxide of 1.6616 g was added slowly to deionized water and stir until clear and homogenous solution appeared for about 5 minutes. The aqueous solution of sodium hydroxide was ready for the preparation of seed gel. The gel was prepared according to the following molar chemical composition:

$$\mathbf{10.67\ Na_2O: 1\ Al_2O_3: 10\ SiO_2: 180\ H_2O}$$

Two milliliter aqueous solution of sodium hydroxide was added to 0.7515g sodium aluminate oxide until a homogenous mixture was formed; 1.5361g Iraqi rice husk was added separately to 5.5 ml sodium hydroxide aqueous until homogenously mixed. Both of the preparations were heated under vigorous stirring to obtain a homogenous mixture. The sample was aged for 24 hours at room temperature in the Teflon bottle. The aluminate and silicate solutions were mixed together in the polypropylene beaker, subsequently stirred for 2 hours with the purpose of making it completely homogenized. This combined solution was used as the feed stock gel. The flow chart of the process is shown in **Figure 1**.

Figure-1. Flow Chart of the Synthesis of Faujasite Type Y–Zeolite Catalyst Using Iraqi Rice Husk(9)



Dealumination Process

The dealumination of type Y-zeolite by acid treatments not only decreases of their aluminum and cation content, but profound modifications of their structure and textural characteristics. For most zeolites, the dealumination has a beneficial influence on catalytic properties. The dealuminated zeolites tend to produce less coke and to exhibit an improved stability of the activity. When the Si/Al ratio goes up, the zeolite become more stable and when the ratio reaches10 and higher, zeolite considered a high silica material. Aluminum can be extracted from certain zeolite structure without the collapse of the crystalline framework. The dealumination process was achieved for the zeolite types prepared from kaolin to increase the Si/Al ratio, by a treatment at high temperatures (550 – 650°C) of the sodium form of synthetic zeolites, followed by leaching with Nitric acid HNO_3 for aluminum extraction. Some details on the applied technique are given in **Table 2 (Abbas, 2011)**.

Table-2. Applied Technique of Dealumination Process (Abbas, 2011)

Sample NO.	Dealumination Methods
(1)	NaY-zeolites, extraction with (2N)HNO_3 for 4h, then calcination at 650°Cfor 4 h.
(2)	Sample (1), extraction with (2N) HNO_3 for 2h, then calcination at 550°C for 4 h.
(3)	Sample (1), extraction with (2N)HNO_3 for 4h, then calcination at 650°C for 4 h, then extraction with (2N)HNO_3 for 6 h, finally calcinations at 650°Cfor 4 h.

Preparation of HY-Zeolite Catalyst

The hydrogen zeolite form was prepared by exchanging Na^+ ions in the sodium form NaY-zeolite with ammonium chloride solution NH_4Cl. In order to obtain ideal degree of ion exchange the technique of multi-steps (three times repeating) was used. Thus, the first step, 2 N of ammonium chloride solution (26.75 g of NH_4Cl in 250 ml of distilled water) contacted with 90 g of faujasite type Y–zeolite (prepared above) with stirring for 2 hours. In the second step, the procedure in the first step was repeated under the same conditions but for 60 g of faujasite type Y–zeolite, which was taken from the total faujasite type Y–zeolite amount produced in the first step. Finally, in the third step, the procedure under the same conditions was repeated again but on about 30 g of faujasite type Y–zeolite, which was taken from the total faujasite type Y–zeolite amount produced in the second step. The exchanged ammonia faujasite type Y–zeolites were filtered off, washed with deionized water to be free of chloride ions, dried overnight at 120°C and then calcined initially at 150°C for two hours. The temperature was increased 75°C per hour until it reached 550°C and it was held constant for 5 hours at this temperature. During calcination, ammonia and water were liberated and decationized HY–zeolite type was formed (Sherman *et al.*, 1978).

Stock solution

In order to avoid interference with other elements in wastewater, the experiments in this paper were carried out using simulated synthesis aqueous solutions of (Zn^{+2})ions.1000 mg/l stock solution of (Zn^{+2}) ions was prepared by dissolving suitable amount of zinc sulfate ($ZnSO_4$) in one liter of double distilled water. All solutions using in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentrations for the experimental work of this investigation. The (Zn^{+2}) ions concentrations were measured using GBC SensAA996Atomic Adsorption Spectrometer.

Laboratory adsorption unit

Semi continuous mode experiments were conducted in this research by treated 250 ml of simulated synthesis aqueous solution (SSAS) of (Zn^{+2}) ions at desired concentrations with the various amounts of the adsorbent material which was faujasite type Y– zeolite prepared from (IRH) using different flow rates of (SSAS) of (Zn^{+2}) ions at various conditions. The pH value was adjusted using 0.1 N KOH and 0.1 N HCl solutions. The adsorption unit using to achieve the experiments of this investigation is shown in **Figure 2**. The adsorption unit consists of packed bed column, feeding burette and sample flask collector. The packed bed column consisted of a clear glass tube of (2.5 cm ID, 2.8 cm OD and 100 cm height) and has a perforated disk in the bottom. The adsorption column packed with type Y– zeolite at different height (40–80 cm) supported from the top and the bottom by spherical glass layer, each sphere has (0.5 cm diameter). Before starting the runs, the adsorption column was rinsed by double deionized water down flow through the column. After the column was accommodation and putting the required amount of adsorbent material type Y– zeolite prepared, the adsorption process started by allowing the desired (SSAS) of (Zn^{+2}) ions of required concentration, pH and feed temperature down flow through the sorption column from a 250 ml feeding burette at a precise flow rate in experiment. For the evaluation of the best operational condition, the experiments were carried out at constant pressure of 1 bar. Outlet samples after treatment in each experiment were collected from the bottom of packed bed column at a regulated running treatment time period (1–60 minute) from entering the initial feed concentrations of (SSAS) of (Zn^{+2}) ions through the packed bed column.

