Mefenamic acid (MA) is a non-steroidal anti-inflammatory drug (NSAID) used to improve the symptoms of viral infection. Its over-dosage may lead to accumulation of toxic metabolites causing nausea and diarrhea. The drug is a potential environmental hazard if present in sewage treatment plants. Innumerable methods including capillary electrophoresis, liquid chromatography, electrochemistry, spectrofluorimetry, chemiluminescence, and spectrophotometry have been employed for the determination of MA from environmental sources. In this study, as a part of our ongoing program of research, we develop a novel electrode material based on 10% magnesium (Mg) loaded zinc oxide (ZnO) nanoparticles pasted onto carbon paste electrode (CPE) for the trace level detection of MA.

In recent years, chemical and biological sensors have created an intense impact in the field of medical diagnosis, personal safety, agriculture, environmental toxin detection, semiconductor processing, and aerospace applications. The emphasis of research in the past few decades has been to develop simple solid-state sensors whose operation is dependent on the production of the measurable signal based on the interaction of an analyte at the active surface of the sensor. In view of this and due to the unavailability of data on the use of Mg-doped ZnO nanoparticles modified glassy carbon electrode (Ba-ZnO/GCE) has shown excellent performance toward the electrochemical determination of MA. The results suggested that the dopant significantly affected the electrochemical behavior of the analyte and better results were obtained with the modified electrode.

In view of these, electrochemical methods are well equipped to determine the analyte in real time to reveal their electron accepting/donating abilities. Further, the applicability of this method for investigating organic and inorganic biomolecules has been witnessed. Electrochemical methods are quite useful in the investigation of redox properties of drugs, which can offer insights into the metabolic fate.

On the other hand, greater efforts are put forward to improve the analytical performance of electrochemical materials by exploring and developing novel time saving, cost-effective and precise sensors. CPE has been widely used as working electrodes in electro-analysis due to their ease of preparation and modification having a wide potential window. Sensitivity and selectivity of CPE toward targeted analyte can be increased by suitable surface modification. Reports on CPE are available in various applications for the detection of different types of biologically active molecules that include nimesulide (at the TiO$_2$ modified CPE), 5-fluorouracil (at glucose and methylene blue dye modified CPE), and erythrosine (at glucose modified CPE). In recent years, transition metal oxides have attracted much interest in developing sensors. In catalysis and environmental monitoring, these metal oxides with specific chemical and physical properties have opened up great perspectives. Amongst the different transition metal-oxides, ZnO with a wide bandgap and higher excitation energy has been extensively studied. ZnO nanomaterials are advantageous in terms of eco-friendly nature and low cost and have the potential for scale-up. ZnO has many technological applications such as in UV light emission devices, chemical and biological sensors, and piezoelectric devices.

Literature survey reveals that oxide-based nanostructures such as Cu and Mg-doped ZnO and, Li, Co, Cr, and other transition metal-doped ZnO have ferroelectric and ferromagnetic properties. The bandgap of ZnO can be tuned, while its electric and optical properties can be improved by Mg doping. Doping with Mg would result in no significant distortion in the lattice structure, resulting in eliminating the defects due to lattice mismatch, because of closer ionic radii of Mg$^{2+}$ and Zn$^{2+}$ viz., 0.057 nm and 0.060 nm, respectively, and the bandgap of ZnO-doped with Mg is proportional to Mg concentration.

In the recent past, we have demonstrated that Ba-doped ZnO nanoparticles modified glassy carbon electrode (Ba-ZnO/GCE) has shown excellent performance toward the electrochemical determination of MA. However, it would be interesting to understand the electrochemical behavior of MA by changing the doping material. In view of this and due to the availability of data on the use of Mg-ZnO nanoparticles for the electrode preparation in sensor applications, we report for the first time, Mg-doped ZnO nanoparticles modified CPE for the analysis of MA. The materials developed are fully characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and Energy-dispersive X-ray spectroscopy (EDX). Furthermore, analysis of MA was carried out in real samples.
of pharmaceutical dosages collected from the human urine samples. The lowest possible detection limit of MA was achieved compared to earlier reports, suggesting the validity of the method for quality control and clinical trials.

