

Full Paper

Construction of Titanium Oxide Nanoparticle/Poly Alizarin Yellow R/Chitosan Nanocomposite: Application to Enhance Electrochemical Determination of Environmentally Pollutant Hydrazine

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Abstract- Hydrazine is a colorless flammable liquid with an ammonia-like odour. Hydrazine is highly toxic and dangerously unstable. In this study, a novel electrochemical sensor was proposed for detection of hydrazine on glassy carbon electrode (GCE). The electrochemical sensor is based on immobilizing titanium dioxide nanoparticle/alizarin yellow R/ Chitosan (TiO₂ NPs/AYR/chit) nanocomposite. The deposited nanocomposite on the GCE was characterized by scanning electron microscopy (SEM). Then its electrocatalytic activity were investigated by CV and amperometry methods. Tests show that TiO₂ NPs/AYR/chit exhibited enhanced catalytic activity towards hydrazine oxidation under optimal conditions. The results show the linear dependence of electrocatalytic response current of the sensor with the hydrazine concentration in the ranges of 5 to 580 μM , with a limit of detection and sensitivity of 3 μM and 0.1727 $\mu\text{A}/\mu\text{M}$, respectively. The modified GCE show many advantages relative to previously reported hydrazine biosensors such as facile preparation, highly sensitive and good catalytic properties at pH 12.

Keywords- Hydrazine, Pollutant, Nanocomposite, Alizarin yellow R, Titanium oxide nanoparticle

1. INTRODUCTION

Hydrazine (N_2H_4) is a colorless, water-soluble, fuming oily liquid, and flammable liquid with an ammonia-like odor and is the simplest diamine. It is employed as fuel and propellant in various rockets, spacecrafts, space shuttles [1] and as a reactant in fuel cell systems since its fuel electro-oxidation process does not have poisoning effects [2]. Also, hydrazine used for many industrial applications such as preparation of polymer foams, gas in air bags, and production of metal films, photographic chemicals, power plants, insecticides, blowing agents for plastics, corrosive inhibitors [3] and DNA damage [4]. Hydrazine has highly toxic fumes and dangerously unstable and explosive chemical, unless handled in solution. It has quite toxic, carcinogenic and hepatotoxic effect and exposure routes include skin adsorption seriously affects blood production, and is harmful to the liver and kidneys [5]. Due to the reasons above, a highly sensitive method is required to for the detection and quantification of hydrazine [6]. Several techniques for the identification and determination of hydrazine have been developed, such as titration [7], HPLC [8], GC [9], and spectrophotometry [10]. However, these methods require complex instruments and, usually require separation, purification and sample pretreatments.

Most of the electrochemical based techniques are sensitive, reliable, compact, economic and fast methodologies. Electrochemical sensors prepared by chemically modified electrodes (CMEs) have attracted more interest due to their high sensitivity and selectivity for the trace analysis of various biologically important compounds [11-13]. One of the main properties of CMEs has been their potential to catalyze the electrode process via decreasing of overpotential and enhancement of the sensitivity and selectivity of the method. To modify electrodes for determination of hydrazine various inorganic and organic materials such as nickel particles [14], calmagates [15], hexacyanoferrate salt [16,17], Pd nanoparticles immobilized on ethylenediamine cellulose [18], cobalt or iron phthalocyanine [19,20] have been used.

The study of conducting polymers has attracted much attention in recent years, and have been applied as an ideal support material for electrochemical sensors due to their high conductivity and stability, homogeneity, reproducibility and their extensive potential applications in the fields of batteries, solar cells and sensors [21]. Electropolymerization is an excellent method to prepare electrodes modified by polymers and film thickness, permeation and charge transport characteristics can be controlled by adjusting the electrochemical parameters. Application of organic dyes as monomer for preparation of conducting polymers have become quite attractive because of their high application potential. Some organic dyes including the neutral red [22], toluidine blue [23], thionine [24] and pyrocatechol violet [25] have been successfully applied for preparation of electrochemical sensors.

Alizarin yellow R, that sometimes used as a pH indicator [26] and a metallochromic indicator, is a yellow colored azo dye with a salicylic acid structure.

