Summary

Chapter I (Introduction and literature review):

This chapter includes an introduction to zeolite structures specially ZSM-5 and also includes the previous published searches in the field of synthesis, characterization and application of ZSM-5.

Chapter II (Experimental):

This chapter includes chemicals, solutions and methods which used for the synthesis of ZSM-5 using different aluminum sources (sodium aluminate, aluminum chloride, aluminum nitrate and aluminum isopropoxide), different silicon sources (tetra ethyl orthosilicate and Ludox AS 30 colloidal silica) and different template sources (tetra propyl ammonium hydroxide and ethylene diamine tetra acetic acid disodium salt), as well as the instrumentation and analytical techniques used for the characterization of the prepared samples using XRD, FT-IR, BET, EDS and TEM. Also, it describes the effect of ZSM-5 on the removing of Pb^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} from aqueous solutions which has the following concentration;27.5, 20, 25.77and 28.56mg/L respectively. Atomic absorption spectroscopy (AAS) was used for measuring concentration. This chapter also describes the methods of the preparation of Pb-ZSM-5, Cu-ZSM-5, Co-ZSM-5 and Ni-ZSM-5.

Chapter III (Results and Discussion):

This chapter deals with the results and discussion

Firstly: **discussion of the results of the prepared ZSM-5 and Pb-ZSM-5, Cu-ZSM-5, Co-ZSM-5 and Ni-ZSM-5.**

(I) XRD studies

XRD has been studied for all the prepared samples. The peaks at ranges of 2Θ =7–9° and 23–25° confirmed ZSM-5 Zeolite. The degree of crystallinity was determined from the peak area between 2θ = 22 and 25° using a highly crystalline ZSM-5 sample (ZSM-5 sample prepared using sodium aluminate, TEOS and TPAOH at 180˚Cand120 hr) as a reference. Average crystal size was measured by Scherer's equation from XRD peak between 2θ =7-10° .In case of using different crystallization times and temperatures; average crystal size increased in the following order; 180 °C (50hr)(63.58nm) < 100 °C (120hr)(71.95nm) < 180 °C (120hr)(78.56nm) < 100 °C (50hr)(88.71nm), whereas degree of crystallinity increased in the following order; 100 °C (50hr)(27.84%) < 100 °C(120hr)(64.66%) < 180 °C (50hr)(70.45%) < 180 °C (120hr)(100%).Aluminum sources can influence different aspects of ZSM-5 crystallization and it leads to change in the final properties of the final product; average crystal size increased in the following order; sodium aluminate (78.56nm)< aluminum nitrate(104.87nm) < aluminum chloride (112.30nm) < aluminum isopropoxide (118.5nm), whereas degree of crystallinity increased in the following order; aluminum isopropoxide (81.83%) < aluminum nitrate (85.58%) < aluminum chloride (90.29%) < sodium aluminate (100%).Silicon sources can influence different

aspects of ZSM-5 crystallization and it leads to change in the final properties of the final product whereas the compound obtained using TEOS was ZSM-5 only but ZSM-5 and analcime in case of Ludox AS30 colloidal silica; average crystal size increased in the following order; TEOS (78.56nm) < Ludox AS 30 colloidal silica (95.80nm), whereas degree of crystallinity increased in the following order; Ludox AS 30 colloidal silica (76.09%) < TEOS (100%). Template sources can influence different aspects of ZSM-5 crystallization and it leads to change in the final properties of the final product; average crystal size increased in the following order; TPAOH (78.56nm) < EDTA disodium salt (107.68nm), whereas degree of crystallinity increased in the following order; EDTA disodium salt (73.41%) < TPAOH (100%).

XRD patterns of all metal –containing ZSM-5 showed the typical spectrum of MFI structure but there is obvious difference in the intensities of peaks of M-ZSM-5near 2θ=7-9° and 2θ=22-25° compared with parent ZSM-5 prepared by using (TEOS,$NaAlO_2$ and TPAOH at 180 ˚C (120 hr)). The intensities of peaks of sample dried at 300 °C higher than that of sample dried at 100 °C.

(II) FT-IR studies

All the prepared samples give the characteristics peaks of ZSM-5 near 1080, 790, 550, 450and 1225 Cm^{-1}. The FT-IR transmission spectra of Pb-ZSM-5,Cu-ZSM-5 ,Co-ZSM-5 and Ni-ZSM-5 has the same spectra of ZSM-5 but the intensities of IR peaks at 447,550,800,1100and 1230 cm^{-1} changes. This indicates the introduction of metal ion.

