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Full Paper

Preparation of Novel Sensors for Potentiometric Determination of Ciprofloxacin Hydrochloride by Green Synthesis of ZnO Nanoparticles

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Abstract- Metal oxide nanoparticles (MONPs) are utilized in many arenas. They can be formulated via various methods for example eco-friendly synthesis, this method contains infinite accession to create MONPs with required properties. Most plants have features as supportable and renewable providers compared with enzymes and microbes, as they have the ability to collect nearly 75% of the energy of light and transform it into energy of chemical, which play fundamental roles in the manufacture of nanoparticles due to containing sugars and antioxidants. In this research green method was applied for the preparation of a novel type of coated wire electrodes for potentiometric determination of ciprofloxacin hydrochloride in pure and pharmaceutical commercial based on metal oxide nanoparticles (ZnO NPs) were synthesized chemical and green sources, leaves extract of Myrtus communis and Mentha, respectively. The electro-active material ciprofloxacin-molybdophosphoric acid (CFX-PM) was made via mixing CFX with molybdophosphoric acid (PM) with used n-Di butyl phthalate (DBP) as a plasticizer. More sensitive sensors were given a Nernst slope equal to 57.89, 58.71, and 59.69 mVdecade-1 with a linear range around 9.0×10^{-9}-1.0×10^{-2}, 1.0×10^{-9}-1.0×10^{-2} and 1.5×10^{-9}-1.0×10^{-2} mol.L^{-1} and the limit of detections were 7.3×10^{-10}, 5.0×10^{-10} and 1.2×10^{-10} mol.L^{-1} with correlation coefficients were 0.9995, 0.9994, and 0.9991 with lifetime equal to 35,36 and 41days for ZnO NPs, ZnO NPs with leaves extract of Myrtus communis and Mentha coated wire electrodes, respectively. The results displayed excellent selectivity and sensitivity of the improved coated wire electrodes with nanometal oxide for the determination of the ciprofloxacin hydrochloride in original samples and marketable formula.

Keywords- Ciprofloxacin hydrochloride; Green synthesis; Nanoparticles; Mentha; Myrtus communis; Sensors

1. INTRODUCTION

Ciprofloxacin hydrochloride,1-cyclopropyl-6-fluoro1,4-dihydro-4-oxo-7-(1- piperazinyl)-3- quinoline carboxilic acid (CPX), Ciprofloxacin is a type of an antibiotic, it utilized to avoid and treat human diseases due to the antibiotic has a very broad antibacterial spectrum, counting the bacteria gram (+), and mainly gram (-) [1]. It is pale yellow, crystalline, a little hygroscopic powder, soluble in water, and a little in methanol [2]. The chemical construction of ciprofloxacin hydrochloride is displayed in Figure 1.

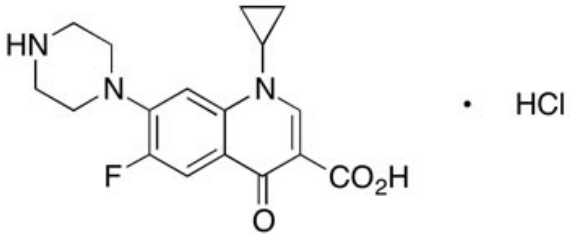


Figure 1. Chemical construction of ciprofloxacin hydrochloride [3]

Metal oxides nanosized have various exceptional properties [4], which including a selectivity of heavy metals and great exclusion capability. They have huge potential as favorable adsorbents to heavy metals. Metal oxide-built nanomaterials consist of oxides of aluminum, oxides of iron, oxides of manganese, oxides of cerium, oxides of zirconium, oxides of zinc, oxides of magnesium, and oxides of titanium nanosized [5]. Zinc oxide NPs have advanced abundant more significance in the last ages because of their great characterizations for example high stability as a chemical, great photostability, great electrochemical coupling factor, and radiation absorption as a varied range [6]. Potentiometry methods include determining the potential in the middle of electrodes without flowing current. Ion selective electrode is a comprehensive subgroup of potentiometry counting pH electrodes prepared from glass. Ion-selective electrodes contain two electrodes known as the indicator electrode (as well named the ISE) and the reference electrode. The difference between the reference electrode and indicator electrode via a membrane at the bottom that is capable of uptake of the chosen species of ion [7]. There are many electrodes were prepared for the determination of ciprofloxacin hydrochloride such as a PVC thin layer ciprofloxacin selective-electrodes with active material is CFX-tetra phenyl borate (CFX-TPB) and using di octyl phthalate DOP as a plasticizer [8]. Electrodes were prepared by mixing Ciprofloxacin hydrochloride (CFH)–Molybdophosphoric acid (MPA), these electrodes were given slopes equal to 53.30, 43.40, 50.10 mV/ decade, respectively [9]. Potentiometric titration is applied for the quantification of ciprofloxacin (CPFX) in pure and dosage forms, with a linear range near 0.0250-2.500 mM (0.10-10 mM) [10]. Simple carbon paste and nano-composite carbon paste constructed on

sensors of potentiometric were utilized for determination of ciprofloxacin [11]. PVC membrane drug selective sensors were constructed for CFX. The electro active materials were CFX- Tetra phenyl borate (CFX-TPB), which plasticized by Di- octyl phthalate (DOP) [12]. In this work a new modified metal oxide ZnO nanoparticle coated wire sensors were prepared to determined CFX in pharmaceutical items with ultra-sensitivity and selectivity. A novel technique established on using the excellent chemical, physical, optical, and conductive constructions of the selected metal oxide has been suggested via applied the potentiometric improved sensor.

2. EXPERIMENTAL SECTION

2.1. Chemicals

All chemicals were of analytical grade, Ciprofloxacin hydrochloride from (SDI), Cipro-Denk (500 mg/tablet) from Germany, Zinc nitrat $Zn(NO_3)_2$, Sodim hydroxide (NaOH), acetone 99.9%, methanol 99.9%, ethanol 99.9%, tetrahydrofuran. Molybdophosphoric acid (PM) 99%, di-n-butyl phthalate (DBP), and high molecular weight PVC, among other analytical chemicals and solvents were from Fluka.