In the present study, the modified electrode fabricated by polymerization of alizarin yellow R (AYR) on the surface of a GCE pre-coated by a thin layer of TiO_2 nanoparticles-chitosan

nanocomposite. To the best of our knowledge, the application of AYR as modifier to fabricate a hydrazine electrochemical sensor had not been reported until our recent work.

2. EXPERIMENTAL SECTION

2.1. Chemicals

All chemicals were of analytical grade and were used as received. AYR was obtained from Sigma–Aldrich. Hydrazine, chitosan and TiO₂ nanoparticles were obtained from Merck. Daily prepared aqueous solutions of hydrazine were used prior to measurements. Double distilled water was used to prepare all solutions. Disodium hydrogen phosphate (Na₂HPO₄) was used for preparation of buffer solutions. The pH of the solution was adjusted by hydrogen chloride and sodium hydroxide (NaOH). All electrochemical experiments were carried out at room temperature 25±0.1 °C.

2.2. Apparatus

Autolab PGSTAT101 voltammetric analyzer with a three electrode system involves an Ag/AgCl (sat. KCl) as reference electrode, a Pt wire as counter electrode and a GCE as working electrode for voltammetric measurements. The Ag/AgCl was used as reference electrode. A rotating electrode system, from pine instruments, was employed. All electrodes were from Metrohm and data storage and processing were done by a personal computer.

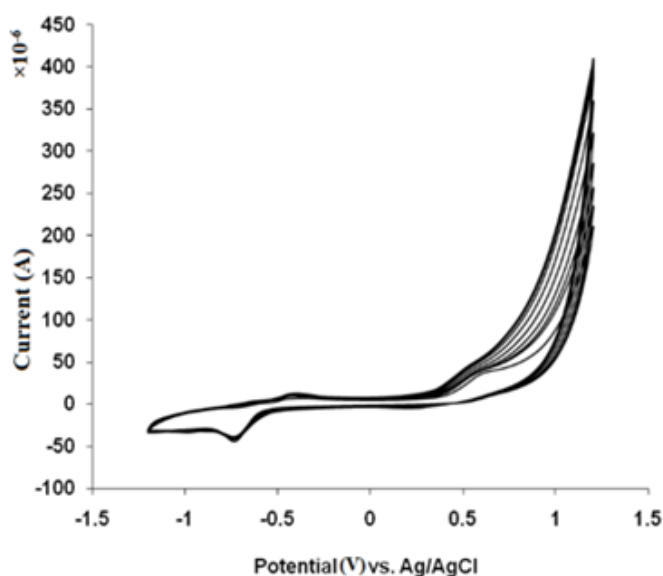
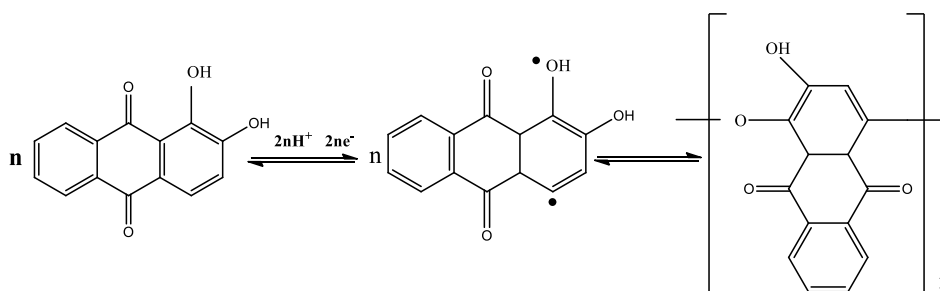


Fig. 1. Cyclic voltammograms of electrochemical polymerization for 0.1 M NaOH containing Alizarine Yellow

2.3. Modification of glassy carbon electrode

The GCE surface was cleaned by polishing with Al₂O₃ slurry, followed by its sonication for 3 min each in ethanol and pure water, respectively. Then the surface of the electrode was electropolymerized by its immersion in a solution containing AYR monomer (17.4 mM) and NaOH 0.1 M by continuous potential cycling from -1.2 to 1.2 V at scan rate of 100 mV/s, for 15 cycles, until a stable voltammogram was obtained (Figure 1).