Activity Test of Synthesized Faujasite Type Y– Zeolite

The activity of faujasite type Y–zeolite prepared from (IRH) was studied by applying removal of (Zn^{+2}) ions. The (Zn^{+2}) ions removal was carried out in a laboratory adsorption unit shown in **Figure 2**and **Figure 3**. This unit is operated under different conditions of initial concentration, feed temperature, flow rate, pH of (SSAS) of (Zn^{+2}) ions, height of adsorbent material (faujasite type Y– zeolite) bed and time of treatment. The (SSAS) enters the adsorption packed bed to pass through the adsorbent material layer where the adsorption takes place. Then the outlet samples from the adsorption bed collected and tested by Atomic Adsorption Spectrometer equipment to find the remaining concentration of (Zn^{+2}) ions.

Figure-2. Laboratory Adsorption Unit

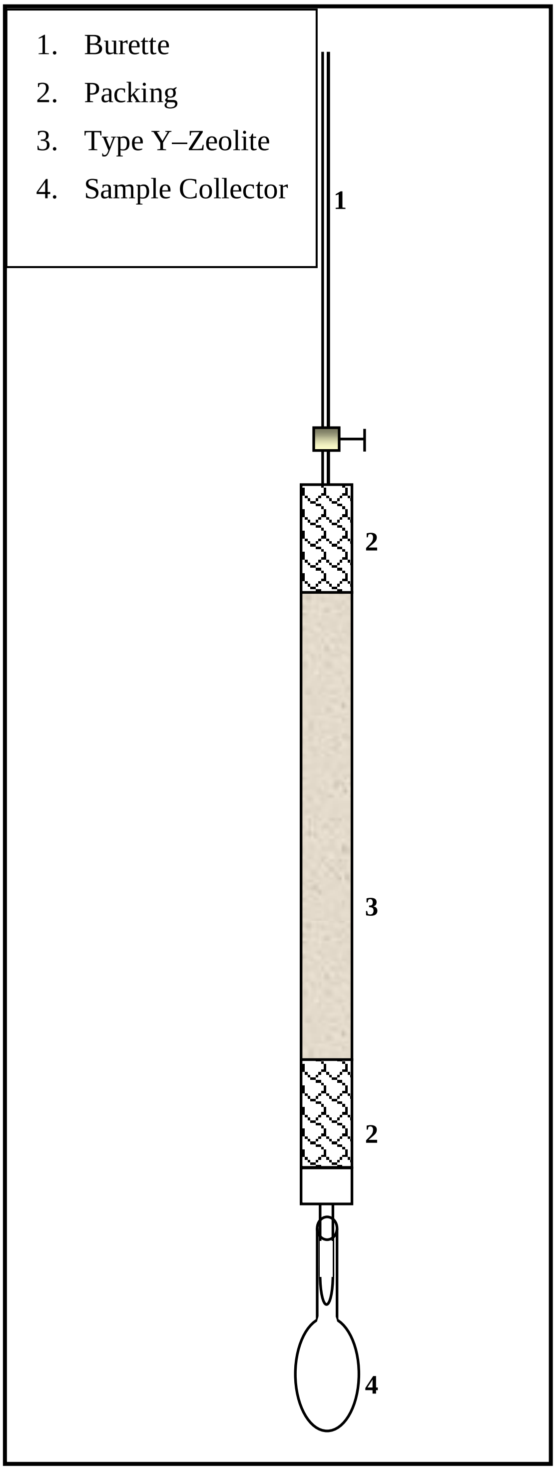
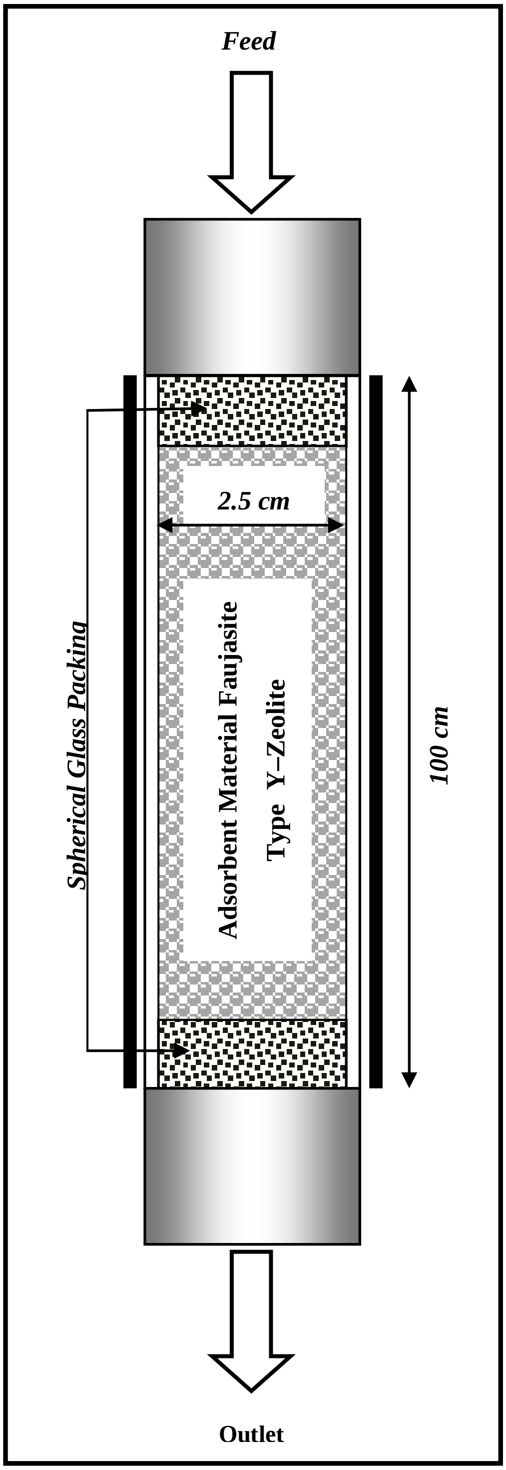


Figure-3. Adsorption Packed Bed



Determination of divalent zinc (Zn^{+2}) ion in the samples after treating

Measurement of unadsorbed (Zn^{+2}) ions in the collected samples after treated with faujasite type Y–zeolite prepared (IRH) in adsorption unit was carried out with Atomic Adsorption Spectrometer. The GBC SensAA996Atomic Adsorption Spectrometer was set up according to manufacturer‘s instruction with the wavelength corresponding to zinc under investigation. The Atomic Adsorption spectrometer was set to zero absorbance using the blank solution. Absorbance at λ=214 nm, using reagent water as reference. Correct absorbance reading of sample by subtracting absorbance of a blank carried through the method. From the correct absorbance, determine (Zn^{+2}) ions present by reference to the calibration curve, prepared prematurely. The absorbance of each sample was read with an automatic calculation. (Zn^{+2}) ions removal was calculated from the equation:

$$\%R = \frac{[Zn^{+2}]_o - [Zn^{+2}]}{[Zn^{+2}]_o} \times 100$$

where: $[Zn^{+2}]_o$ and $[Zn^{+2}]$ are initial and residual divalent zinc (Zn^{+2})ion concentration respectively.