2.2. Apparatus

Double beam UV-Visible spectrophotometer model (UV-1650 PC) Shimadzu, Japan, infrared spectrophotometer SHIMADZU, FTIR-8000 (Japan), XRD Phillips xpert PA analytical, Holland, Field Emission Scanning Electron Microscopy (FE-SEM) and transmission electron microscopes, French MIRA3, Atomic forces microscope (AFM), AA2000, Angstrom, HANNA instruments pH 2110UK, Romania, Reference electrode: Saturated calomel electrode (RE-2BH), atomic forces microscope (AFM), AA2000, Angstrom were used.

2.3. Preparation of CFX-PM Electro-active Material

Ion-pair of complex CFX-PM was prepared via mixing a similar concentration (1.0×10^{-2} mol. L^{-1}) of CFX in 100 ml. A precipitate was formed of CFX-PM. The precipitate was washed through deionized water and filtered by Whatman filter paper No. 41, then it left for 24 h to dry.

2.4. Synthesis of ZnO_2 nanoparticles

To synthesized ZnO NPs were prepared 100 mL of 0.1 mol.L^{-1} of zinc nitrate hexahydrate in deionized water. 0.1 mol.L^{-1} of NaOH was dripped slowly at room temperature with constant stirring. The final solution shown the difference in color to white color slowly, then left the solution stirring it for 2 h. The mixture was centrifuged at normal room temperature. The gel

obtained put it in Petri dish which contain the gel is placed for dry at overnight and then put it in the furnace at 500^0C for 3h for calcination [13] as shown in Figure 2.

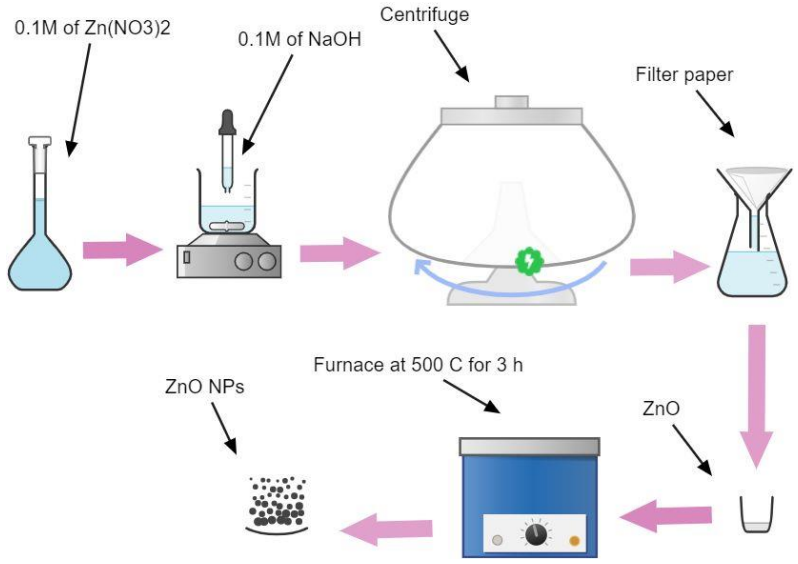


Figure 2. Chemical synthesis of ZnO nanoparticles

2.5. Green Synthesis of ZnO_2 nanoparticles

Firstly, preparation of leaves extract of *Myrtus communis* and *Mentha*. The fresh leaves of *Myrtus communis* and *Mentha* were washed numerous times via utilizing deionized water to clean it.

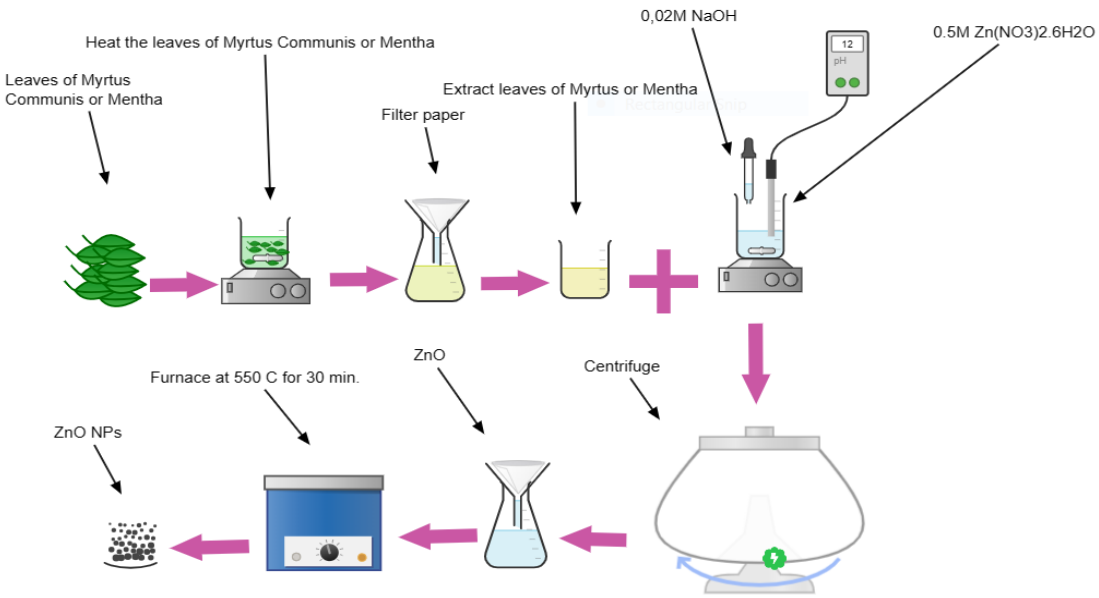


Figure 3. Green synthesis of ZnO NPs with leaves extract of *Myrtus communis* and ZnO NPs with leaves extract of *Mentha*

