Nano Biomed Eng
2017, 9(2): 152-161. doi: 10.5101/nbe.v9i2.p152-161.

Research Article

# New Voltammetric Study of $MgCl_2$ as Alternative Contrast Media in MRI Molecular Imaging

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**Received:** Apr. 29, 2017; **Accepted:** Jun. 26, 2017; **Published:** Jun. 30, 2017.

**Citation:** Muhammed Mizher Radhi, Haydar Abdulkadeer Taheer Al-Shimmari, Emad Abbas Jaffar Al-Mulla, Ali Abdulabbas Abdullah, and Ahmed Ghanim Wadday, New Voltammetric Study of $MgCl_2$ as Alternative Contrast Media in MRI Molecular Imaging. *Nano Biomed. Eng.*, 2017, 9(2): 152-161.
**DOI:** 10.5101/nbe.v9i2.p152-161.

## Abstract

Gadolinium compounds have been used as a common contrast media in MRI technique; however, they have oxidation-reduction current peaks in blood medium. To propose a solution for this problem, the alternative of contrast media in magnetic resonance imaging (MRI) was studied by electrochemical method using cyclic voltammetric technique. Magnesium compound was chosen such as $MgCl_2$ which has a good electrochemical properties especially in blood medium. It was found that Mg (II) ions in blood medium acted as an antioxidative reagent. The results of this study focused on the effect of magnesium chloride ions in normal saline, KCl solution and blood medium in presence with ascorbic acid (AA) and folic acid (FA) and understanding the redox current peaks of Mg (II) ions in these conditions. We obtained good results by using $MgCl_2$ solution as an alternative contrast medium in MRI technique instead of using of gadolinium compounds.

**Keywords:** MRI contrast media; Cyclic voltammetry (CV); $MgCl_2$; Ascorbic acid (AA); Folic acid (FA)

## Introduction

In the last two decades, that gadolinium compounds can be approved of using as magnetic resonance imaging (MRI) contrast media particularly in biological events or biomarkers has been the focal point of MRI contrast media research [1-3]. The main groups of MRI contrast agent are commonly determined in terms of relaxivity, as a result of the longitudinal relaxation time of protons in combined with (1 mmol) paramagnetic ion concentration. Agents based on $Mn^{2+}$, $Mn^{3+}$, $Fe^{3+}$ and $Cu^{2+}$ paramagnetic ions have been covered in previous studies, but Gd (III) complexes are out of the main group of contrast media used in clinical practices [4]. Recent studies show that gadolinium involved contrast agents have been correlated with the complication of nephrogenic systemic fibrosis (NSF), for which reason more caution should be taken with patients with renal failure in further studies [5, 6].

The electrochemistry of $GdCl_3$ in LiCl-KCl eutectic salt was studied in the temperature range of 683-813 K by using Mo working electrode. The Gd (III)

/ Gd (0) redox reaction was evaluated with respect to its major thermodynamic, kinetic and initial electrocrystallization properties. According to cyclic voltammetry (CV) and square wave voltammetry, the reduction of Gd (III) ions to Gd (0) metal is a one-step three-electron reaction. The exchange current density was determined by linear polarization of Mo electrode coated with gadolinium metal [7].

Electrochemical fabrication of Mg-Ca mixture was studied by code-position of Ca (II) and Mg (II) ions in KCl–$CaCl_2$-$MgCl_2$ melts at 943 K on electrodes made of tungsten. CV showed that the reduction of Ca (II) and Mg (II) ions took place at −2.23 V in KCl–$CaCl_2$ eutectic melts at 943 K. The bulk composition of Mg-Ca alloys were analysed by inductively coupled plasma atomic emission spectrometer [8].

Oxygen is transported in the red blood cell by the haemoglobin; the electrochemical method is more suitable to investigate the electroactive characterization of the reaction between oxygen and haemoglobin which occurs by uptake or release of protons depending on the pH. The phenotypes were determined expeditiously by using sufficient distinct values of the peak current. The feasibility of this method made it more efficient and unrelated to the detected values of peak current. In addition, the concentration haemoglobin samples were determined accurately because the good relation between the concentration and the peak current of haemoglobin samples [9].

The electrochemical impedance spectroscopy (EIS) and the CV could detect the bilayer lipid membrane through membrane formation process which was affected by $Mg^{2+}$. The EIS showed an obvious increasing of the distance between the peaks of CV waves which were detected and a decreasing of charge transfer resistance for the formed membrane [10].

The contrast media with $MgCl_2$ electrolytes which were in U (VI) voltammetric technique with electrodes of graphite had two processes in the range of 2.4-6.6 pH. Most of the features of this process were associated with solid uranium oxide compounds reduction that were attached to graphite electrodes. The mass transport mechanism was provided by the diffusion of applied $Mg^{2+}$ ions from the electrolytes [11].

One of the studies investigated the electrochemical redox Cu (II), and Cu (II) in ascorbic acid by glassy carbon electrode (GCE) with various pH of aqueous phosphate buffer solution (PBS). This study found that electrochemical reactions were diffusion-controlled according to the linear relation between the square root of scan rate and the peak current. In presence of ascorbic acid, both of the cathodic and anodic peak currents of Cu (II) reduced and peak positions shifted compared to those of Cu (II) alone [12].