(III) N_2 adsorption -desorption studies

The different surface characteristics of various investigated zeolitic materials were determined from N_2 adsorption /desorption isotherms conducted at 77 k. These characteristics include surface area data, Pore volume data and Pore size data. In case of using different **crystallization temperatures and times;** the BET surface area increased in the following order; 100°C (120hr) (151m^2/g) <100°C (50hr) (168.5 m^2/g) <180°C (50hr) (184.1 m^2/g) <180°C (120hr) (290.1 m^2/g). In case of using different **aluminum sources** the BET surface area increased in the following order; aluminum chloride (153.1m^2/g) < aluminum isopropoxide (171.8m^2/g) < aluminum nitrate (212.4m^2/g) <sodium aluminate (290.1m^2/g). In case of using different **silicon sources** the BET surface area increased in the following order; LudoxAS30 colloidal silica (109.8m^2/g) <TEOS (290.1m^2/g). In case of using different **template sources** the BET surface area increased in the following order; EDTA disodium salt (141.4m^2/g) <TPAOH (290.1m^2/g).

(IV) EDS studies

EDS has been studied for the prepared ZSM-5 samples and the results show that the prepared samples are chemical compounds of Si-O-Al-Na composition. But the sample prepared using aluminum chloride contains carbon in addition to the previous elements.

(V) TEM studies

The results show that the sample, which were prepared at 100 °C (50 hr) crystallized in spherical shape crystals due to very low degree of crystallinity. The sample that were prepared at 100 °C (120hr) crystallized in orthorhombic shape crystals. The sample that were prepared at 180 °C (50hr) crystallized in both of spherical and subhedral shape crystals. The sample that were prepared at 180 °C (120hr) crystallized in cubical shape crystals. The samples that prepared using aluminum chloride, aluminum nitrate and Ludox AS 30 colloidal silica crystallized in hexagonal shape crystals, whereas the sample prepared using aluminum isopropoxide crystallized in orthorhombic shape crystals but the sample prepared using ethylene diamine tetra acetic acid crystallized in both of tabular and hexagonal shape crystals.

Secondly: **discussion of the results of the removing of heavy metals from aqueous solutions**

ZSM-5 has a great effect on the removing of Pb^{2+}, Cu^{2+}, Co^{2+} and $Ni^{2+}$from aqueous solutions which has the following concentration 27.5, 20, 25.77and 28.5mg/L respectively. The adsorption of these metal ions is greatly dependent on contact time with adsorbent (ZSM-5).Such experiments provide equilibrium time after which adsorption could not be achieved due to saturation of adsorbent's active sites. It was found that equilibrium time was 120 min for both of Pb^{2+} and Cu^{2+} whereas 60 min for both of Co^{2+} and Ni^{2+}. These results suggest that the pseudo – second order sorption mechanism is predominant for sorption of Pb^{2+}, Cu^{2+} and Co^{2+}, whereas pseudo first- order sorption mechanism is predominant for sorption

of Ni^{2+}.The effect of pH has been studied; In case of lead the uptake efficiency gradually increase as the pH increase from 2.13 to 4.99 then above 4.99 uptake efficiency Reduced to a small extent. In case of cupper the uptake efficiency gradually increases as the pH increase from 2.44 to 6.60.In case of cobalt the uptake efficiency gradually increases as the pH increase from 2.31 to 6. In case of nickel the uptake efficiency gradually increases as the pH increase from 2.50 to 5.84.The effect of both of concentration and temperature has been studied and it was found that the % uptake increase as the concentration decrease and the temperature increase. Both of Langmuir and Freundlish isotherms has been studied and it was found that adsorption process for all metals was fit to Langmuir model than the Freundlish model. Thermo dynamic parameters, standard free energy ΔG^0, standard enthalpy ΔH^0 and standard entropy ΔS^0 were determined. It can be stated that Pb^{2+}, $Cu^{2+}$and Co^{2+} adsorptions on ZSM-5 are an endothermic phenomenon, whereas Ni^{2+} adsorption on ZSM-5 are an exothermic phenomenon. Adsorption process of Pb^{2+} is chemical in nature, whereas adsorption process of Cu^{2+} Co^{2+} and Ni^{2+} is physical in nature. The negative Gibbs' free energy ΔG values for Pb^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} confirm the feasibility of the adsorption process and that adsorption is spontaneous. positive values of entropy for Pb^{2+}, $Cu^{2+}$and Co^{2+} means that they have high degree of freedom whereas, negative values of entropy for Ni^{2+} means that they have low degree of freedom.