Then, the leaves were left to dry and grind to well powder via a mortar. About 5 g of the powder leaves were put in beaker of 250 mL mixed with 50 mL of deionized water, and heated at 45℃ for 20 minutes. The mixture was filtered in extra beaker with Whatman No. 1 Then the extract was utilized for synthesis of ZnO NPs via 25 mL of 0.05 M aqueous solution of $Zn(NO_3)_2.6H_2O$ was mix up with 4 mL of the aqueous leaves extract of *Myrtus communis* and *Mentha* in a 250 mL beaker as shown in Figure 3 Then, the pH of the mixture would be at pH equal to 12 via the slow addition of NaOH solution at concentration of 0.02 $mol.L^{-1}$. The finals solution, was stirred for nearly three hours at room temperature under a magnetic stirrer, then centrifuged at 8000 rpm for 20 min. This outcome a solid product with light-orange color which was then dried for 12 h in an oven at 60℃. The solid product was collected and calcined in a furnace at 550℃ for 30 minutes. After cooling the powder was kept in a desiccator for the procedure of green synthesis of ZnO nanoparticles shown in Figure 3 [14].

2.6. Preparation of Standard CFX Solution

A CFX standard solution (0.1 $mol.L^{-1}$) was prepared via addition 3.678 g of CFX powder to deionized water (100 mL). The solution was be dilute by utilizing the deionized water at the range of 1.0×1.0^{-10}-1.0×10^{-2} $mol.L^{-1}$.

2.7. Preparation of Sensor

To preparing a solution of polymeric functionalized ZnO nanoparticles by weighting suspending approximately 0.5 gm of ZnO nanoparticles with 0.1 gm of CFX-PM complex, 0.19 gm of matrix (PVC), and 0.35 mL of n-di butyl phthalate (DBP) in 7 mL of THF. By stirring to make a polymeric solution of CFX-PM-ZnO nanoparticles which is then used to make the surface of wire wire-coated electrode based on CFX-PM-ZnO nanoparticles. The formation of a thin layer on the surface of the electrode for using it as a mixture of the generated membrane.

2.8. Calibration of Sensors

The data of potentials of (CFX-PM-ZnO NPs) sensors were quantified and plotted *vs.* concentrations of CFX ($mol.L^{-1}$). The range of linear was valued separately utilizing CFX standard solutions (50 mL) in the concentration range 1.0×10^{-10}-1.0×10^{-2} $mol.L^{-1}$and the constructed functional CFX-PM-ZnO NPs sensors were utilized.

3. RESULTS AND DISCUSSION

3.1. UV-Visible Spectroscopy of ZnO NPs ,ZnO NPs with leaves extract *Myrtus communis* and ZnO NPs with leaves extract *Mentha*

The spectra of UV-Vis were documented for structure of ZnO NPs which shown in Figure 4. These peaks are registered at 380.0, 370.0 and 381.0 nm for ZnO NPs, ZnO NPs with leaves extract of *Myrtus communis*, and ZnO NPs with leaves extract of *Mentha*, respectively, is in agreement with the range of spectral of ZnO nanoparticles between300–500 nm [15,16].

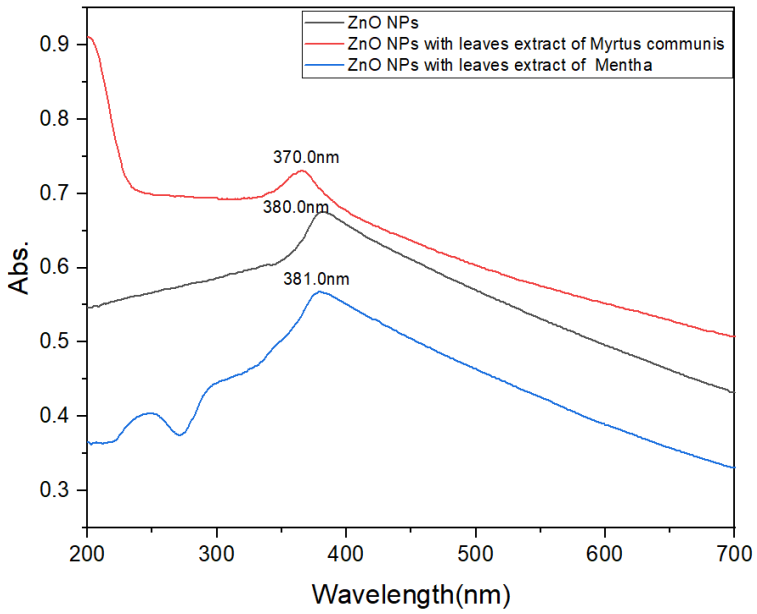


Figure 4. UV-Visible spectrum of Zinc oxide nano particles

From Figure 4, the various peaks exist at various wavelength, which were generally related with Zn defects, for example moves of an electron from conduction to the valance band and O_2 vacancies [17]. The O_2 vacancies alteration the characterization of oxide materials via making F centers of ionic oxides which may cause the foundation of metal-metal bonds in covalent bond. In other case, O_2 vacancies variation the state of composites of transition metal atoms with empty d orbitals, which can finally change the local electronic construction of atoms [18].

3.2. Analysis of FTIR of ZnO NPs, ZnO NPs with leaves extract of *Myrtus communis* and ZnO NPs with leaves extract of *Mentha*

In Figure 5 all zinc oxide nanoparticles prepared method the stretching band (3322.56-3277.12) cm^{-1} and bending bands (1636.84- 1636.05) cm^{-1}appear to hydroxy group, the Zn-O spectrum bands show at (455.94) cm^{-1} for ZnO NPs and (472.15,434.37) cm^{-1} for ZnO NPs with leaves extract of *Myrtus communis* and (466.21) cm^{-1} appear Zn-O bands for leaves extract of *Mentha*. That indicated that the zinc oxide nanoparticles prepared from was form in one phase (Zn-O) matched with values in reference [19].