Experimental

Instrumentation and chemicals.—Electrochemical oxidation of MA was studied at the surface of Mg-doped ZnO modified carbon paste electrode (Mg-ZnO/CPE). The current generated was measured using a platinum wire as the counter electrode and Ag/AgCl (3.0 M KCl) as the reference electrode. Electrodes were connected to an electrochemical analyzer (CHI Company, D630, USA). MA was used as received from Sigma Aldrich to prepare the stock solution (0.1 mM) in ethanol. The pH of the supporting electrolyte was maintained between 3.0 and 11.2 using 0.2 M phosphate buffer solution (PBS) that was prepared by mixing the stock solutions of Na2HPO4 and NaH2PO4.36 Interference studies were performed using the most widely used excipients such as urea, glycine, starch, gum acacia, dextrose, sucrose, citric acid and oxalic acid. All the experiments were performed using the analytical grade reagents (Sigma Aldrich). Double distilled water was used.

Preparation of Mg-ZnO nanoparticles.—The Mg-doped ZnO nanoparticles (Mg-ZnO NPs) were prepared by a simple co-precipitation method. A 100 mL of the solution containing 0.1 M zinc acetate, 0.01 M magnesium acetate and 10 mg of SDS (capping agent) were taken in a clean 500 mL beaker to which 100 mL of NaOH (0.2 M) was added dropwise under constant stirring at 1000 rpm speed for 50 min. The obtained slurry was centrifuged to separate the nanoparticles. The resulting Mg-ZnO nanoparticles were washed repeatedly with distilled water and alcohol to remove any impurities and dried at 80°C in an oven for 5 h. Finally, the nanoparticles were calcined at 500°C for 3 h in a muffle furnace.

Preparation of electrodes.—To fabricate the unmodified electrode, graphite powder was mixed with binder paraffin oil in a mortar. The paste was kept overnight after homogenizing for 1 h and then filled into a polytetrafluoroethylene tube with copper wire for establishing electrical contact. The electrode was activated by recording the voltammograms in pH 7.0 for 20 cycles to minimize the background current. The resulting CPE was modified by mixing 10% doped Mg-ZnO NPs during the preparation of paste.

Initially, electrochemical experiments were conducted with several wt% of Mg-ZnO NPs ranging from 0.1 to 5 wt%, with respect to the weight of the carbon paste. The results showed that the peak current for MA oxidation reached a maximum with addition of 2 wt% of NPs. Further, addition of NPs did not alter the peak current and that is probably due to the limited mass transport of analyte inside a thicker film. Hence, 2 wt% NPs was used for the preparation of the modified Mg-ZnO/CPE.

Results and Discussion

Characterization of Mg-ZnO nanoparticles.—XRD analysis.—Effect of Mg doping on lattice parameters as well as crystal structure was investigated by XRD (Fig. 1A), which confirmed the polycrystalline, hexagonal wurtzite structure. Ba-doped ZnO NPs in our previous work were also found to be polycrystalline, hexagonal wurtzite.35 The absence of impurities and substitution of Mg into ZnO lattice were confirmed by the absence of diffraction peaks of Mg and their oxides. This also confirmed the hexagonal wurtzite structure of ZnO, which was not altered by doping with Mg. The expanded 20 region within 30° - 35° shows that the (002) diffraction peaks shifted to lower 20 values indicating Mg incorporation in ZnO lattice.