The mechanism of the reaction proposed as below:



After 15 cycles electrode was washed by water and was dipped into the PBS in order to test its electrochemical behavior. TiO₂ nanoparticles (1 mg/mL in water) was added to 1 mg chitosan in 1 mL acetic acid thoroughly mixed. Then 5 μ L of TiO₂/Chit solution was dropped on the surface of GCE/AYR/Chit and dried in air to form a thin film. The SEM image of TiO₂/AYR/Chit/GC was shown in Figure 2.

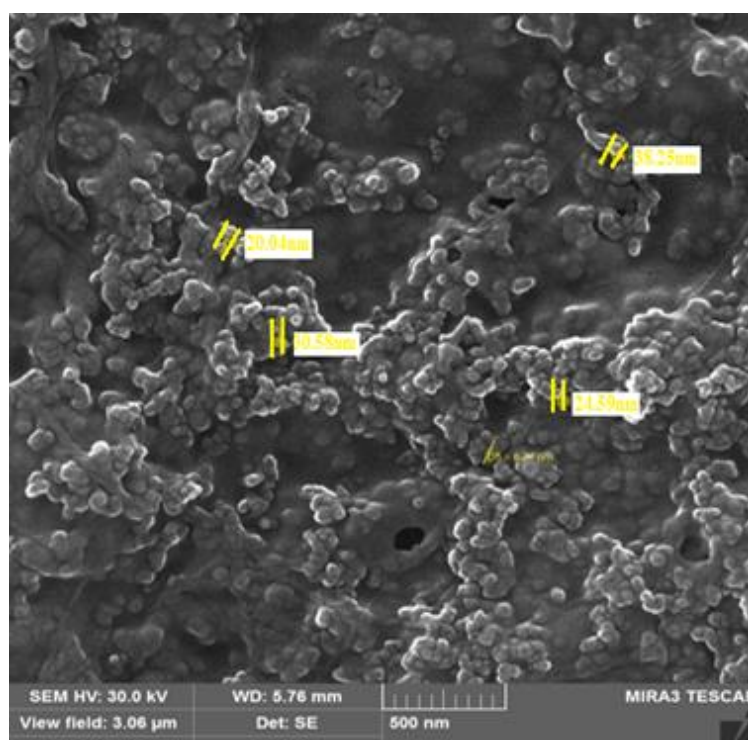


Fig. 2. Scanning electron microscopy image of TiO₂/Chit/GCE

3. RESULTS AND DISCUSSION

3.1. Hydrazine oxidation on AYR/TiO₂/chit/GCE

The application of the modified GCE for *electrocatalytic* oxidation of hydrazine was studied by cyclic voltammetry. As can be seen in Figure 3b, no redox response of hydrazine can be seen in the potential range from 0 to 0.6 V for chitosan modified electrode. However, at the bare GCE (Figure 3c) and AYR/GC (Figure 3a) electrodes, the current slowly increased due to catalytic oxidation of hydrazine. At the AYR/TiO₂/Chit/GCE (Figure 3d), the catalytic oxidation of the modified electrode, increases the hydrazine oxidation current. A dramatic increase of current indicating significant catalytic ability of AYR/TiO₂/Chit/GCE to hydrazine oxidation. Then at the surface of GCE modified by AYR/TiO₂/Chit the overvoltage for hydrazine oxidation decreased and reproducibility of the modified electrode improved by its antifouling properties. Therefore, AYR/TiO₂/Chit is suitable as mediator to shuttle electron between hydrazine and modified electrode, and facilitate electrochemical regeneration following electron exchange with hydrazine.