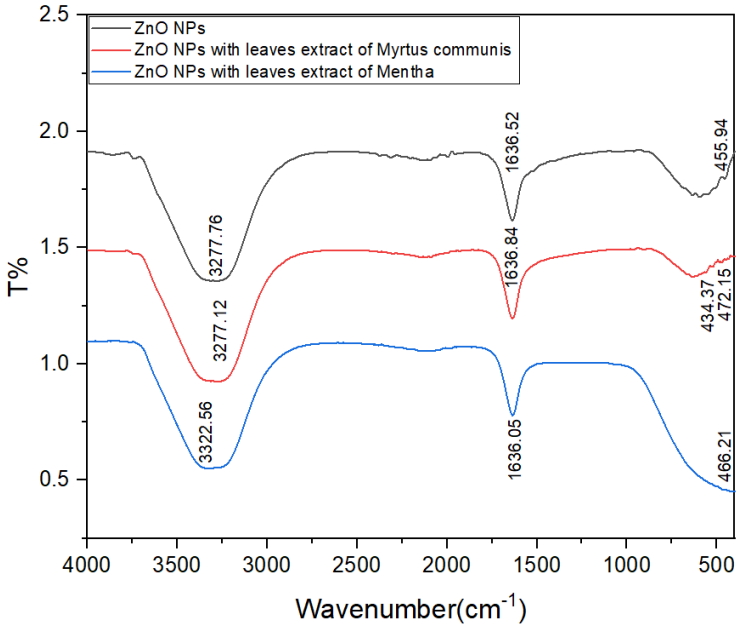


Figure 5. FTIR spectrum of ZnO NPs, ZnO NPs with leaves extract of *Myrtus communis* and ZnO NPs with leaves extract of *Mentha*

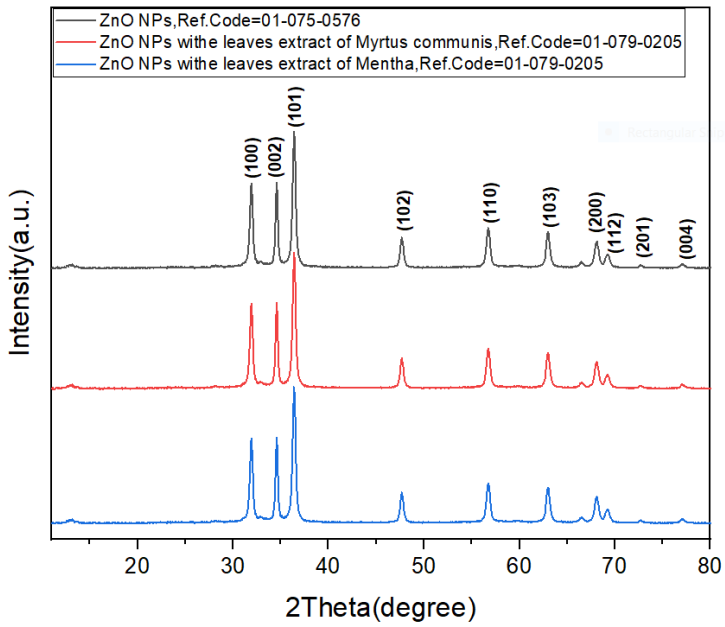


Figure 6. XRD pattern of ZnO NPs, ZnO NPs with leaves extract of *Myrtus communis* and ZnO NPs with leaves extract of *Mentha*

3.3. XRD Analysis

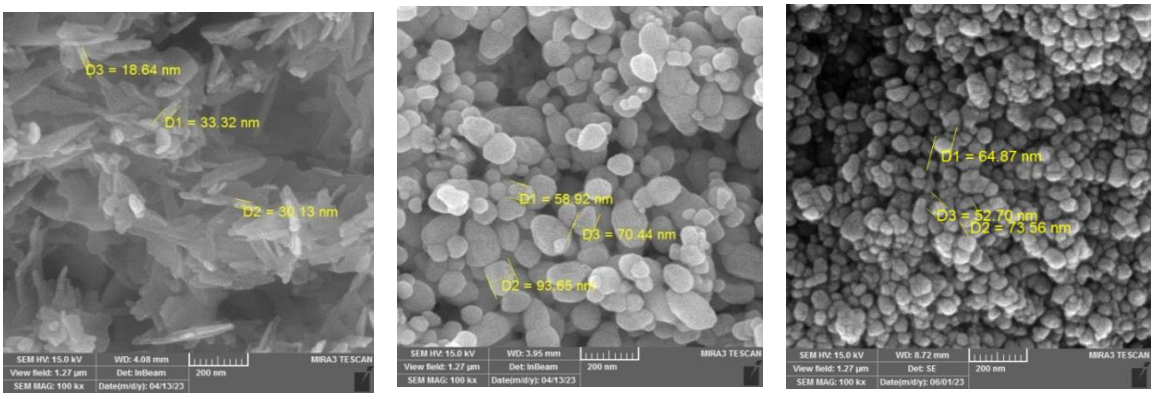
To value the nature of crystalline of the synthesized nanoparticles, the diffract gram was examined. The peaks of X-ray diffraction for chemical and green synthesized ZnO

nanoparticles at 2θ obtained are at 31.92◦, 34.57◦, 36.37◦, 47.67◦, 56.72◦, 63.02◦, 66.51◦, 68.11◦ and 69.20◦ for ZnO NPs with 31.07◦, 34.67◦, 36.52◦, 47.77◦, 56.82◦, 63.07◦, 66.57◦, 68.17◦ and 69.37◦ for ZnO NPs with leaves extract of *Myrtus communis* and 31.97◦, 34.62◦, 36.42◦, 47.77◦, 56.77◦, 63.02◦, 66.56◦, 68.12◦ and 69.32◦ for ZnO NPs with leaves extract of *Mentha*, respectively as shown in Figure 6.