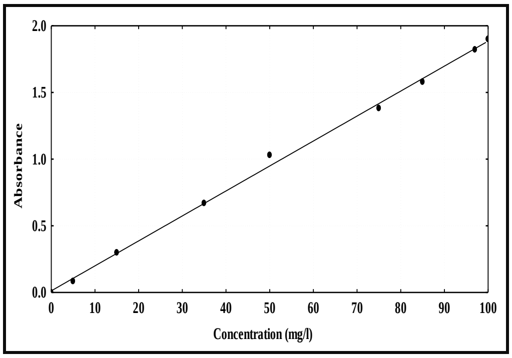


Figure 4: Calibration Curve of Divalent Zinc (Zn^{+2})Ion

Reusability of Synthesized Faujasite Type Y– Zeolite

In order to check the reusability of adsorbent material, synthesized faujasite type Y–zeolite was firstly dried at 105°C for 24 h, after that tested in adsorption unit using the same conditions of experiment gives the best percent removal of (Zn^{+2}) ions from (SSAS) aforementioned which was as follow: T_f = 50°C, pH = 10, F = 1 ml/min, t = 1 h of (SSAS) (Zn^{+2}) ions, and 80 cm height of adsorbent material. The capacity of the adsorbent was found to be decreased until be constant at 3.54% after 12 times repeated use and constant for initial concentration C_o = 5 mg/l; thus multiple use of adsorbent was seen to be feasible.

Catalytic Activity of Synthesized Promoted and non-promoted Faujasite Type Y–Zeolite Catalyst

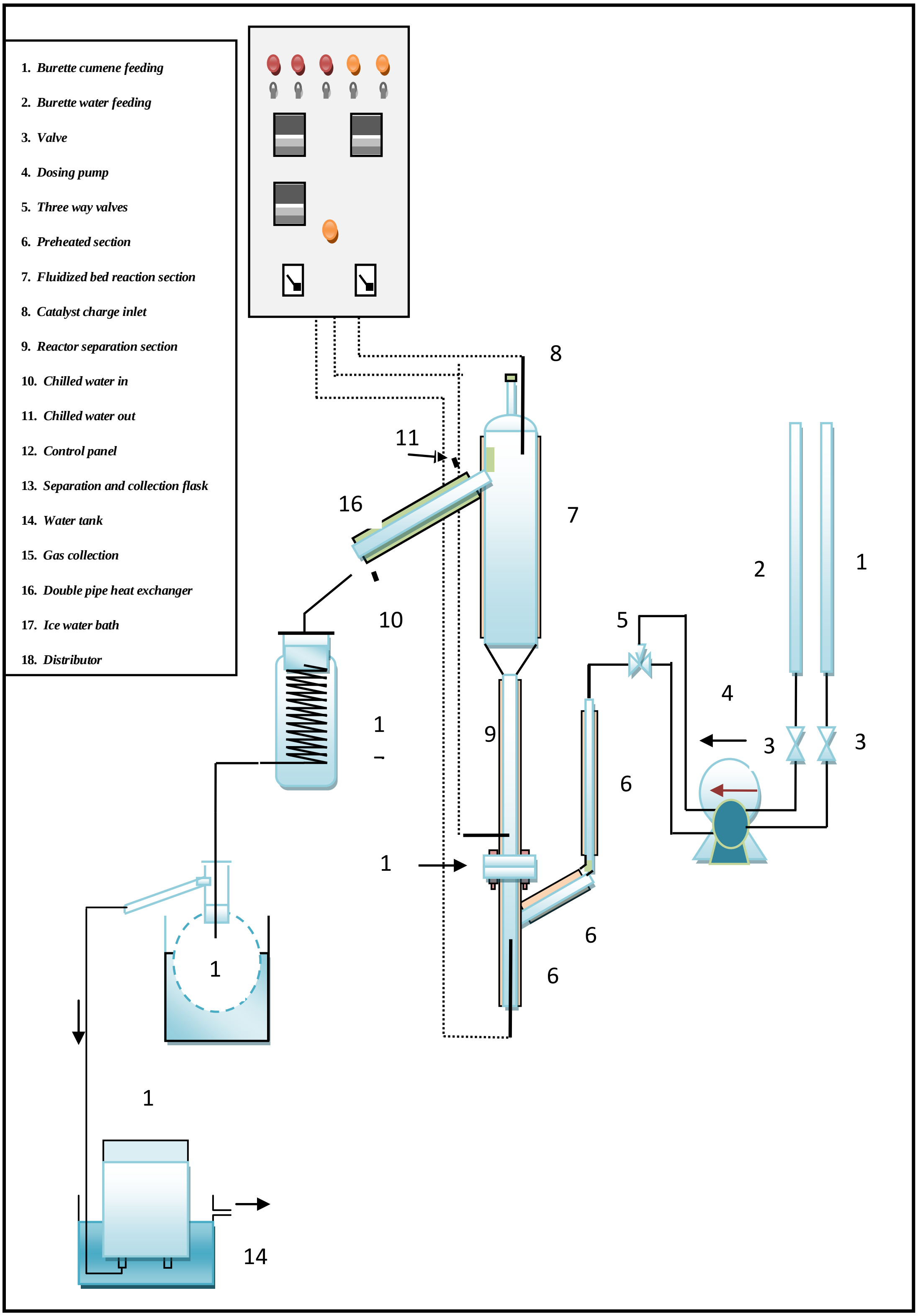
The promoted and normally faujasite type Y zeolite catalyst activity was studied by applying n-heptane catalytic cracking reaction. The n-heptane catalytic cracking reaction was carried out in catalytic cracking unit shown in **Figure 5**. This unit is operated under atmospheric pressure and the experiments of catalytic cracking were performed in an experimental fluidized bed unit. The unit consists of n-heptane storage tank, gas flow meter, dosing pump, evaporator, condenser/separator, cooler with appropriate control, and power supply box. A suitable amount of faujasite type Y–zeolite catalyst prepared from (IRH) was charged in the reactor from the top of it. At preheating section, the feed was preheated at 400°C before entering to catalytic bed. The temperature controlled was setting at desired reaction temperature between (400-550°C) in the reaction zone. The first condenser was supplied with water from chiller and second charged with ice. A suitable quantity of water was charged to the preheater to remove air from the reactor. This water changed to steam used for air stripping from the reactor. The temperature in preheater kept at 400°C. After stripping air from the reactor, the flow of water was stopped and began to n-heptane flow at a rate4.5 ml/min to the reactor for ten minute period. The reaction products were flown through double pipe heat exchanger, internal tube ice bath, separation and collection for liquid storage, while the gaseous products passed through the liquid products and were collected in a vessel over water. The gas volume is determined by water displacement. A sample of gaseous product was collected and then analyzed by gas chromatography device (GC) (Dani, Model GC 1000 DPC), to determine the chemical composition of the gaseous product. Cracking liquid products also collected in a tube and then analyzed by gas chromatography, to determine the chemical composition of the liquids product. The catalyst was replaced after the end of each experiment.