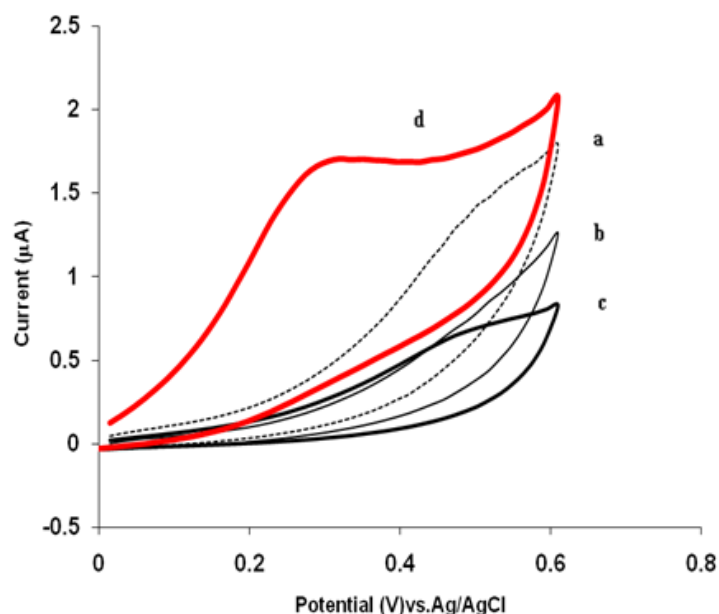


Fig. 3. Cyclic voltammograms of unmodified GCE (a), GCE modified by chitosan (b), GCE modified by AYR (c), and GCE modified by AYR/TiO₂/Chit (d), in the 10 mM hydrazine, supporting electrolyte: 0.1 M PBS (pH 12) and scan rate: 30 mV/s

3.2. Effect of pH on the modified electrodes

The effect of solution pH on the electrocatalytic oxidation of the modified electrode for hydrazine was investigated.

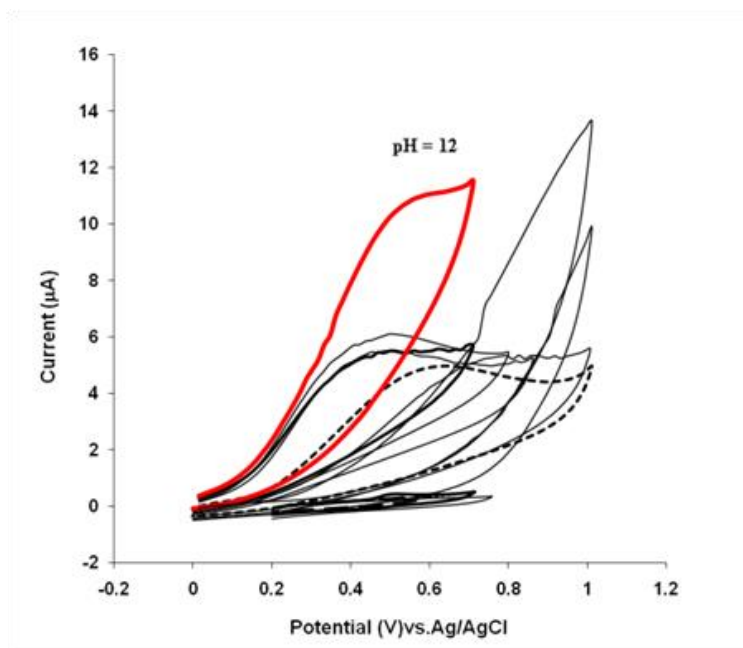


Fig. 4. Cyclic voltammograms of AYR/TiO₂/Chit/GCE in different pH solutions, from right to left, 2 to 12, in the presence of 100 µL hydrazine and scan rate of 100 mV/s

The cyclic voltammograms of the modified electrode in 0.5 mL of 0.1 M hydrazine at different pH values were studied. As can be seen in Figure 4, at pH of 12 maximum peak current and most reproducible results were achieved, and, at pH values lower than 12, the voltammetric signal decreases significantly. Therefore pH 12 was considered as optimum pH for detection of hydrazine.

3.3. Effect of potential scan rate

Figure 5 shows the CV of 0.01 M hydrazine on the AYR/TiO₂/Chit/GCE at the different scan rates (from 10 to 150 mV/s). The inset of voltammogram at Figure 5 shows that the peak current of hydrazine oxidation is proportional to square root of the scan rate, signifies a diffusion control process which is related to the relatively slow diffusion of counter ions into the electrode surfaces [27]. The slope value of the plots is 0.422 (Figure 5 Inset). Thus, the redox reactions in the electrode is diffusion controlled processes.