The peaks were agreed with the JCPDS cards No. 01-075-0576 for ZnO NPs, and JCPDS cards No.01-079-0205 for ZnO NPs with leaves extract of *Myrtus communis* and leaves extract of *Mentha*, respectively. The average size of Zinc oxide nanoparticles from calculation of Scherer equation is equal to 23.32,17.30 and 18.93nm for ZnO NPs, ZnO NPs with leaves extract of *Myrtus communis* and ZnO NPs with leaves extract of *Mentha*, respectively.

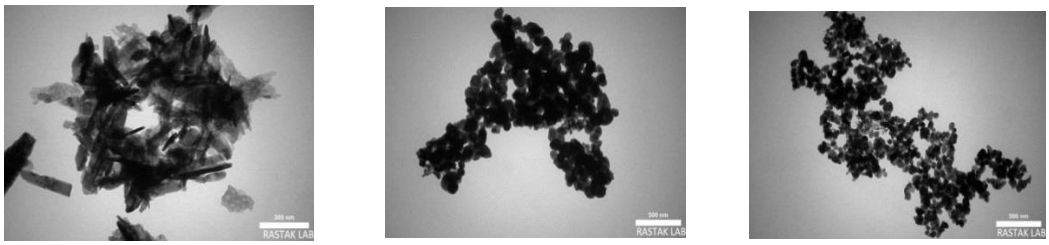
3.4. SEM, TEM and AFM Analysis

The Scanning Electron Microscopic and transition electron microscopic images were taken to check the finding of nanoparticles. Figure 7 shows SEM images which taken for ZnO NPs, ZnO NPs with leaves extract of *Myrtus communis* and *Mentha*. SEM discovered the particle to be in its nano formula. The partly agglomerated state could be because of that no hard-acting chemical filtration methods were working in green synthesis. Extra factor that supports combination can be the smaller size of the nanoparticles. The average size of ZnO NPs were 27.36,74.33 and 63.71nm for ZnO NPs, ZnO NPs with leaves extract of *Myrtus communis* and *Mentha*, respectively. The average size of ZnO NPs which were calculated from atomic forces microscopy were 21.10, 79.79, and 64.42 for ZnO NPs, ZnO NPs with leaves extracted from *Myrtus communis* and *Mentha*, respectively. Also, Figure 8 shows the TEM images of ZnO NPs, ZnO NPs with leaves extract of *Myrtus communis* and *Mentha*, respectively, which display the distribution and morphology and Figure 9 shows the AFM images for ZnO NPs with leaves extract of *Myrtus communis* and *Mentha*, respectively.



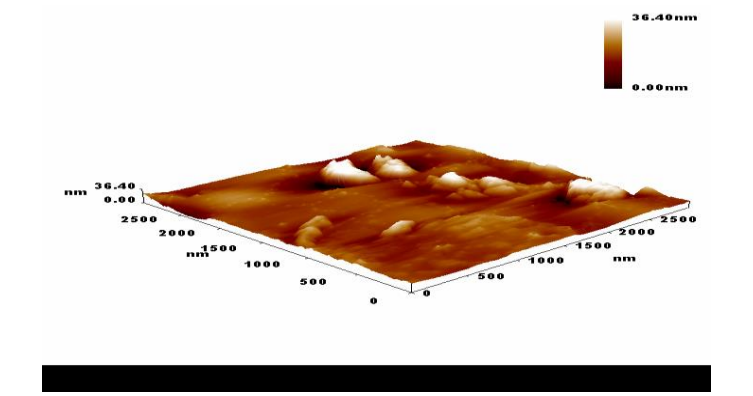
(a) (b) (c)

Figure 7. SEM images of Zinc oxide NPs where (a) for ZnO NPs and (b) for ZnO NPs with leaves extract of *Myrtus communis* and (c) for ZnO NPs with leaves extract of *Mentha*

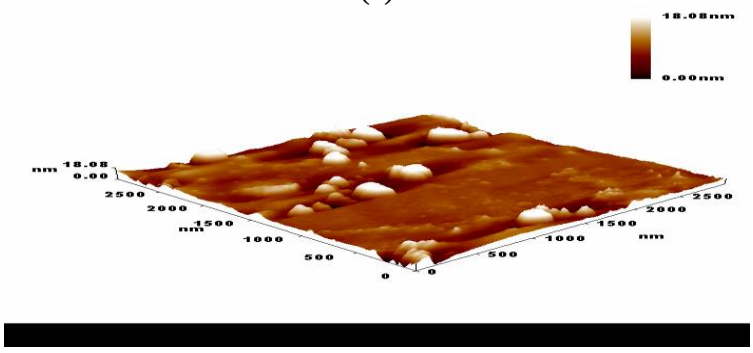


(a) (b) (c)

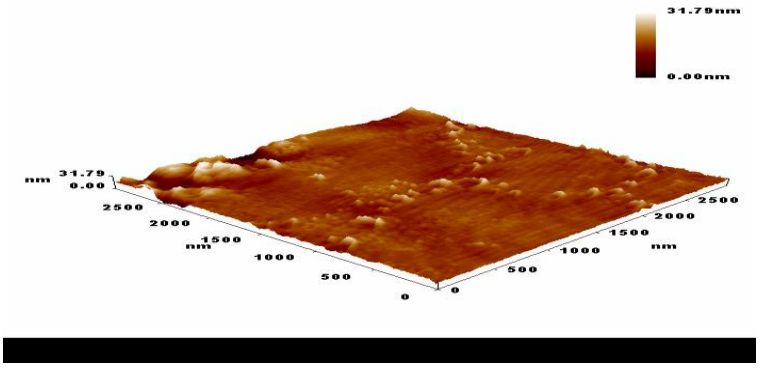
Figure 8. TEM images of Zinc Oxide NPs where (a) for ZnO NPs and (b) for ZnO NPs with leaves extract of *Myrtus communis* and (c) for ZnO NPs with leaves extract of *Mentha*



(a)



(b)



(c)

Figure 9. AFM images of Zinc oxide NPs where (a) for ZnO NPs and (b) for ZnO NPs with leaves extract of *Myrtus communis* and (c) for ZnO NPs with leaves extract of *Mentha*