MATHEMATICAL MODEL

Fixed bed dynamics are describing by a set of convection-diffusion equations, coupled with source terms due to adsorption and diffusion inside adsorbent particles. Inside the particle, molecules of adsorbate diffuse into the inner portions of particle via surface diffusion, pore diffusion, or both. The solution of these equations will give rise to the prediction of the needed concentration distribution. This investigation focuses on understanding the mechanism of both surface diffusion and pore diffusion. To formulate a generalized model corresponding to the dispersion flow, surface diffusion and pore diffusion mechanism, following assumptions are made:

1. The system operates under isothermal conditions.
2. The equilibrium of adsorption is described by Langmuir isotherm.
3. Intraparticle mass transport is due to Fickian diffusion, and it is characterized by the pore diffusion coefficient, D_p and the surface diffusion, D_s.
4. Mass transfer across the boundary layer surrounding the solid particles is characterized by the external-film mass transfer coefficient, k_f.
5. Film transfer resistance for mass transport from the mobile to the stationary phase.
6. Local adsorption equilibrium between the adsorbate adsorbed onto the adsorbent surface and the adsorbate in the intraparticle stagnation fluid.
7. Both surface and pore diffusion are included in the mass transport mechanism.
8. Axial dispersion.

Figure 5: Schematic flow diagram of the catalytic cracking unit (Yousif, 2010)



Simulation Technique

Equations used in simulation technique represent a set of simultaneous, nonlinear, partial differential equations (PDEs) that can be solved numerically. The discretatization was applied to space coordinates (Z and r) to convert the PODs to a set of ordinary differential equations (ODEs). The resulting ODEs can be solved using an existing ODE solver provided by MATLAB (Lazo, 1999).

RESULTS AND DISCUSSION

The ability of (IRH) to remove (Zn^{+2}) ions from (SSAS) of (Zn^{+2})ions in semi continuous packed bed column at various parameters which are pH's of (SSAS) of (Zn^{+2})ions solution (*pH*), height of adsorbent material (faujasite type Y–zeolite prepared from (IRH)) (*h*), flow rates (*F*), feed temperature (T_{feed}) and time of treatment (*t*) of (SSAS)was investigated. More than 1000 experiments were achieved by varying all above parameters for different initial concentrations (C_o) of (SSAS) of (Zn^{+2}) ions. Thus, the results obtained are explained below. The results showed that using adsorbent material, the percent removal of (Zn^{+2}) ions was decreased when the initial concentration (C_o) of (SSAS) of (Zn^{+2}) ions was increased at constant other variables as shown in **Figure 6**. This can be explained by the fact that the initial concentration of (Zn^{+2}) ions had a restricted effect on (Zn^{+2}) ions removal capacity; simultaneously the prepared adsorbent material had a limited number of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the number of (Zn^{+2}) ions molecules competing for the available functions groups on the surface of adsorbent material. Since the solution of lower concentration has a small amount of (Zn^{+2}) ions than the solution of higher concentration of it, so the percent removal was decreased with increasing initial concentration of (Zn^{+2}) ions. For adsorbent material, higher percent removal was 99.32% at initial concentration of (Zn^{+2}) ions5 mg/l, so adsorbent material was found to be very efficient to (Zn^{+2}) ions removal from (SSAS).

The results indicated that using adsorbent material, the percent removal of (Zn^{+2}) ions was increased when the pH of (SSAS) of (Zn^{+2}) ions was increased at constant other variables as shown in **Figure 7**.The influence of initial pH of (SSAS) was studied in the range of 1–10. It was noticed that when the pH value is higher than 8, the adsorption amount of (Zn^{+2}) ions increased dramatically, which was attributed to the fact that (Zn^{+2}) ions started to precipitate leading to the reduction of the (Zn^{+2}) ions in the aqueous solution at higher pH value. The effect of pH can be explained by ion-exchange mechanism of sorption in which the important role is played by functional groups that have cation exchange properties. At lower pH values zinc removal was inhibited, possibly as a result of the competition between hydrogen and zinc ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligand functional groups in adsorbent material would be exposed, increasing the negative charge density on the Y–zeolite surface, increasing the attraction of metallic ions [(Zn^{+2}) ions] with positive charge and allowing the sorption onto adsorbent material cell surface. The results elucidated that when the adsorbent material bed height was increased the percent removal of (Zn^{+2}) ions was increased too at constant other variables as shown in **Figure 8**. The increased of bed height (*h*) meaning increased in the surface area of adsorbent material, as a result increased the number of active sites in the adsorbent material surface i.e. increased the availability of binding sites for adsorption and consequently increase the (Zn^{+2}) ions removal capacity on faujasite type Y–zeolite. This lead to increase the ability of adsorbent material to adsorb greater amount of (Zn^{+2}) ions from (SSAS) at different initial concentrations and ultimately the percent removal of (Zn^{+2}) ions increased.