GCE was modified with different microparticles to increase the efficiency of analyzing $Mn^{2+}$ in blood samples by CV, and it was applied to detecting the trace of Mn (II) by oxidation process [13, 14].

In this work, a new study in cyclic voltammetric technique using blood medium as an electrolyte to determination the effects of AA and FA on the redox current peaks of $MgCl_2$ as an alternative of MRI contrast medium and comparative study with gadolinium compounds.

## Experimental

### Reagents and chemicals

Magnevist 0.5 mmol/mL solution for injection (gadopentetate dimeglumine) used as contrast media in MRI test was from Bayer Schering Pharma (Berlin Germany); Normal saline (0.9% NaCl W/V) from Alcon Parenterals (India) Ltd; Magnesium chloride ($MgCl_2$) from Fluka (Germany); Ascorbic acid (AA) from Technicon chemicals Co. (Oreq. Tournai Belgique); KCl from SCRC (China), and other chemicals and solvents were of annular grade and used as received from the manufacturers. Double distilled water was used for the preparation of aqueous solutions. All solutions were deaerated with oxygen with nitrogen gas for 10-15 min prior to making the measurement.

### Apparatus and procedures

Instruments: EZstat series (potentiostat/glvanostat), NuVant Systems Inc., USA. Electrochemical workstations of bioanalytical system with potetiostate driven by electroanalytical measuring softwares were connected to personal computer to perform CV. An Ag/AgCl (3 mol NaCl) and platinum wire (1 mm of diameter) were used as a reference and a counter electrode respectively. The GCE was used in this study after cleaning with alumina grand and sonic technique for 10-15 min.

## Results and Discussion

There have been many studies on the use of contrast

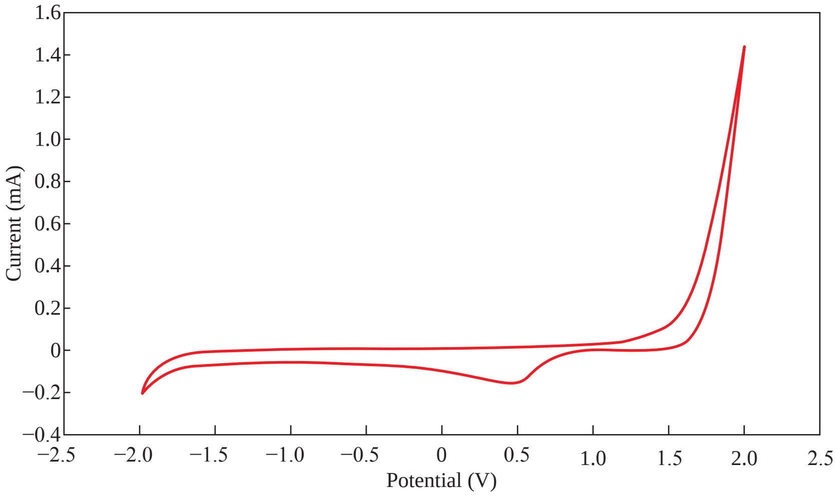


**Fig. 1** CV of Mg (II) in KCl as an electrolyte using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

media in MRI screening device and the applied contrast medium is exclusively gadolinium compounds. It is very important to find alternatives to this contrast medium given to the emergence of fumbling in some patients using gadolinium. The study on these compounds for electrochemical contrast media identify the extent of their impact on the blood composition.

## Effects of different electrolytes on Mg (II) ions

Three different electrolytes were chosen to study the interference effect of these electrolytes on Mg (II) by electrochemical analysis of redox current peaks for $MgCl_2$ in different electrolytes, and the studies are as follows.

In 0.1 mol KCl: Fig. 1 shows that the reduction current peak of Mg(II) in KCl as an electrolyte appeared at 500 mV, which means magnesium ions acted as an antioxidative agent in KCl solution. It was found that the cathodic current peak of magnesium ions increased with the increasing of the concentration of $MgCl_2$, as shown in Fig. 2. The relationship between the cathodic current peak versus

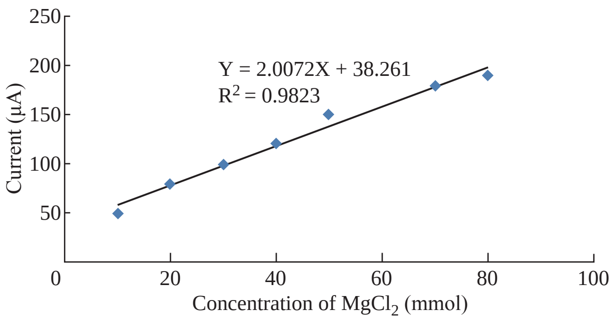


**Fig. 2** Plot of cathodic current peak (Ipc) for $MgCl_2$ against different concentrations in 0.1mol KCl using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

the different concentrations of Mg (II) was represented by the equation Y = 1916.7X + 41.25, with a high sensitivity of $R^2$ = 0.9583. The relationship shows that the behavior of magnesium ions in KCl solution as an antioxidant reagent could enhance the reduction current peak of magnesium ions which have good electrochemical properties in medical applications [15].