Energy-dispersive X-ray spectroscopy analysis (EDX).—EDX was used to analyze the composition of Mg-ZnO NPs (Fig. 1B). The spectrum confirms the presence of Zn, O and Mg. Three peaks obtained at 1.0, 8.7 and 9.4 keV confirmed the presence of Zn. The peaks obtained were analogous to that reported for the Ba-doped ZnO NPs.35 Peaks corresponding to Mg and O are observed at 1.25 and 0.5 keV. The atomic percentages for Zn, O, and Mg were found to be 48.39, 49.89 and 1.73 respectively. These results are somewhat different from the results obtained for Ba-doped ZnO which were 71.26, 41.5 and 4.78 respectively for Zn, O and Ba. Further, EDX confirms the successful incorporation of Mg into the ZnO nanostructure.

Scanning electron microscopy (SEM).—The microstructure of Mg-ZnO NPs was investigated by SEM (Fig. 1C). The ZnO nanoparticles have the granular and well-dispersed structure. The Mg-ZnO crystals are more uniform and well defined. Additions of Mg do not seem to have a significant impact on the particle size of ZnO; however, our careful particle size distribution studies (by comparison of SEM images, not shown) suggested that a marginal decrease in the overall particle size has happened with Mg doping. More number of Mg ions can be segregated onto the surface of ZnO, which might have restricted the growth to tiny grains.37

Electrochemical investigation.—Area of the electrode.—The electrode active surface area was investigated using the cyclic voltammetric technique. The voltammograms were recorded at different scan rates for 1.0 mM K3Fe(CN)6 in 0.1 M KCl solution. Using Eq. 1 for a reversible process, the area of the electrode surface was calculated:

\[ I_{pa} = 0.4463 \left( \frac{F^{1/2}}{RT^{1/2}} \right) n^{3/2} A_D^{1/2} v^{1/2} C_o \]  

Where \( I_{pa} \) refers to anodic peak current, \( n \) is the number of electrons transferred, \( A_o \) is surface area of the electrode, \( D_c \) is diffusion coefficient, \( v \) is scan rate and \( C_o \) is the concentration of K3Fe(CN)6. For 1.0 mM K3Fe(CN)6 in 0.1 M KCl electrolyte, \( n = 1 \), \( D_c = 7.6 \times 10^{-6} \) cm2 s−1, then from the slope of the plot of \( I_{pa} \) vs. \( v^{1/2} \), the electroactive surface area was calculated to be 0.04 cm2 for CPE and 0.075 cm2 for Mg-ZnO/CPE, respectively.

Effect of accumulation time.—The observed peak current is directly related to the amount of analyte present near the vicinity of the working electrode. Hence, accumulation time exerts an effect on the electrochemical behavior as well as the peak current of MA during its oxidation. Experiments performed in the range of 10–120 s (Fig. 2A) for 0.1 mM MA show that peak current was maximum at 20 s. Initially, the linear increase in the peak current with a rise in accumulation time suggests that accumulated amount of MA at the interface region increases linearly as the time increases up to 20 s. Further from 20 to 70 s, a decrease of peak current is observed and that suggested that with the longer duration of accumulation, an equilibrium between the diffusional and the adsorbed concentrations of the electroactive compound take place. At higher accumulation times, < 70 s, the constant peak current suggests saturation in surface coverage. Hence, further experiments were performed at the accumulation time of 20 s. However, the accumulation time required for Ba-ZnO/GCE was 60 s.35 This difference could be due to the difference in the adsorption properties of the electrode material.

Detection of MA.—The electro-catalytic activity of carbon paste electrode and the fabricated electrodes with ZnO NPs as well as Mg-ZnO NPs was investigated by cyclic voltammetry. The voltammograms (Fig. 2B) obtained showed no peaks in the absence of MA, but in its presence at 0.1 mM MA, voltammograms showed an MA oxidation peak (at +0.75 V for CPE and +0.70 V for Mg-ZnO/CPE) for both the modified and the unmodified electrode. In our previous work similar results were observed for GCE and ZnO/GCE, but for Ba-ZnO/GCE, the oxidation peak was at +0.65 V.35 The peak current was much higher for Mg-ZnO/CPE than those of CPE and ZnO/CPE and Ba-ZnO/GCE. Due to the presence of Mg-ZnO nanoparticles, an enhancement in the active surface area of the modified electrode was observed, reflecting an increased peak current. It was also observed...
that the peak was absent on reversing the scan direction, indicating the irreversibility of the electrochemical process.