The results illustrated that when the flow rate of (SSAS) of metal ion $Zn^{+2}$was increased, the percent removal of (Zn^{+2}) ions was decreased at constant other variables as shown in **Figure 9**. This may be due to the fact that when the flow of (SSAS) increasing, the velocity of solution in the column packed with the adsorbent material was increasing too, so the solution spend shorter time than that spend it when the flow rate decreased, thus the adsorbent material uptake low amount of (Zn^{+2}) ions from (SSAS), therefore the percent removal of (Zn^{+2}) ions from (SSAS) was decreased. The results demonstrated that when the temperature of feed (SSAS) of metal ion $Zn^{+2}$was increased the percent removal of (Zn^{+2}) ions was increased too at constant other variables as shown in **Figure 10**.The effect of temperature is fairly common and increasing the mobility of the metal cation. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the adsorbent material enabling (Zn^{+2}) ions to penetrate further. It was indicated that (Zn^{+2}) ions adsorption capacity increased with increasing feed temperature from 5 to 50°C. This effect may be due to the fact that at higher temperature an increase in active sites occurs due to bond rupture. The results demonstrated that when the treatment time of (SSAS) of (Zn^{+2})ions increased the percent removal of (Zn^{+2}) ions increased at constant other variables as shown in **Figure 11**. This may be due to the fact that when the time of treatment of (SSAS) increasing and the velocity of solution in the column packed with the adsorbent material was remaining constant, the solution spend longer time than that spend it when the time of treatment decreased, so the adsorbent material uptake more amount of (Zn^{+2}) ions from (SSAS), therefore the percent removal of (Zn^{+2}) ions from (SSAS) was increased.

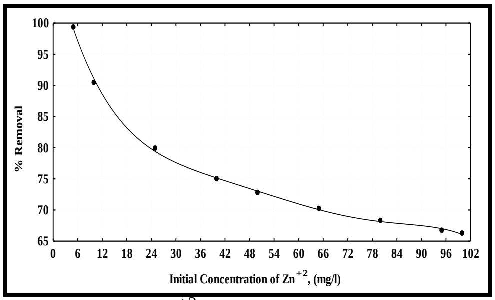


Figure 6: Effect of (Zn^{+2}) ions Initial Concentration on the % Removal of (Zn^{+2}) ions@ ***T* = 50°C, *t* = 60 min, h_{cat}=0.8m,*F* = 1 ml/min, *P* =1 bar,** and ***pH* = 10**

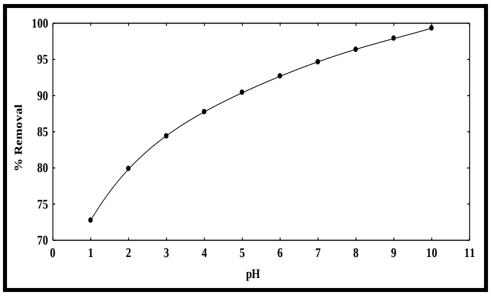


Figure 7: Effect of pH on the % Removal of (Zn^{+2}) ions@ ***T* = 50°C,h_{cat}=0.8m,*F* = 1, *t* = 60 min, ml/min, *P* =1 bar,** and **C_o = 5 mg/l**

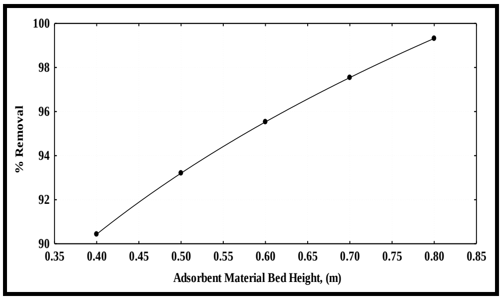


Figure 8: Effect of Adsorbent Material Bed height on the % Removal of (Zn^{+2}) ions@ **$T = 50°C$, $t = 60$ min ,** **$C_o = 5$ mg/l, $F = 1$ ml/min, $P = 1$ bar,** and ***$pH = 10$***

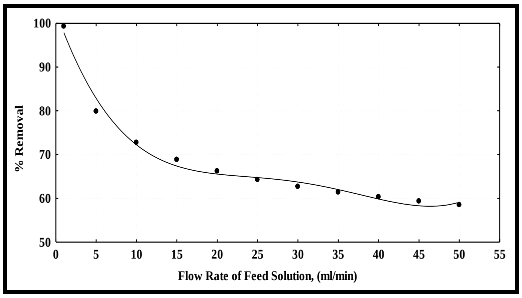


Figure 9: Effect of Feed Flow Rate on the % Removal of (Zn^{+2}) ions@ **$T = 50°C$, $t = 60$ min,** **h_{cat}=0.8m, $C_o = 5$ mg/l, $P = 1$ bar,** and ***$pH = 10$***

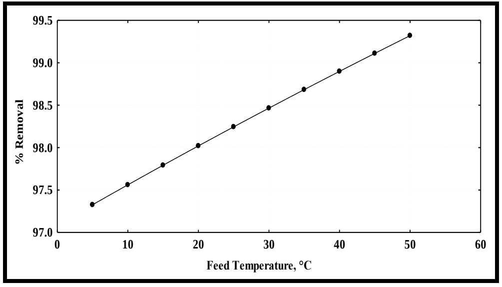


Figure 10: Effect of Feed Temperature on the % Removal of (Zn^{+2}) ions@ **$C_o = 5$ mg/l, $t = 60$ min** **h_{cat}=0.8m, $F = 1$ ml/min, $P = 1$ bar,** and ***$pH = 10$***

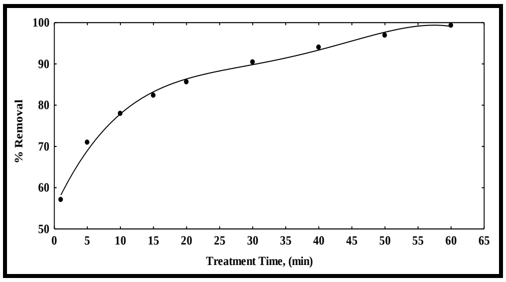


Figure 11: Effect of Treatment Time on the % Removal of (Zn^{+2}) ions@ **$T = 50°C$, $C_o = 5$ mg/l** **h_{cat}=0.8m,$F = 1$ ml/min, $P = 1$ bar,** and ***$pH = 10$***