In normal saline (0.9% NaCl): The other study on Mg (II) was in normal saline as an electrolyte. It is shown in Fig. 3 that two reduction peaks of Mg (II) in normal saline appeared at 100 mV and –250 mV as illustrated in the following two chemical equations [16, 17]:

$$Mg^{2-} + e = Mg^{1-}, e = 100 \text{ mV} \quad (1)$$

$$Mg^{1-} + e = Mg^{0}, e = -250 \text{ mV} \quad (2)$$

Normal saline acted as an electrocatalyst for the cathodic current peak of Mg (II). Therefore, increasing the concentration of Mg (II) in normal saline increased the current as shown in Fig. 4. The relationship between the second cathodic current peak of Mg (II) at 100 mV against different concentrations of Mg (II) was illustrated by a good straight line, with the equation Y = 560X + 16.4 and with the good sensitivity of $R^2$ = 0.9495. Other evidences also proved that magnesium chloride solution in normal saline as an electrolyte had the cathodic current peak enhanced at different concentrations and acted as a electrocatalyst [18].

In normal human blood sample: It was found that no redox current peak appeared for the effect of Mg (II) in blood medium as shown in Fig. 5. It means that magnesium ions had no effect in blood components especially when used as a human body tonic in pharma medicines. This characteristic of magnesium chloride

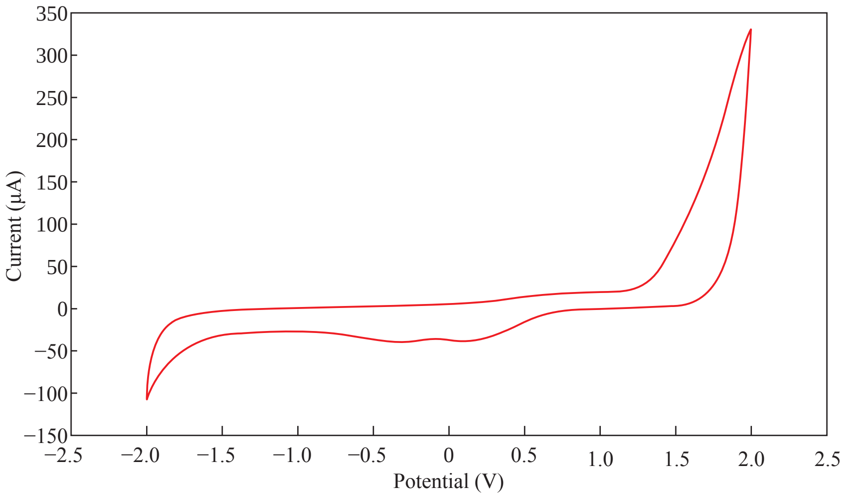


**Fig. 3** CV of Mg (II) in normal saline (0.9% NaCl) as an electrolyte using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

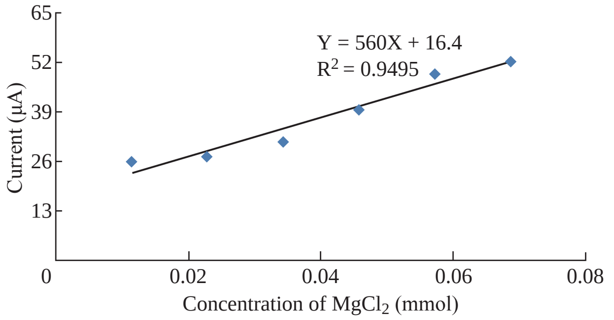


**Fig. 4** Ipc of $MgCl_2$ against different concentrations in normal saline using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

in blood medium is very important for medical purposes as it may be used as alternative contrast in different techniques for radiographic diagnosis [19].

## Effect of ascorbic acid (AA) on redox current peaks of Mg (II) in normal saline

Fig. 6 shows the anodic current peak of AA enhanced the cathodic current peak of Mg (II) in normal saline. Also, it was shown that AA solution effected directly on the two reduction current peaks of Mg (II) by reducing them to a single reaction of Mg (II). The reaction is expressed by equation 2, and the deposition of Mg layer on the surface of the working electrode could be seen. Here ascorbic acid acted as an electro-catalyst for the redox process of magnesium ions in normal saline as an electrolyte [20].