The conductivity of the electrode material requires the electrons to occupy the partially filled orbital which is attained by occupancy conduction band. The electrons in a semiconductor can be easily moved to conduction band leaving behind positively charged vacancy (holes) in valence band since the bandgap is smaller. Doping of the semiconductor material is an alternative strategy for generating charge carriers. Further, doping changes the electron distribution and the Fermi level. For an n-type semiconductor as for our electrode material the Fermi level lies just below the conduction band. At the interface between an electrolyte solution and semiconductor electrode, the two phases are in equilibrium when the electrochemical potential is the same. If they do not lie at the same energy level a movement of charge between electrode and solution is required to attain an equilibrium. If they do not lie at the same energy level a movement of charge between electrode and solution is required to attain an equilibrium. If they do not lie at the same energy level a movement of charge between electrode and solution is required to attain an equilibrium. If they do not lie at the same energy level a movement of charge between electrode and solution is required to attain an equilibrium.

**Effect of pH on the oxidation of MA.—**The pH of the supporting electrolyte for the determination of analyte has an important effect due to the charge on the electrode surface and dissociation of the analyte. The results of the variation of pH of the supporting electrolyte and the electrochemical behavior of 0.1 mM MA are shown in Fig. 3A. Experiments were performed over the pH range of 3.0–11.2 using the linear sweep voltammetric technique. It was observed that oxidation of MA is predominant in pH 7.0. However, in our previous work, on Ba-ZnO/GCE suggested that pH 5.0 is more suitable. The results obtained can thus be related to the point of zero charge (pzc) of ZnO nanoparticles. The pzc value as proposed by Benhebal et al. is 8.6 and below the pzc, the surface is positively charged but above which it is negatively charged. At pH 3.0, very low response signals were observed due to the dissolution of ZnO nanoparticles. In addition, at
acidic pH, MA would be in its protonated form, which is repelled by the positive electrode surface. As the pH increases to 7.0, the MA predominates in its anionic form and hence, the static force of attraction between the positively charged electrode and the anionic form of MA would allow more analyte at the surface of the electrode (Fig. 3B). Hence, pH 7.0 was used for further investigations. The electrode reaction involved the participation of protons since the voltammograms recorded at increased pH showed a shift of peak potential in the negative direction (Fig. 3C). A linear regression equation of the data fitting was found to be:

\[ E_p = -0.034 \text{pH} + 0.875; \quad R^2 = 0.983 \quad \text{[2]} \]

Effects of scan rate variation.—Cyclic voltammograms were recorded for 0.01 mM MA between 0.20 and 1.0 V with increasing scan rate between 10 mVs\(^{-1}\) and 100 mVs\(^{-1}\) (Fig. 4A). Linear plots for Ip vs square root of \(\nu\) suggests that the electrode process is diffusion-controlled (Fig. 4B) and the linear equation for Ip was as followed

\[ I_p = 5.0923 \nu^{1/2} - 0.0297; \quad R^2 = 0.9973. \quad \text{[3]} \]

From the plot of logarithm of scan rate vs log of peak current (Fig. 4C), the linear equation obtained is:

\[ \log I_p = 0.5059 \log \nu + 0.7072; \quad R^2 = 0.9957. \quad \text{[4]} \]

The slope of 0.505 is closer to the theoretical value of 0.5 for purely diffusion-controlled process. Adsorption-controlled process was observed on the surface of Ba-ZnO/GCE. In addition, the relationship between the peak potential and log \(\nu\) (Fig. 4D) showed good linearity and the regression equation obtained is:

\[ E_p = 0.719 + 0.0491 \log \nu; \quad R^2 = 0.9950. \quad \text{[5]} \]

Analytical application.—Square wave voltammetric technique was used to record the voltammograms (Fig 5A) (Table I). The linear
Figure 3. A) Effect of variation of pH of phosphate buffer solution on electrochemical oxidation of 0.1 mM MA; B) Plot for variation of pH versus peak current for oxidation of MA (Accumulation time 20 s; scan rate 0.05 Vs$^{-1}$); C) Plot for variation of pH versus peak potential for oxidation of MA (accumulation time 20 s; scan rate 0.05 Vs$^{-1}$).