Table 1 shows the different values of characterization of CFX sensors which prepared by coated wire electrodes with nanoparticles. The applied using nanoparticles such as ZnO NPs gave an excellent Nernstian response, the slopes for CFX coated wire electrode is 57.89, 58.71 and 59.69 mV.decade^{-1} for CFX-PM-ZnO NPs,CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrodes, respectively for CFX concentration. Linear range to the CFX concentration was from 9.0×10^{-9}-1.0×10^{-2},1.0×10^{-9}-1.0×10^{-2} and 1.5×10^{-9}-1.0×10^{-2} mol.L^{-1} for CFX-PM-ZnO NPs ,CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract *Mentha* coated wire electrodes, respectively (Figure 10). Coated wire electrodes were gave a detection limit equal to 7.3×10^{-10}, 5.0×10^{-10} and 1.2×10^{-10} mol.L^{-1} for CFX-PM-ZnO NPs, CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha*, respectively. CFX electrodes lifetime were by weekly check the response of slope were 35,36 and 41 days for CFX-PM-ZnO NPs, CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract *Mentha* coated wire electrodes respectively.

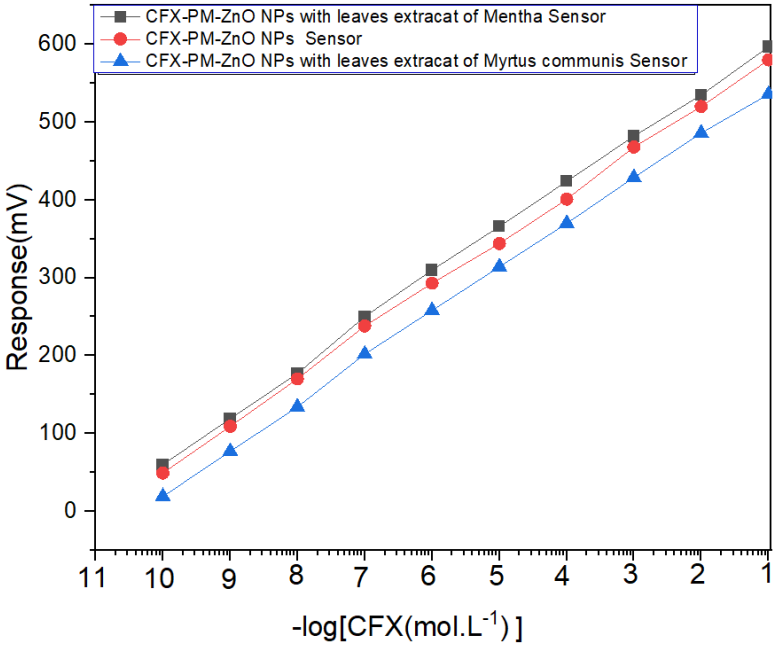


Figure 10. Calibration curve of CFX-PM-ZnO NPs,CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrodes

On the other hand, another type of sensors was prepared for determination of ciprofloxacin hydrochloride-based nano-composite carbon paste and simple carbon paste based potentiometric sensors of cirprofloxacinium-phosphotungstate, as well as a highly lipophilic cation-exchanger, sodium tetrakis(trifluoromethyl)phenyl borate were constructed and used for

determination of ciprofloxacin at different pH values. The slope were equal to 55.7 and 66.6 mV.decade $^{-1}$ with concentration range were of 1.0×10^{-5} to 1.0×10^{-2} mol.L^{-1}, detection limits were 1.0×10^{-5} and 7.9×10^{-6} mol.L^{-1} for bare carbon paste and MWCNTs-based sensors, respectively. Optimized sensors were successfully applied for the determination of ciprofloxacin in its pure form, pharmaceutical preparations, as well as spiked urine and serum samples, with high recovery [11]. The utmost important component in improving ultrasensitive sensors with essential features is the select materials of nanostructured and sensor suggest method. The ratio of surface volume which is a significant component in increasing contact reactions on the overall electrical conductivity of nanomaterials, is detected via the size and shape of the nanoparticles which used. Therefore, because of these nanomaterials have a high chemical stability, the morphology of the nanoscale will influence not just the sensitivity of the sensor but also the dynamic responsiveness and lengthy-term stability of the sensor. The polymeric media and molecular structure, for example, long-chain polymer and crystallinity, may well affect the electrical conductivity of metal oxide nanocomposite-made-up sensors [20].

Table 1. Parameters of CFX-PM-ZnONPs, CFX-PM-ZnONPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of and *Mentha* coated wire electrodes

Parameters	CFX-PM- ZnO NPs coated wire electrode	CFX-PM-ZnO NPs with leaves extract *of Myrtus communis* coated wire electrode	CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrode
Slope (mV.decade^{-1})	57.89	58.71	59.69
Correlations Coefficient(R^2)	0.9995	0.9994	0.9991
Range of Conc. (mol.L^{-1})	9.0×10^{-9}-1.0×10^{-2}	1.0×10^{-9}-1.0×10^{-2}	1.5×10^{-9}-1.0×10^{-2}
LOD (mol.L^{-1})	7.3×10^{-10}	5.0×10^{-10}	1.2×10^{-10}
Intercept(mV)	600.87	640.07	660.27
Range of PH	5.5-9.5	5.0-9.0	4.5-9.5
Life of time(day)	35	36	41

3.5. Effect of pH on the Electrodes Responses

To measure the result of pH response of on CFX-PM-ZnO NPs, CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrodes, the potential of the ciprofloxacin hydrochloride (CFX) solution was measured at 1.0×10^{-3} mol.L^{-1} from the pH value of 0.5 to 14.0 by using solutions of HCl or

NaOH as concentrated to adjustment the pH. The results displayed in Figure 11 show that the value of potential stayed constant in spite of the pH variation in the variety of 5.5-9.5,5.0-9.0 and 4.5-9.5 for CFX-PM-ZnO NPs,CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrodes, respectively The variations above the pH value of 9.5 might be justified via confiscating the positive charge on the molecule of drug. Variations under the value of pH of 3.0 were caused via removal of the ion-pair from the coated wire electrodes or analyte in the solution [21].