It was found that AA in normal saline had an enhancing effect on the cathodic current peak of Mg (II) and the peak appeared at 525 mV. As shown in Fig. 7, the relationship between the cathodic current peak of Mg (II) against different concentrations of AA in normal saline was according to the equation Y = 1590X + 36, with the sensitivity of $R^2$ = 0.9901. The redox process of AA was the same with that of magnesium ions in normal saline. It was noticed that the magnesium ions were anti-oxidative reagents,

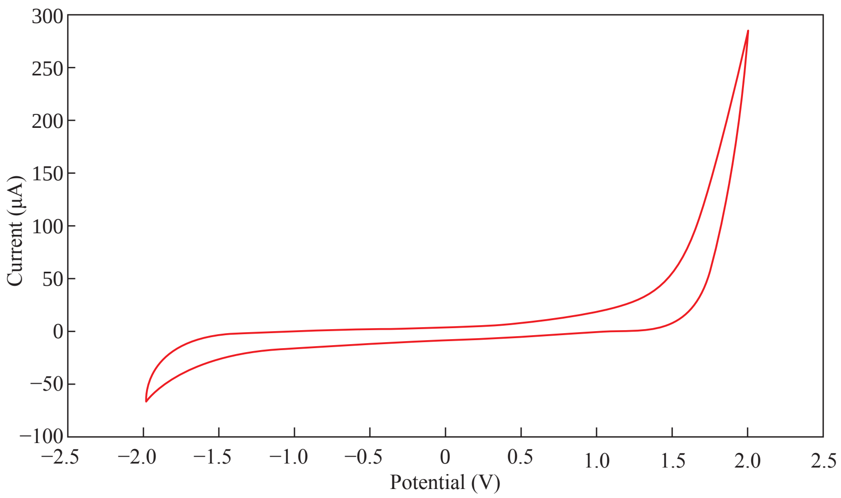


**Fig. 5** CV of Mg (II) in normal human blood sample as an electrolyte using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

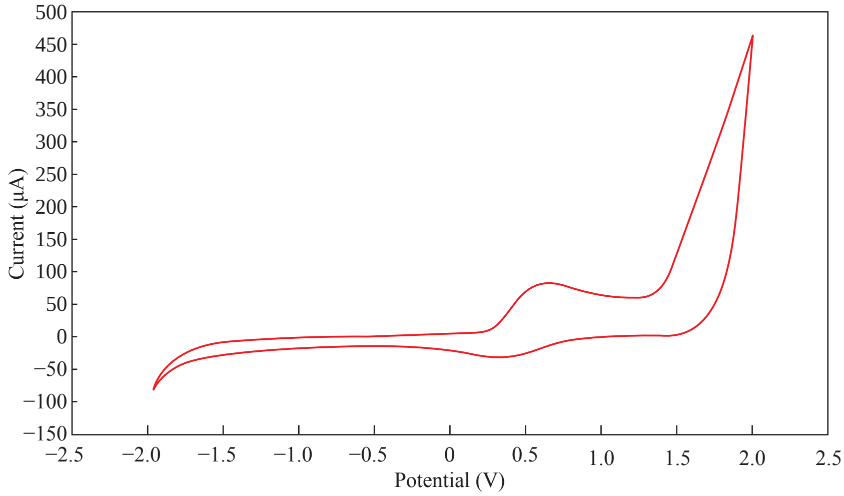


**Fig. 6** CV of Mg (II) in normal saline in presence of AA using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

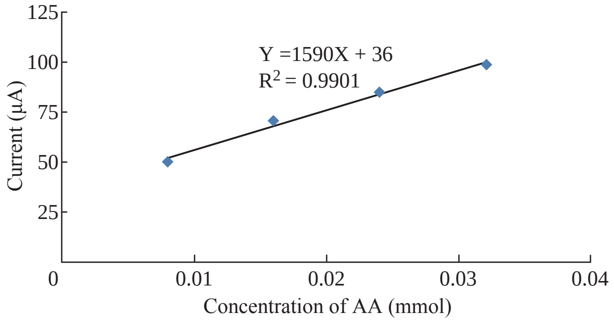


**Fig. 7** Ipc of $MgCl_2$ against different concentrations of AA in normal saline using GCE at 100 mV/ and Ag/AgCl as a reference electrode.

which was also true when they were in AA. Therefore, AA can be considered as supplementary to magnesium ions in enhancing the cathodic current peak [21].

## Effect of folic acid (FA) on the redox current peaks of Mg (II) in normal saline

Fig. 8 shows the effect of FA solution on the two reduction current peaks of magnesium ions in normal saline. It was found that folic acid acted as an anti-oxidative reagent with the enhancement of the two reduction peaks of Mg (II) in normal saline. FA acted as an electro-catalyst for magnesium ions in normal saline by the equation Y= 580X + 40.8 and with the sensitivity of $R^2 = 0.9723$ as shown in Fig. 9. FA is one of the complementary medicines for different drugs [22]. In this study, FA acted as a good anti-oxidative reagent which enhanced the cathodic current peak of magnesium chloride in normal saline [23].