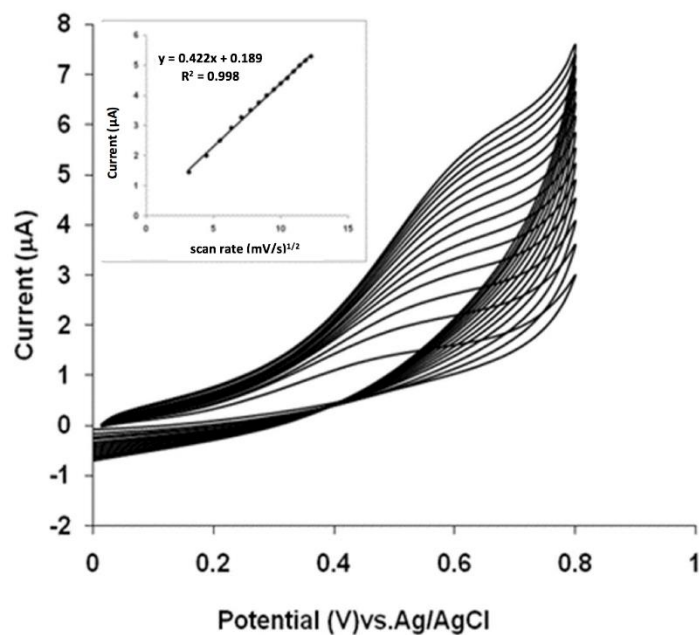


Fig. 5. CV of 100 μM hydrazine in PBS of pH 12 on the surface of AYR/TiO₂/Chit in various sweep rates from 10 to 150 mV/s. Inset, plot of peak current of hydrazine vs. scan rate^{1/2}

3.4. The effect of concentration

To study the electrocatalytic activity of GCE modified by AYR/TiO₂-Chit, the cyclic voltammograms of the AYR/TiO₂-Chit/GCE in the presence of different concentrations of hydrazine were investigated and results are presented in Figure 6.

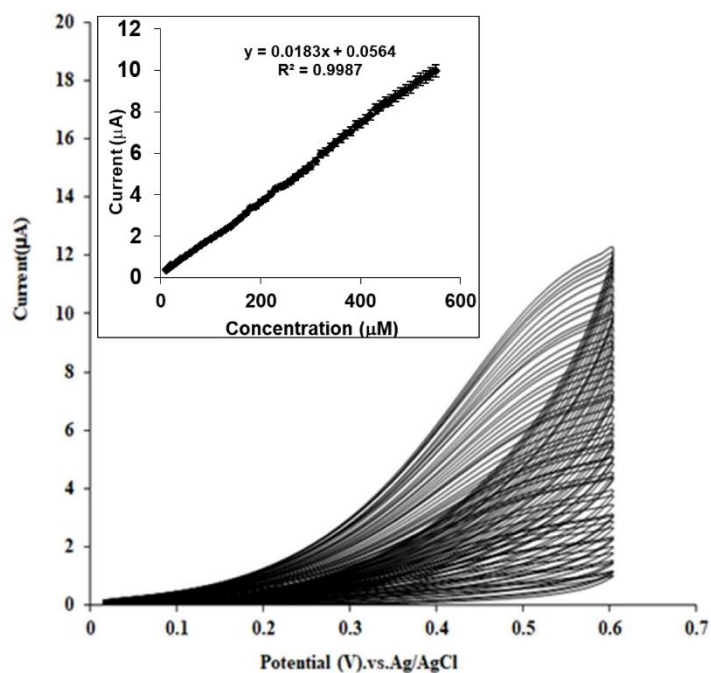


Fig. 6. Cyclic voltammograms of GCE modified by AYR/TiO₂/Chit/ in 100 mM of PBS and pH of 12 containing different concentrations of hydrazine from 10 to 550 μM

Results shows that the anodic peak current of hydrazine increases by increasing the hydrazine concentration in solution.

The inset of Figure 6 shows that the oxidation peak current of hydrazine is proportional to analyte concentrations. This suggest that the oxidation process is controlled by diffusion as expected for a catalytic system [27]. The plot of the peak current response versus hydrazine concentrations (Figure 6, inset), reveals one linear ranges from 10 to 550 μM with an excellent linear correlation using CV technique.