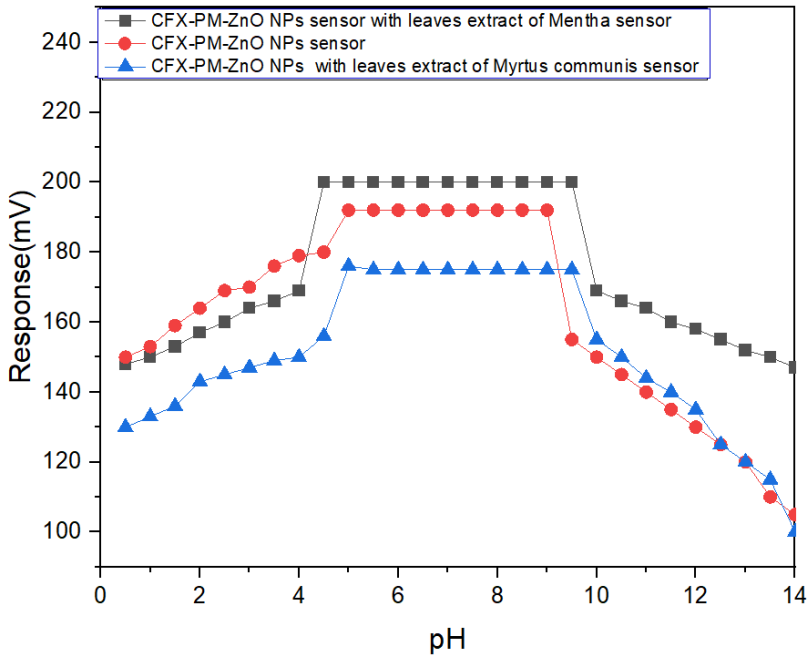


Figure 11. pH range for CFX-PMA-ZnO NPs , CFX-PM-ZnO NPs with leaves extract *of Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrodes

3.6. Electrode Selectivity

Coefficients of selectivity $K_{pot\ CFX,j\ +z}$ of the sensors towards various cations, anions and some pharmacologically related composites were calculated via applied the separate solution method [22] as shown in an equation below:

$$\text{Log } K_{Pot\ CFX.J\ z+} = (E_2\text{-}E_1)/S + \log [CFX] - \log (Jz+)\ _{1/z}$$

where, K_{Pot} is the coefficient of selectivity, E_1 is the potential of sensor in 1.0×10^{-3} mol L^{-1} GFX solution. E_2 is the potential of electrode in 1.0×10^{-3} mol L^{-1} solution of the interferent ion J_{Z+} and S is the slope. The values of selectivity for CFX-PM-ZnO NPs, CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha* sensors as shown in Table 2.

Table 2. Values of selectivity for CFX-PM-ZnO NPs,CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrodes

Ions interference	CFX-PM-ZnO NPs coated wire electrode	CFX-PM-ZnO NPs with leaves extract of *Myrtus communis*	CFX-PM-ZnO NPs with leaves extract of *Mentha*
K^+	2.2175×10^{-1}	1.0775×10^{-1}	1.9561×10^{-1}
Na^+	4.9102×10^{-1}	1.2527×10^{-1}	1.5013×10^{-1}
CO_3^{2-}	3.0990×10^{-1}	1.6678×10^{-1}	1.6398×10^{-1}
NO_3^-	2.0395×10^{-1}	1.9013×10^{-1}	1.7910×10^{-1}
Mg^{2+}	3.9833×10^{-2}	1.8538×10^{-3}	2.9650×10^{-4}
Zn^{2+}	4.5161×10^{-2}	1.3654×10^{-4}	2.7147×10^{-4}
Al^{3+}	2.9339×10^{-4}	4.6715×10^{-6}	4.2275×10^{-7}
Fe^{3+}	7.0789×10^{-5}	4.0977×10^{-6}	4.6173×10^{-7}
Glucose	6.9224×10^{-7}	8.0271×10^{-8}	5.0509×10^{-8}
Starch	9.6743×10^{-3}	6.7402×10^{-8}	9.4741×10^{-9}

Table 3. Measurements of CFX-PM-ZnO NPs, CFX-PM-ZnO NPs with leaves extract of *Myrtus communis*, and CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrode for determination of ciprofloxacin hydrochloride (CFX)

Wire coated Type of Electrode	Concentration(M)				
	Sample	Response by potentiometric method			
		Direct	SAM	SAMS	Titration
CFX-PM-ZnO NPs coated wire electrode	1×10^{-3}	0.9887×10^{-3}	0.9521×10^{-3}	0.9834×10^{-3}	0.9862×10^{-3}
	RSD %	0.49	1.23	-	-
	Rec %	98.87	95.52	98.34	98.62
	RE%	-1.13	-4.48	-1.66	-1.38
CFX-PM-ZnO NPs with leaves extract of extrac *Myrtus communis coated wire electrode*	1×10^{-3}	0.9858×10^{-3}	0.9952×10^{-3}	09912×10^{-3}	0.9687×10^{-3}
	RSD %	0.62	0.63	-	-
	Rec %	98.58	99.52	99.12	96.87
	RE%	-1.42	-0.48	-0.88	-3.13
CFX-PMA-ZnO NPs with leaves extract Mentha coated wire electrode	1×10^{-3}	0.9916×10^{-3}	$0.99.81\times10^{-3}$	0.9983×10^{-3}	0.9689×10^{-3}
	RSD %	0.26	1.90	-	-
	Rec %	99.16	99.81	99.83	96.89
	RE%	-0.84	-0.19	-0.17	-3.11

*n=5
%Rec=Percentage of Recovery
%RE=Relative error

3.7. Quantification of Ciprofloxacin hydrochloride in pure form and its tablets

For evaluate of the sensors that have been developed, CFX was determined in its pharmaceutical formula (Cipro-Denk (500mg/tablet) from Germany/tablet). Potentiometric methods were applied by using 1.0×10^{-3} mole.L^{-1} such as direct, standard addition, multi addition and titration methods. The results of percentage of recoveries were 98.87, 95.81, 98.34 and 98.62 for CFX-PM-ZnO NPs with 98.58, 95.78, 98.12 and 96.87 for CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and 99.16, 97.52, 97.83 and 96.89 for CFX-PM-ZnO NPs with leaves extract of *Mentha* sensors, respectively.