## Effect of ascorbic acid (AA) on redox current peaks of Mg (II) in blood medium

Fig. 10 shows that the anodic current peak of AA acid appeared at 750 mV. AA acted as an electro catalyst enhancing the reduction current peak of Mg (II) ions in blood medium. The previous results of

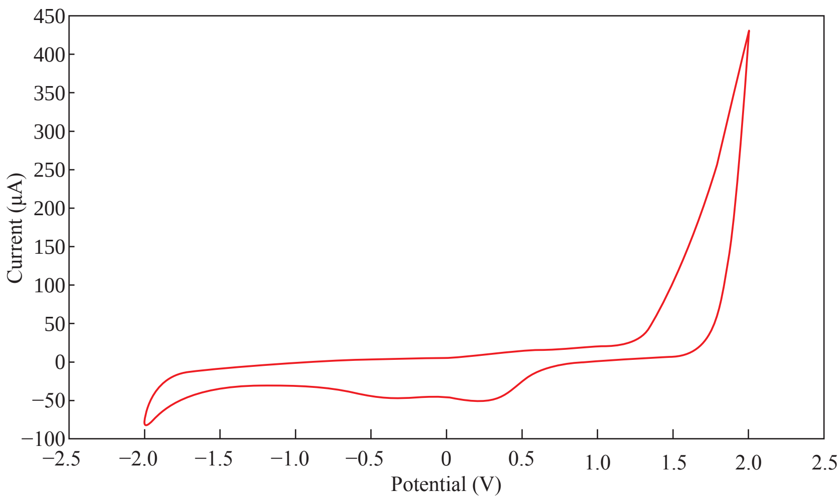


**Fig. 8** CV of Mg (II) in normal saline in presence of FA using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

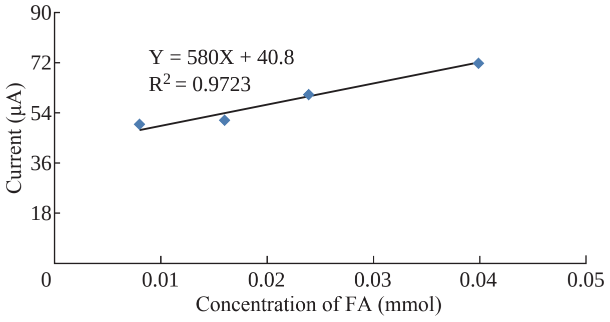


**Fig. 9** Ipc of $MgCl_2$ against the different concentrations of FA in normal saline using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

Mg (II) in blood samples as in Fig. 3 which shows no significant signals of Mg (II) in CV. But when using AA with blood medium, the reduction peak of Mg (II) appeared at –500 mV as shown in Fig. 11. Magnesium ions in blood medium had a cathodic current peak which was enhanced by AA as illustrated by the relationship in Fig. 11 with the equation Y = 54.286X + 16.6 and with the sensitivity $R^2$ = 0.9377. Hence, AA is a very important anti-oxidative reagent to support magnesium ions in blood as a contrast medium for radiological diagnosis [24].

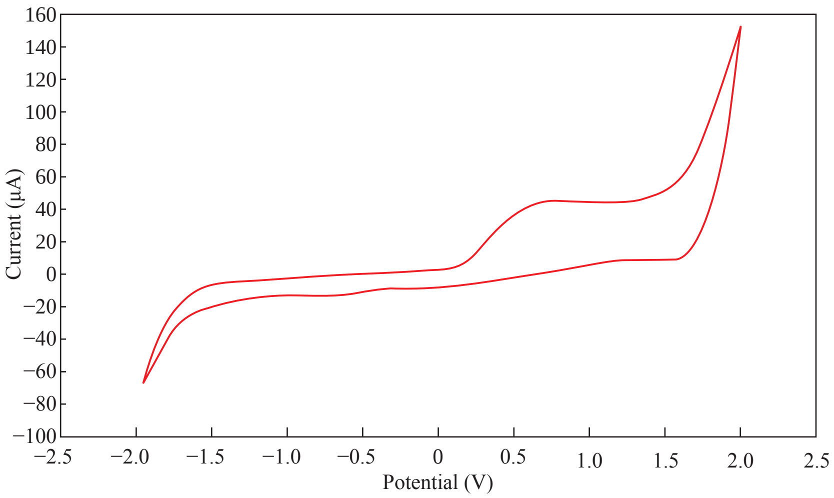


**Fig. 10** CV of Mg (II) in blood medium in presence of AA using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

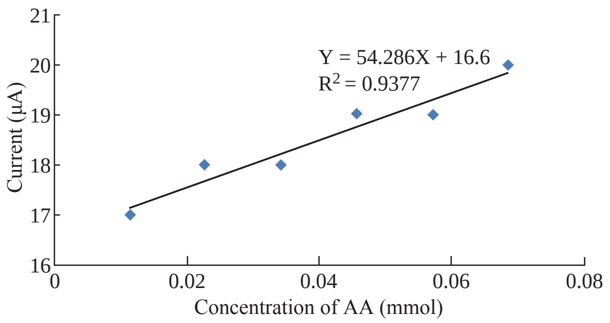


**Fig. 11** Ipc of $MgCl_2$ against different concentrations of AA in blood medium using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

## Effect of folic acid (FA) on redox current peaks of Mg (II) in blood medium

Fig. 12 shows the CV of Mg (II) in blood medium in presence of FA solution. The results showed two oxidation and reduction current peaks at 1 V and –750 mV respectively. FA acted as an electro-catalyst by enhancing both redox current peaks. Hence, it is very important to use FA with Mg (II) as a contrast medium in MRI technique so as to achieve high-resolution images in diagnosis of different diseases. Fig. 13 illustrates the relationship between the cathodic (reduction) current peak of magnesium ions at 750 mV in presence of FA and different concentration of FA in blood medium, which is a good straight line by the equation Y= 30.357X + 16.982, with the good sensitivity of $R^2$ = 0.9383.