CHARECTRIZATION OF PREPARED ZEOLITE TYPE Y CATALYST

In general, the characterization of a zeolite catalyst has to provide information about structure and morphology, the chemical composition, the ability to sorb and retain molecules and the ability to chemically convert these molecules. Information on the structural, chemical and catalytic characteristics of zeolites is essential for deriving relations between their chemical and physicochemical properties on the one side and the sorptive and catalytic properties on the other. Such relations are of high importance, as they allow the rational development of sorbents, catalyst and advanced structural materials. In this paper, zeolite was synthesized from Iraqi rice husk. The main uses are as an adsorbent material to adsorb divalent zinc (Zn^{+2}) ions from simulated aqueous solution and use the remaining samples as a catalyst for n-heptane isomerization, thus only characterizations with respect to these applications are being dealt with in depth. There are many characterization techniques but the important ones in this study are X-ray diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM) and determination of BET surface area and pore volume of prepared zeolite catalysts.

X-Ray Diffraction (*XRD*)

Powder X-ray diffraction (XRD) studies were performed on the finally calcined samples in order to identify or detect different crystalline phases present in the adsorbent material. **Figure 12** illustrated XRD patterns of zeolite type Y catalyst prepared from (IRH). The comparison between the prepared HY-zeolite catalyst and standard HY-zeolite indicates that the preparation method results in a material almost compatible with the crystal structure as HY-zeolite. This leads to conclusion that the preparation method gives a nearly synthesized indigenous HY-zeolite. XRD also shows that there is small reduce in the intensity of the peaks located around differences regions, which can be explained by the prepared zeolite type Y in addition to the nature of raw materials, which were used in the preparation method.

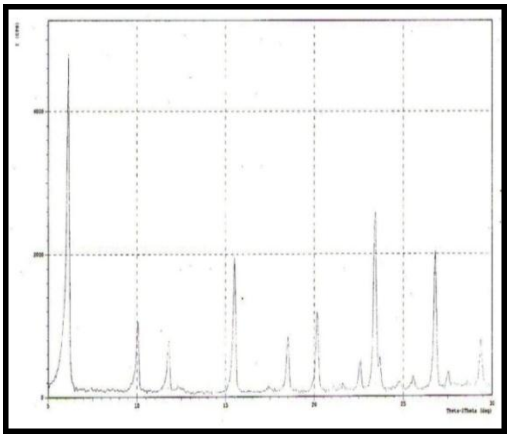


Figure-12. XRD pattern of HY-zeolite

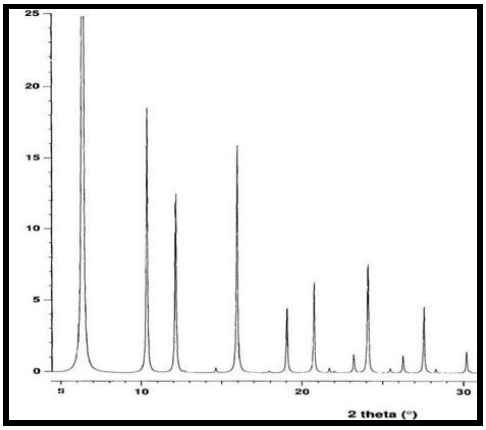


Figure-13. Standard XRD of Y-Zeolite

Scanning Electron Microscopy (SEM)

The morphologies and crystal sizes of zeolite type Y were observed by Leo 435VP (Variable Pressure Scanning) Zeiss-Leica Scanning Electron Microscope. The micrographs of SEM were taken in the magnification range of × 20,000 times. SEM images zeolite type Y prepared from (IRH) as shown in **Figure 14** show that all contain particles of 20 to 50 μm and these particles are in agglomerate form. This SEM gives the idea about particles size and their distribution also showing the way it agglomerated under the effect of Van Der Waal's forces, regarding the fact that on nanoscale the active forces become the Van Der Waals and the surface tension (Hari, 2002) . In fact the particles sizes affected by crystallization process in presence of structure directing agent therefore, the difference in particles sizes due to size of the nucles formed and crystallization method progress (Eric, 2006). In general, the sample of zeolite prepared from (IRH) gives a similar morphology of the crystal but with a difference in size.

Fourier Transform Infra-Red (FTIR) Spectroscopy

The FTIR spectroscopy for zeolite type Y catalysts prepared from (IRH) is shown in **Figure 15**. In **Figure 15** the spectrum demonstrates a very strong, intense and broad peak at 1041 cm^{-1} which corresponds to the Si-O-Si asymmetric vibration and due to the greater ionic character of the Si-O group, this band is much more intense than the corresponding C-O band. This spectrum also exhibits bands at 794 cm^{-1} and 470 cm^{-1} which correspond to the symmetric stretching of SiO_4 tetrahedral and Si-O bending band vibrations, respectively. This data indicates that the silica phase found in (IRH) was completely amorphous due to the absence of bands near 622 cm^{-1} which is identical to tridymite (crystalline phase) that shows the presence of the cristobalite phase.

