Abstract

The study includes sixth chapters, the chapter I gave an introduction to some of the qualities of amine organic compounds such as ANI and its derivatives, and also it included some of the qualities of phenolic compounds such as phenol and its derivatives. It also included the types of polymer from conductivity; conductive and insulator to electricity. Moreover, the types of the polymerization process; chemical and electrochemical polymerization processes. It also focused on the electropolymerization process because of its advantages, and also the study mentions some of the factors that depended upon electropolymerization process and the characterization and analysis of the electroprepared polymer. Finally, it mentioned some of the previous studies of the electropolymerization process that carried out on the amino compound such as ANI and *m*-toluidine compounds, and phenolic compounds such as phenol and *m*-cresol.

Chapter II included the anodic electropolymerization of *m*-toluidine on Pt-electrode from a deoxygenated aqueous acid medium was carried out using cyclic voltammetry technique. The effect of different parameters on the electrochemical polymerization such as a monomer, sulfuric acid, sodium sulfate concentrations, scan rate, and temperature were investigated using a conventional three-electrode cell. The results showed the presence of an oxidation peak (anodic current peak) at approximately +1110 mV vs. saturated calomel electrode in all cases of the investigated parameters. A gradual increased of the anodic current peak density (Ip) was observed with repeating number of cycles accompanied with the appearance of a new peak at low positive potential from the second repeating cycle. In addition, the effects of *m*-toluidine, sulfuric acid, sodium sulfate concentrations, scan rate, and temperature values have the same behavior on Ip values, in which there were increasing in I_p values till certain values (different for each parameter) and then decreased. The experimentally obtained kinetic equation was deduced from the values of Ip and a simplified mechanism for the electrochemical anodic polymerization of m-toluidine was proposed. Moreover, the diffusion coefficient, activation energy (E_a), and thermokinetic parameters such as entropy (ΔS^*) and enthalpy of reaction (ΔH^*) were calculated. The prepared polymer was characterized by Elemental analysis, UV-visible, IR, ^{1}H-NMR, X-ray diffraction, SEM, and TGA.

Chapter III included the electrochemical anodic polymerization of *m*-cresol on platinum electrodes using cyclic voltammetry technique was performed. The cyclic

voltammetric data showed the presence of an oxidation peak (anodic current peak) at approximately +1010 mV vs. saturated calomel electrode. The effects of *m*-cresol, sulfuric acid, and sodium sulfate concentrations, scan rate, and temperature were studied, and they have the same behavior on Ip, in which there was an increasing of Ip till certain value (different for each parameter) and then decreased. The experimentally kinetic equation was deduced from values of Ip, and simplified mechanism for the electrochemical anodic polymerization was proposed. Moreover, the diffusion coefficient, activation energy (E_a), and thermokinetic parameters such as entropy (ΔS^*) and enthalpy of reaction (ΔH^*) were calculated for the polymer. Finally, the chemical structure and morphology of the prepared polymer were characterized by Elemental analysis, UV-visible, IR, ^{1}H-NMR, X-ray diffraction, SEM, and TGA analysis.

Chapter IV included the electrochemical anodic polymerization of *m*-toluidine and *m*-cresol monomers together on the platinum electrode using cyclic voltammetry technique. The cyclic voltammetric data showed the presence of an Ip at approximately + 1060 mV vs. saturated calomel electrode in cases of all investigated parameters. The effects of *m*-toluidine and *m*-cresol monomers, sulfuric acid, sodium sulfate concentrations, scan rate, and temperature were studied, and they have the same behavior on the Ip values, in which there were increasing of Ip untill certain value (different for each parameter) and then decreased. In addition, the effect of repetitive cycles was studied, in which the Ip disappeared from the second repeating cycle. The experimentally kinetic equation was deduced from the Ip values, and simplified mechanism for the electrochemical anodic polymerization reaction was proposed. Moreover, the diffusion coefficient, activation energy (E_a), and thermokinetic parameters such as entropy (ΔS^*) and enthalpy of reaction (ΔH^*) were calculated. Finally, the chemical structure and morphology of the prepared polymer were characterized by elemental analysis, UV-visible, IR, ^{1}H-NMR, X-ray diffraction, SEM, and TGA.