## Effect of gadolinium compound in normal saline

Gadopentetate dimeglumine is one of the contrast media used in magnetic MRI technique. The study of electrochemical properties of this compound in normal saline is shown in Fig 14; there is no oxidation reduction current peak in the CV.

## Effect of gadolinium compound in blood medium

The gadopentetate dimeglumine was used as a contrast media in MRI technique to provide high resolution of imaging. It was found that oxidation and reduction current peaks of this contrast appeared in the CV when using blood medium as an electrolyte at 900 mV and –750 mV respectively (Fig. 15).

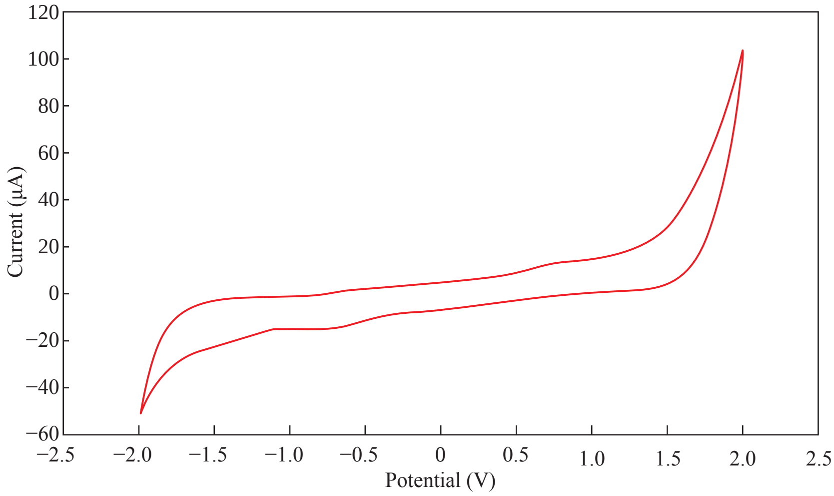


**Fig. 12** CV of Mg (II) in blood medium in present of FA using GCE at 100 Mv/s and Ag/AgCl as a reference electrode.

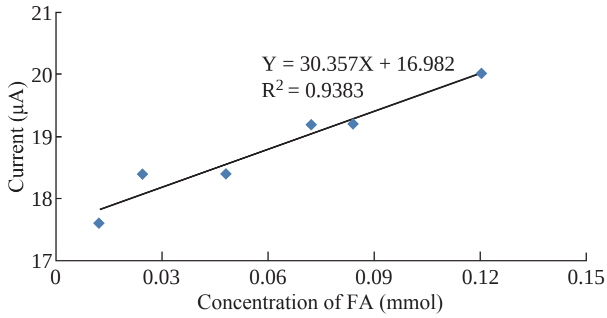


**Fig. 13** Ipc of $MgCl_2$ against different concentrations of FA in blood medium using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

Fig. 16 and 17 show the voltammogram of oxidative and antioxidative current peaks of gadopentetate dimeglumine at 900 mV and –750 mV respectively. Its being an oxidizing substance and causing disadvantages in some patients lead to lack of use and thereby depriving the patient of diagnosis by MRI technique [25].

## Effect of AA on gadolinium compound in blood medium

Fig. 18 shows the CV of gadopentetate dimeglumine which illustrates its electrochemical properties in blood medium in presence of AA. It was found that the oxidation current peak of AA at 600 mV effected on the redox current peaks of the contrast medium, causing the disappearance of anodic (oxidation) current peak of the contrast medium and the enhancement of cathodic (reduction) current peak at –900 mV. Hence, AA acted as an electrocatalyst reagent for safely using gadolinium compounds in blood medium [26-29].

## MRI finding with new contrast medium ($MgCl_2$)

Fig. (19(a)) provides the MR imaging (T1-weighted imaging) of rabbit's kidney without using any contrast media, and it has the mean clearness value of 622.5