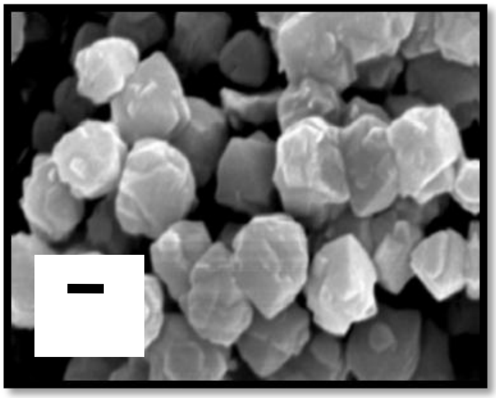


Figure-14. SEM of normally zeolite type Y catalyst

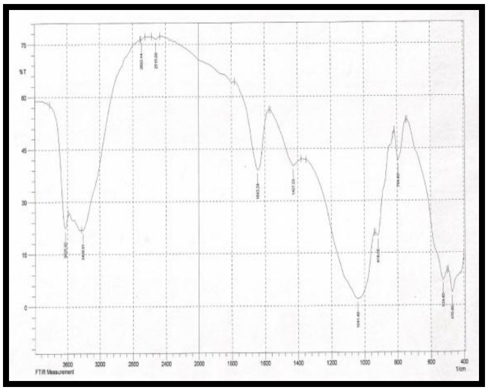


Figure-15.FTIR of normally zeolite type Y catalyst

BET Surface area and pore volume

Brunauer, Emmett and Teller (BET) theory is a well-known rule for the physical adsorption of gas molecules on a solid surface. The concept of the theory is an extension of the Langmuir theory. The Langmuir theory states that *the adsorbent surface is pictured as an array of* N^s *equivalent and independent sites for localized adsorption (one molecule per site)*. The fraction of sites occupied by N^a molecules is $\theta = N^a/N^s$. BET were able to extend the Langmuir mechanism to multilayer adsorption (Françoise Rouquerol. *et al.*, 1999). A measuring technique of specific surface area and pore volume developed on the bases of BET theory. From the kinetic theory of gases, the rate of adsorption is dependent on the pressure and the fraction of bare sites $(1-\theta)$ which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (***i***) gas molecules physically adsorb on a solid in layers infinitely; (***ii***) there is no interaction between each adsorption layer; and (***iii***) the Langmuir theory can be applied to each layer. Surface area and pore volume of zeolite type Y prepared from Iraqi rice husk were determined by BET N_2 absorption and the results are shown in **Table 3**.

Table-3. Surface Area and Pore Volume of Prepared Zeolite Catalysts

Catalyst	Surface Area, m^2/g	Pore Volume, cm^3/g
Zeolite Type Y Prepared from IRH	239.55	0.4235

Catalytic Activity of Prepared catalysts

The activity of normally zeolite type Y and promoted zeolite type Y catalysts (using to remove divalent zinc (Zn^{+2}) ion) were tested by n-heptane catalytic cracking. This is achieved in a catalytic cracking laboratory unit as described in section ***2.7*** above. n-Heptane supplied from *Sigma Aldrich Co.* and used as a raw material for catalytic cracking process. The catalytic cracking of n-heptane experiments were carried at a temperature range of 400 to 550°C and atmospheric pressure for different quantities of two types of zeolite type Y catalysts. The products of n- heptane catalytic cracking over two prepared zeolite type Y catalysts are given in **Table 4** and **Figures 16** and **17**. Results listed in **Table 9** were calculated based on the amount of n-heptane in the output of the reactor measured by GC investigation with corresponding input of 99% n-heptane purity by the equation:

$$Conversion=\frac{initial\ wt\ \%\ of\ n\text{-}heptane - final\ wt\ \%\ of\ n\text{-}heptane}{initial\ wt\ \%\ of\ n\text{-}heptane}\times 100$$

It can be seen from **Table 4** and **Figure 16** and **Figure 17** that the conversion of n-heptane catalytic cracking was increased for both prepared zeolite type Y catalysts as the temperature increasing. This may be due to the considerable enhancing effect of acid sites in zeolite catalyst in both type of catalysts normally or promoted, which emerged when the HY-zeolite had been adsorbed the n-heptane at higher temperature and may be due to the fact that when an increase in reaction temperature lead to increase the reaction rate (*for all reactions*) with respect to n-heptane catalytic cracking to produce benefit material. Also It can be seen from tables and figures referred above that the conversion and selectivity of n-heptane catalytic cracking was increasing when use promoted zeolite type Y than the conversion and selectivity using normally zeolite type Y for the same temperature. This result may be due to the metal cracking reactions activity increases for the catalyst has metal promoter which is Zn^{+2}. Therefore, the increasing in the conversion and selectivity of n-heptane catalytic cracking may be due to the existence of divalent zinc ion Zn^{+2} in the raw material (zeolite type Y prepared from (IRH)) before preparation of catalyst which activates the cracking reactions activity than the other zeolite type Y catalyst which prepared from (IRH) only (without treated Zn^{+2} ionsaqueous solutions).

Comparison between the theoretical and experimental results

The model used, as described above, determines the percent removal of Zn^{+2} ionsat different times based on different operating conditions. The results simulated using the model is compared with the experimental data obtained from sorption unit. The comparison between two models is carried out in order to obtain the most acceptable values for the model parameters as illustrated in **Table 5**, and to find the effect of each parameter on the prediction of the results. The results predicted by our proposed model show a good agreement with the experimental data with 93.5% accuracy as in **Figures 18** and **19**.

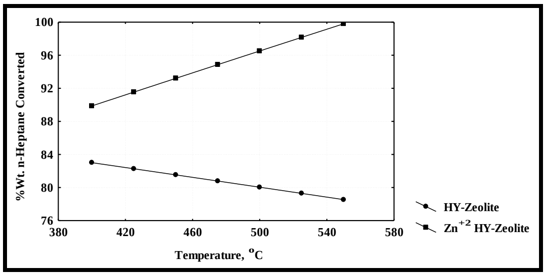


Figure 16: Effect of Temperature on n-heptane Converted (Cracked)

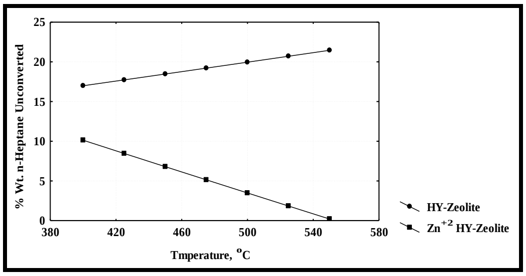


Figure 17: Effect of Temperature on n-heptane Unconverted (Uncracked)