The equation observed for the plot of peak current vs concentration of MA (Fig. 5B) was:

$$I_p = 1.024C + 0.3729; \quad R^2 = 0.9956.$$  \[6\]

Further, the value of LOD and LOQ were calculated by the equation:

$$LOD = 3Sb/m, \quad LOQ = 10Sb/m,$$

where $Sb$ and $m$ are standard deviations of the blank and slope of the calibration graph. The value of the limit of detection and quantification were found to be 2.05 nM and 6.85 nM, respectively. In comparison to the reported methods in the literature, it can be noticed that we found the lowest possible limit of detection (Table I).

Interference studies.—The prepared electrode was investigated for the selectivity in the presence of interferents, which are usually present with MA in biological fluids and pharmaceutical formulations (Fig. 6). Investigations were performed using the square wave voltammetric technique (Fig. S1) by adding interfering species at a concentration 1000 fold higher than concentration of MA (0.01 mM). The addition of filler materials, organic species and adhesives (urea, glycine, starch, gum acacia, dextrose, citric acid and oxalic acid) caused no effect of the SWV response of MA. The plot of % interference vs excipient shows that none of the above interferents executes the threshold limit. The voltammetric signals obtained for MA was within the threshold limit (within ±5% variations in the voltammetric signals).

### Table I. Characteristics of MA calibration plot using square wave voltammetric technique at Mg-ZnO/CPE.

| Characteristic                     | Value     |
|-----------------------------------|-----------|
| Linearity range (μM)              | 0.1–6.0   |
| Slope of the calibration plot     | 10.24     |
| Intercept                         | 0.372     |
| Correlation coefficient (r)       | 0.995     |
| RSD of slope (%)                  | 0.190     |
| RSD of intercept (%)              | 0.188     |
| Number of data points             | 12        |
| LOD (nM)                          | 2.05      |
| LOQ (nM)                          | 6.85      |
| Repeatability (RSD %)             | 1.89      |
| Reproducibility (RSD %)           | 2.61      |

Figure 4. A) Effect of variation of scan rate on electrochemical oxidation of 0.01 mM MA: a) 0.01; b) 0.05; c) 0.1; d) 0.2; e) 0.3; f) 0.4; g) 0.7; h) 0.8; i) 1.0 Vs$^{-1}$; B) Plot for peak current versus square root of scan rate; C) Plot for log peak current versus log scan rate; D) Plot for log scan rate versus peak potential.
Figure 5. A) Square wave voltammogram for varying concentration of MA: a) 0.01; b) 0.02; c) 0.03; d) 0.1; e) 0.15; f) 0.20; g) 0.25; h) 0.35; i) 0.45; j) 0.50 μM; B) Plot for peak current Vs concentration of MA.

Table II. Comparison of detection limits of MA with different reported methods.

| Method | LOD (nM) | References |
|--------|----------|------------|
| a      | 3.0 × 10^3 | 4          |
| b      | 5.0 × 10^4 | 12         |
| c      | 6.02      | 35         |
| d      | 15 × 10^3 | 44         |
| e      | 4.97      | 45         |
| f      | 2.48      | 46         |
| g      | 2.05      | Present work |

*Capillary zone electrophoresis;  
Chemiluminescence detection;  
Ba-ZnO/GCE;  
GCE;  
Magneto carbon paste electrode using molecularly imprinted magnetic nano-spheres;  
Ni–Al layered double hydroxidenano-particles;  
Mg-ZnO/CPE.