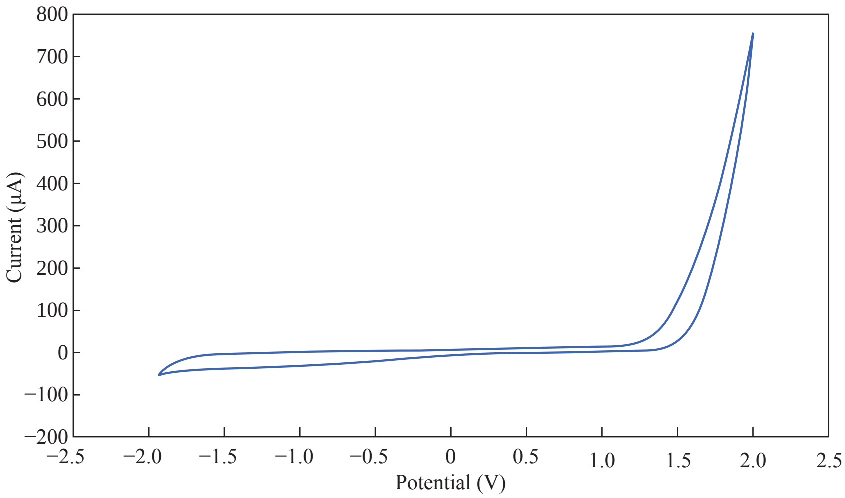


**Fig. 14** CV of gadopentetate dimeglumine in normal saline using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

units. In comparison, Fig. (19(b)) provides the MR imaging (T1-weighted imaging) of the kidney using $MgCl_2$ as a new contrast mediium, and it has a mean clearness value of 1,003 units. The MRI of rabbit's kidney was more accurate in diagnosis when using the $MgCl_2$ contrast. Thus, $MgCl_2$ as T1 contrast medium is

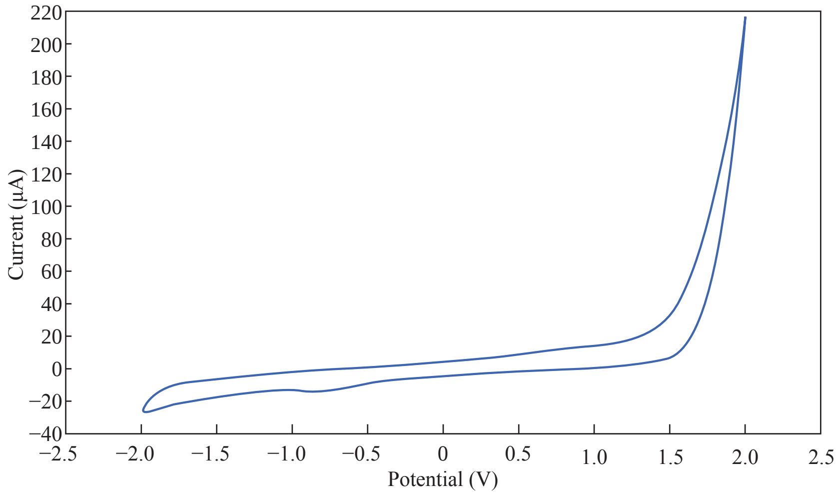


**Fig. 15** CV of gadopentetate dimeglumine in blood medium using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

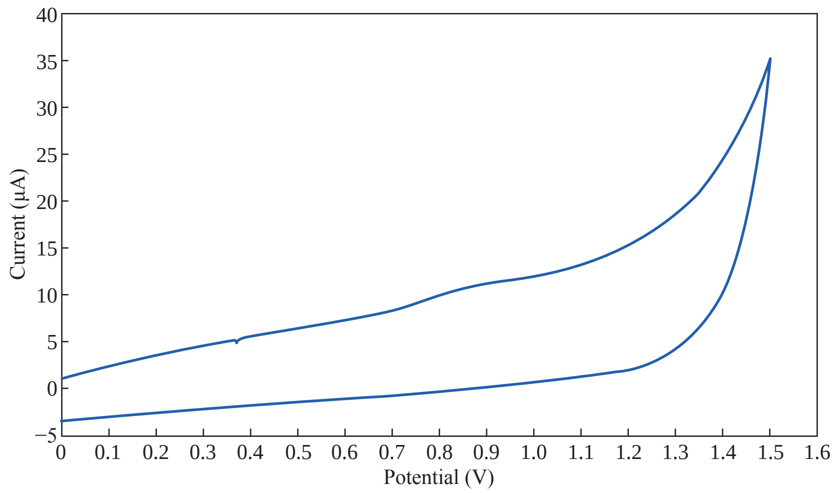


**Fig. 16** CV of anodic current peak of gadopentetate dimeglumine in blood medium using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

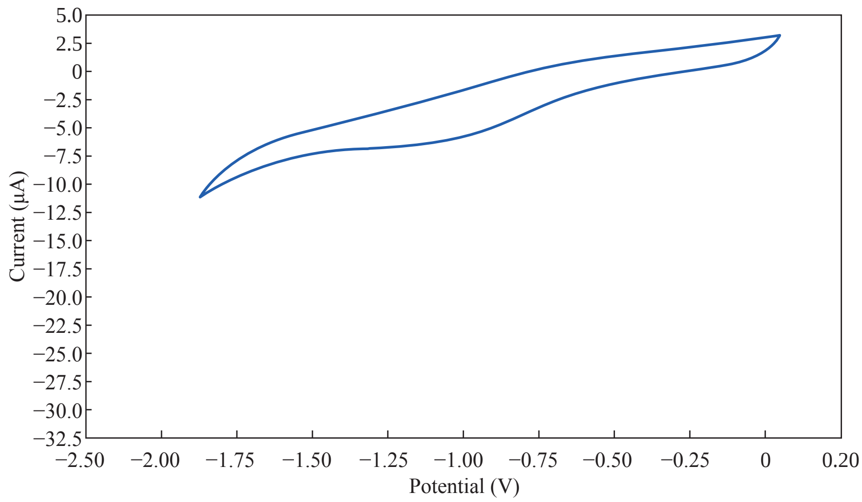


**Fig. 17** CV of cathodic current peak of gadopentetate dimeglumine in blood medium using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