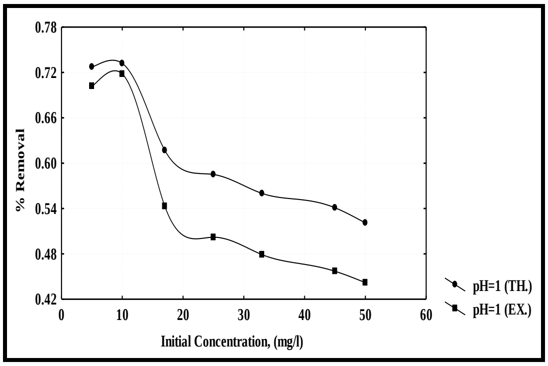


Figure 18: Comparison of experimental and modeling results for data obtained from sorption unit for **@ T_f= 50 °C, t = 60 min, h_{cat}= 0.8m, F = 1 ml/min, P =1 bar,** and **pH = 1**(**EX.:** Experimental Results, **TH.:** Theoretical Results)

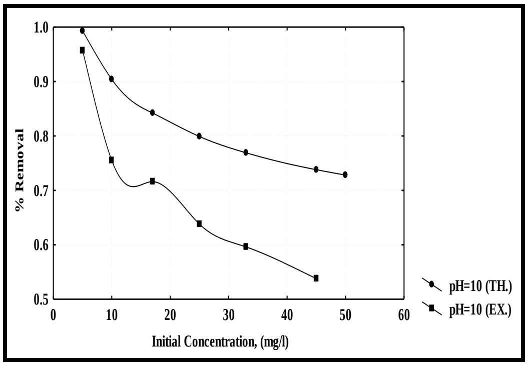


Figure 19: Comparison of experimental and modeling results for data obtained from sorption unit for **@ T_f= 50 °C t = 60 min, h_{cat}= 0.8m, F = 1 ml/min, P =1 bar,** and **pH = 10** (**EX.:** Experimental Results, **TH.:** Theoretical Results)

Table-4. n-heptane catalytic cracking using prepared zeolite catalysts

Catalyst	Temp., °C	Substances (wt%)								
		Methane	Ethane	Propylene	Butane	2-Butene	2-Pentene	1-Hexene	2-Hexene	n-Heptane (unreacted)
Normally Zeolite Type Y	400	7.7732	–	31.9448	26.1188	6.57335	–	6.19373	4.40557	16.9906
	425	7.87033	–	32.8477	24.1718	6.64756	–	6.29086	4.44308	17.7287
	450	7.96568	–	33.7523	22.2262	6.72027	–	6.38621	4.47967	18.4697
	475	8.05934	–	34.6587	20.2817	6.79157	–	6.47987	4.51539	19.2134
	500	8.15141	–	35.5666	18.3384	6.86153	–	6.57194	4.55031	19.9598
	525	8.24194	–	36.4761	16.3961	6.93021	–	6.66247	4.58446	20.7087
	550	8.33103	–	37.387	14.4547	6.99769	–	6.75156	4.61788	21.4601
Promoted Zeolite Type Y	400	8.42035	20.9538	39.6537	–	7.06983	9.05058	4.72121	–	10.1305
	425	8.50674	21.3501	40.6514	–	7.15622	9.13697	4.73917	–	8.4594
	450	8.59187	21.7442	41.6492	–	7.24135	9.2221	4.75673	–	6.79455
	475	8.67579	22.1359	42.6469	–	7.32527	9.30602	4.77392	–	5.1362
	500	8.75855	22.5256	43.6446	–	7.40803	9.38878	4.79076	–	3.48368
	525	8.8402	22.9131	44.6423	–	7.48968	9.47043	4.80725	–	1.83704
	550	8.92079	23.2986	45.6399	–	7.57027	9.55102	4.82343	–	0.19599

Table-5. Model and Required Parameters

Model Designation	Solution Method	Required Parameters
Dispersed flow, pore and surface model	Numerical solution	Pe, D_s, D_p, k_f, K, n

Statistical Model

A statistical model was carried out on the experimental results obtained from this study. Regression Analysis and π Theorem was adopted to maintain a relation between the percent removal of divalent zinc Zn^{+2} ions and the feed temperature, flow rate, pressure, pH of feed solution, initial concentration of divalent zinc Zn^{+2} ion, zeolite catalyst bed height, treatment time and column diameter. This relation is shown in equation (1), which has a correlation coefficient (R^2) equal to 99.32%.

$$\% R = 9.4566 \times 10^{-4} \left(\frac{T_f \; P \; h_{cat} \; C_{p_{sol}} \; t \; pH}{F \; d \; C_o \; g} \right)^{0.1352}$$

where: **%*R***: Percent Removal of Divalent Zinc Zn^{+2} Ions from Aqueous Solution

T_f: Feed Temperature, (K)

P: Pressure, (Pa)

h_{cat}: Catalyst Bed Height, (m)

Cp_{sol}: Heat Capacity of Aqueous Solution, (J/g.K)

F: Aqueous Solution Flow Rate

d: Internal Diameter of Sorption Column, (m)

C_o: Initial Concentration of Divalent Zinc Zn^{+2} Ion, (g/m^3)

g: Gravity Acceleration, (m/s^2)

COCLUSIONS

The following conclusions can be drawn:

1. The maximum removal of divalent zinc Zn^{+2} ions was 99.32% performed at initial concentration =5 mg/l, aqueous solution flow rate = 1 ml/min, pH = 10, pressure = 1 bar, feed temperature = 50 °C, zeolite catalyst bed height = 80 cm and treatment time = 1 h.
2. The percent removal of divalent zinc Zn^{+2} ions was increased with decreeing aqueous solution flow rate and initial concentration of divalent zinc Zn^{+2} ions while the percent removal was increasing with increasing feed temperature, treatment time, pH and the bed height of faujasite type Y–zeolite catalyst prepared from Iraqi rice husk.
3. It can be prepared a good catalyst (which is faujasite type Y–zeolite) for divalent zinc Zn^{+2} ions removal from Iraqi rice husk that remove divalent zinc Zn^{+2} ions from aqueous solution or industrial wastewater to remove the toxic waste in economic and eco-friendly method.

4. It can be prepared a good promoted catalyst (which is Zn^{+2} HY-zeolite) for catalytic cracking process from the left samples of faujasite type Y-zeolite that adsorb the divalent zinc ion Zn^{+2} from aqueous solution to produce a benefit materials and remove the toxic waste in economic and eco-friendly method.

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