The modified sensors CFX-PM-ZnO NPs,CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of Mentha coated wire electrodes were more sensitive to CFX, also the results in Table 3 and Figure 12, 13 and 14 showed that the suggested sensors have a high sensitivity for detecting CFX in pure forms.

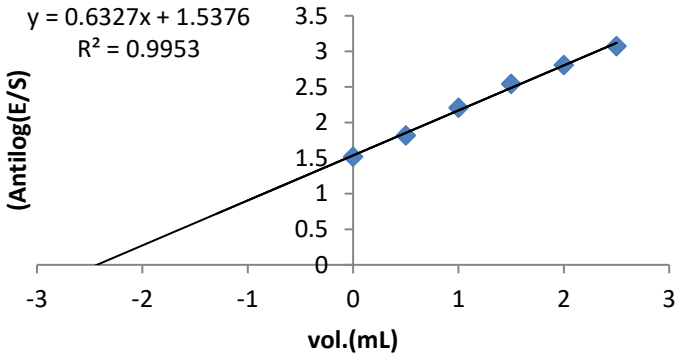


Figure 12. Standard addition method for determination of CFX by using sensor of CFX-PM-ZnO NPs

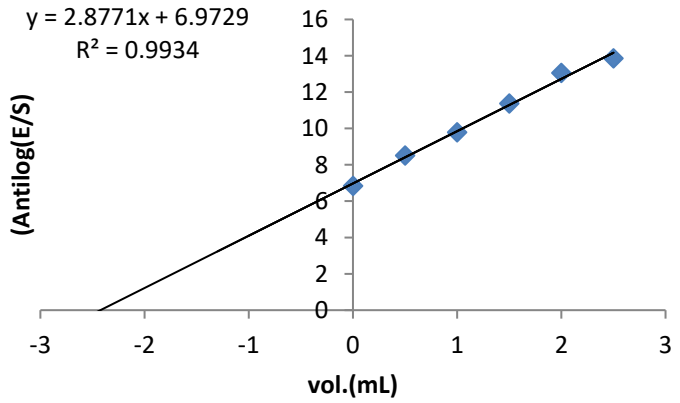


Figure 13. Standard addition method for determination of CFX by using sensor of CFX-PM-ZnO NPs with leaves extract of *Myrtus communis*

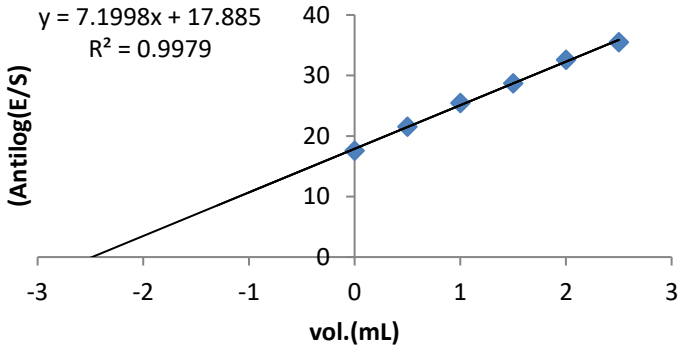


Figure 14. Standard addition method for determination of CFX by using sensor of CFX-PM-ZnO NPs with leaves extract of *Mentha*

3.8. Analytical applications for pharmaceutical tablets of CFX

For determination of CFX in commercial product was applied a direct method at 1×10^{-4} mol.L^{-1} of ciprofloxacin hydrochloride with CFX-PM-ZnO NPs,CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrodes. The average recovery for ciprofloxacin determination in tablets was around 98.08% for three type of coated wire sensors and the values of RSD% were 1.28,0.90 and 0.58 for CFX-PM-ZnO NPs,CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrodes, respectively. as shown in Table 4.

Table 4. Results of direct method of CFX-PM-ZnO NPs,CFX-PM-ZnO NPs with leaves extract of *Myrtus communis* and CFX-PM-ZnO NPs with leaves extract of *Mentha* coated wire electrodes for determination of ciprofloxacin hydrochloride(CFX)

Type of coated wire electrodes	Conc. of Cipro-Denk CFX(prepared) (Tablet/mg)	Conc.of Cipro-Denk CFX(found) (Tablet/mg)	RSD%	Rec%
CFX-PM-ZnO NPs	1×10^{-4}	0.9700×10^{-4}	1.28	97.00
CFX-PM-ZnO NPs with leaves extract of *Myrtus communis*	1×10^{-4}	0.9850×10^{-4}	0.90	98.50
Myrtle CFX-PMA-ZnO NPs with leaves extract of *Mentha*	1×10^{-4}	0.9875×10^{-4}	0.58	98.75

%Rec=Percentage of Recovery
%RSD=Relative Standard Deviation

4. CONCLUSION

Three sensors modified with CFX-PM-ZnO NPs, CFX-PM-ZnO NPs with leaves extract of Myrtus communis, and CFX-PM-ZnO NPs with leaves extract of Mentha coated wire electrodes were utilized for detection of ciprofloxacin hydrochloride. For their sensitivity and selectivity, the formed sensors shown to be higher to other old-style sensors. Moreover, the usage of metal oxide nanoparticles as coated membrane modifiers caused in good selectivity in calculating the selected medication, with a wide range of linear concentration and low detection limit. As a result, the metal oxide developed membrane sensors can be used for systematic ciprofloxacin hydrochloride analysis in research labs, companies of pharmaceutical, and hospitals.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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