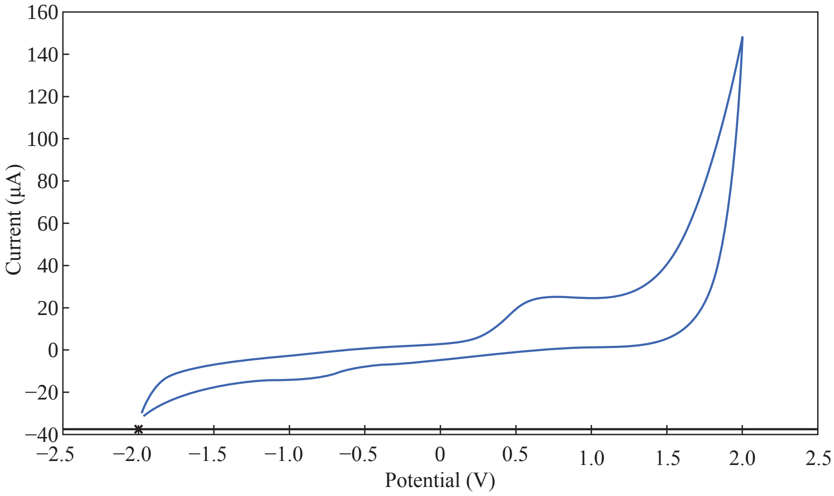


**Fig. 18** CV of gadopentetate dimeglumine in blood medium in presence of AA using GCE at 100 mV/s and Ag/AgCl as a reference electrode.

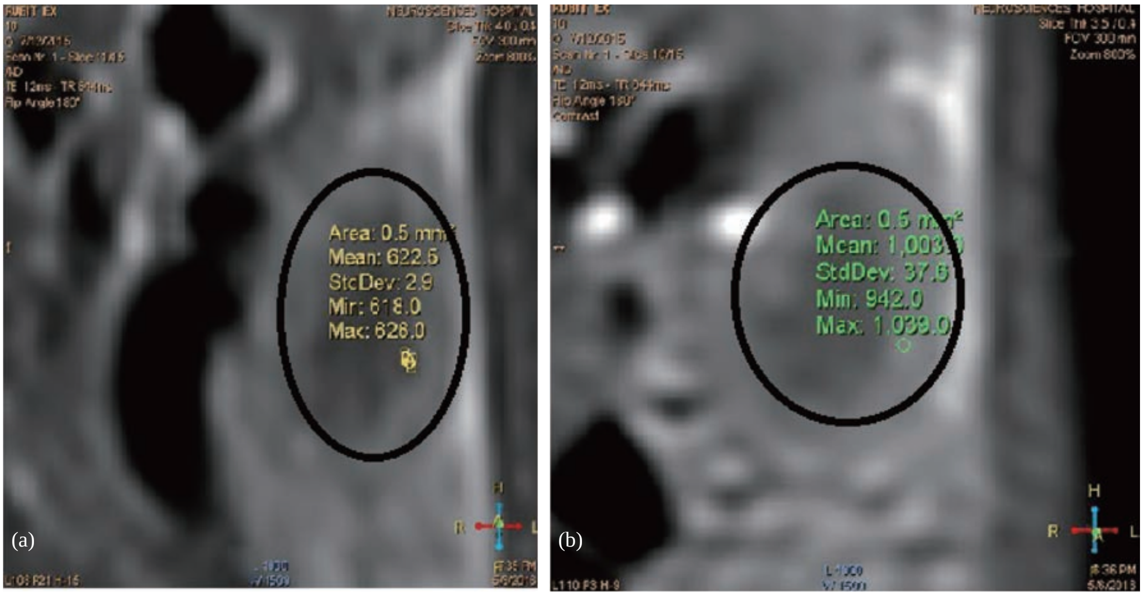


**Fig. 19** MR imaging of rabbit's kidney **(a)** without contrast medium (clearness: 622.6 units) and **(b)** with $MgCl_2$ as contrast medium (clearness: 1,003 units).

alternative to gadolinium compound. Simultaneously, due to the safety and high resolution of MR imaging, this new contrast medium is prospectively applicable in clinical diagnosis.

## Conclusions

Through behavioral electrochemical studies on each of the contrast media used in MRI, this paper looked into gadolinium compound. Its electrochemical properties in terms of redox current peaks of Mg (II) were presented, It was found that magnesium chloride was a suitable chemical compound as an antioxidant reagent without any side effects, more useful than gadolinium compound, and could be used as an alternative contrast medium in MRI technique.

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