Chapter V included the applications of the prepared polymer films as pH and heavy metal sensors. A sensor of *m*-toluidin polymer film coated platinum electrode was fabricated by the electropolymerization using cyclic voltammetry technique for the detection of mercury ions (Hg^{2+}) in aqueous solution. The study was carried out using simple potentiometric method and confirmed by cyclic voltammetry technique. The effects of the polymer film thickness and pH of Hg^{2+} ions solution on the response of the sensor were studied. Moreover, the stability, sensitivity, and selectivity of the *m*-toluidine sensor were studied. The best thickness of polymer film was found to be ten cyclic voltammetric runs. This film has a Nenstian response slope of 29.19

mV/decade with a detection limit of $3.54x10^{-5}$ M at 293 K by the simple potentiometric method. In addition, it has a sensitivity of 4×10^{-7} AM^{-1} with a detection limit of $1.33x10^{-7}$ M by the cyclic voltammetry method. Moreover, the sensor is a specific to Hg^{2+} ions in the presence of other ions such as Na^{+}, $K^{+,}$ Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+}. Also, the highest response of the sensor to Hg^{2+} ions in a solution of pH ranged from 4.0 to 6.4 for lifetime of about eleven weeks. Moreover, the sensor was applied for detection of four natural samples; tap water, underground water, first distillated water, and another sample wasted with Hg^{2+} ions.

Moreover, *m*-toluidine polymer film coated platinum electrode used as pH sensor in aqueous solution. The study was carried out by simple potentiometric method by measuring its potentiometric response slope, and it was confirmed by cyclic potentiometer technique method. The effects of thicknesses of the sensor polymer film in term of number of cyclic voltammetric runs, different buffer solutions, and stability of the sensor with days on proton ions determination was studied. Linear calibration curve in pH range from 6.0 to 10 for ten cyclic voltammetric runs was obtained by simple potentiometric method with Nenstian response slope of 57.34 mV/decade at 293 K. From the two methods of studying, the best thickness of the sensor polymer film was ten cyclic voltammetric runs. In addition, the best range of pH solutions was from 6.0 to 10. The sensor has good sensitivity and selectivity to proton ions in the presence of a variety of other cations such as Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}. Moreover, the lifetime of the sensor was about nine days, which enhanced to reach nine weeks.

In addition, *m*-cresol polymer film coated a platinum electrode was used as sensor for the detection of lead (II) ions (Pb^{2+}) in aqueous solutions. The study was carried out by the simple potentiometric method by measuring its potentiometric response slope and was confirmed by the cyclic voltammetry technique. The effects of the polymer film thicknesses and the pH of Pb^{2+} solution on the response of the sensor were studied. Moreover, the stability, sensitivity, and selectivity of the *m*-cresol sensor were studied. The best thickness of polymer film was about three cyclic voltammetric runs. This film has Nenstian response slope of 26.5 mV/decade with a detection limit of $2.75x10^{-5}$ M at 293 K by the simple potentiometric method. In addition, it has a sensitivity of $1.1x10^{-6}$ AM^{-1} with a detection limit of $7.0x10^{-7}$ M by the cyclic voltammetry method. Moreover, the sensor is selective to Pb^{2+} ions in the presence of other ions such as Na^{+}, $K^{+,}$ Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}. Also, the highest response of the sensor to the Pb^{2+} ions is achieved over a pH range of 4.0 – 5.3. The lifetime of the sensor is more than one month. Moreover, the sensor was applied for the detection of four natural samples; tap water,

underground water, first distillated water, and another sample wasted with the Pb^{2+} ions.