The maximum interference was from oxalic acid, which was about 4.8%. Hence, the developed sensor showed admirable selectivity for the determination of MA. This can be due to the strong adsorption of the negatively charged MA onto the surface of the positively charged electrode surface.

Table and human urine analysis.—Pharmaceutical dosage form and human urine samples were analyzed by the proposed method to estimate the concentration of MA. Ten tablets consisting of mefenamic acid (100 mg meftal SPAS tablets) available in the market were purchased from local pharmacy shop. Using mortar and pastel the tablets were finely grounded and the weight corresponding to stock solution was dissolved and diluted up to 100 ml with phosphate buffer solution, pH 7.0. Sonication for ten minutes was performed to attain proper dissolution of the content. Square wave voltammetric technique was used to carry out the analysis. Standard addition method was used to investigate the recovery and the results obtained were in the range of 93.5–100.8%. In addition, low percentage of RSD (2.7%) affirmed the accuracy of the proposed method (Table III).

The proposed method was then applied for the determination of MA in human urine samples. Urine samples from five healthy volunteers were collected and were centrifuged at ambient temperature for 6 min. The samples were diluted with phosphate buffer solution, pH 7.0. Further, the urine samples were spiked with addition of analyte solution of known concentration. The SWV technique was utilized for recovery measurements (Fig. S2). The recovery studies were performed and the results obtained are in the range of 96–100.6% with a low percentage of RSD (1.3%), suggesting a good recovery from the human urine samples (Table IV).

Table III. Analysis of MA in tablets by square wave voltammetric technique and recovery studies.

| Percentage of interference | MA tablet (Meftal SPAS) |
|---------------------------|-------------------------|
| Urea                      | 100                     |
| Glycerine                 | 97.6                    |
| Starch                    | 2.79                    |
| Gum Acacia                | 0.47                    |
| Dextrose                  | 1.03                    |
| Sucrose                   | -2.4                    |
| Citric Acid               | 1.0                     |
| Oxalic Acid               | 0.97                    |
| Recovered (%)             | 97                      |
| RSD (%)                   | 1.74                    |
| Bias (%)                  | -2.6                    |

Reproducibility and stability of Mg-ZnO/CPE.—Six electrodes were prepared to test the reproducibility of the developed sensor. The peak current was recorded within a day (24 h) for every few hours and the RSD was calculated to be 1.8%. The repeatability was carried out in a day for the same concentration of the analyte and the deviation was found to be 2.6%. This indicates the excellent reproducibility and stability of the sensors.
repeatability for Mg-ZnO/CPE. In addition, the excellent sensor was stored frozen for two weeks and the peak current was observed, the obtained response was up to 98.2% of the initial response. Hence, the developed sensor can be recommended for routine analysis of biological and pharmaceutical dosages.

Conclusions

The present work describes a novel, facile, and versatile method for the preparation of Mg-ZnO nanoparticles to develop a novel electrochemical sensor for the trace level detection of MA. The sensor exhibited the highest sensitivity and selectivity for analyzing oxidation products of MA with the LOD and LOQ values that were lower than those of the earlier reported methods. The electrode assembly showed excellent reproducibility and repeatability, suggesting its application in clinical and pharmaceutical areas. The method is simple and less expensive compared to other techniques for similar applications including complex situations. Low detection limit, wide linear range and good selectivity with a high electrochemical performance of Mg-ZnO/CPE allows this method for future biosensor applications of environmental contaminants.

The present results were compared with our recent work on the use of Ba-ZnO nanoparticles as the sensor for MA. Comparison of voltamograms at different pH showed that pH 5.0 is suitable for Ba-doped ZnO system whereas pH 7.0 is preferable for Mg-doped ZnO and the variation is attributed to the difference in the pzc of the two systems. Overall, the study reconfirmed that doping of ZnO nanoparticles increases its electrochemical sensitivity toward MA and it varies with the nature of the dopant.

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