The inset of Figure 6 shows a linear plot of anodic peak current vs. hydrazine concentrations. Based on above results, a possible 4-electron process mechanism can be proposed, leading finally to the generation of nitrogen gas. (equations 1 to 3):



3.5. Amperometric detection of hydrazine at AYR/TiO₂/Chit/GCE

To achieve a lower detection limit, a more sensitive method than cyclic voltammetry such as amperometry under rotating condition was studied.

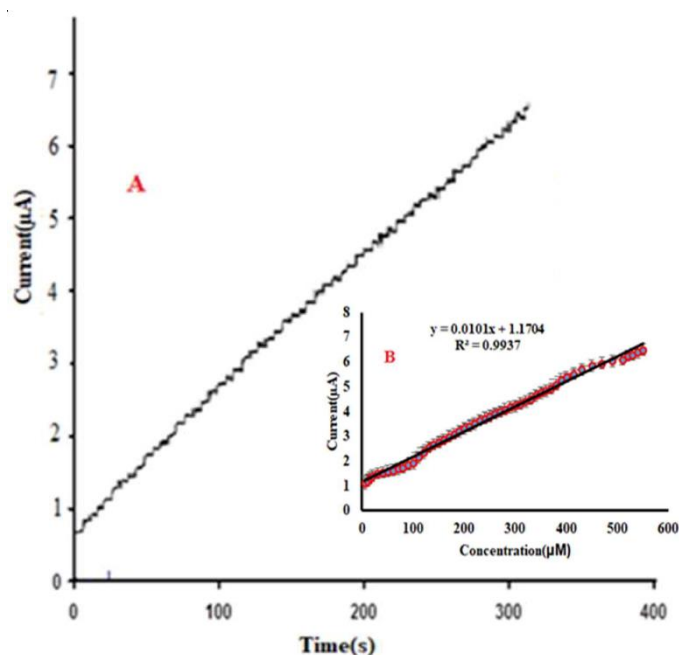


Fig. 7. Amperometric responses of GCE modified by AYR/Chit/TiO₂ NPs (rotating speed 2000 rpm) held at 0.45 V in PBS (pH 12). The inset shows the linear dependence of peak currents vs. concentration

Figure 7 shows the hydrodynamic amperograms of the rotating GCE electrode modified by AYR/Chit/TiO₂ NPs (rotating speed of 2000 rpm) with successive injection of hydrazine at an applied potential of 0.45 V vs. Ag/AgCl reference electrode.

As illustrated in Figure 7, during the successive additions of hydrazine from 5 μM to 580 μM, a well-defined response is observed (Figure 7A). The measured currents increases, by increasing the hydrazine concentrations in the solution. The calibration plot for hydrazine determination is linear for a wide concentration up to 580 μM (Figure 7B). A linear least square calibration curve over the range of 5–550 μM shows a slope of 0.1727 μA/μM (sensitivity) and a correlation coefficient of 0.998. The detection limit was 1 μM when the signal to noise ratio was 3.

3.6. Comparison of the recent biosensor with previously reported electrochemical methods

The linear range and detection limit of proposed biosensor was compared with other modified electrodes that have been developed for hydrazine determination (Table 1). As can be seen, the presented biosensor has better or comparable linear dynamic range and detection limit compared to those of other methods that are shown in Table.1.

Table 1. Comparisons of linear range and detection limit of the present biosensor with those of some other modified electrodes applied for hydrazine determination

Electrode	Modifier	Linear range (M)	Detection limit (M)	Ref.
Graphite paste	Au Nanoparticle	0.05-250×10 ⁻⁶	3.07×10 ⁻⁶	[1]
Ti	gold nanoparticles	500-4000×10 ⁻⁶	42×10 ⁻⁶	[29]
Carbon ceramic	Ni hexacyanoferrate	20-2000×10 ⁻⁶	8×10 ⁻⁶	[30]
Carbon paste	Co phthalocyanine	125-980×10 ⁻⁶	73.5×10 ⁻⁶	[31]
Al	Hexacyanoferrate Pd	390-1000×10 ⁻⁶ and 2000-7500×10 ⁻⁶	4.6×10 ⁻⁶	[32]
Cu	Thiourea	135-5000×10 ⁻⁶	7.6×10 ⁻⁶	[33]
GCE	Overoxidized polypyrrole	13-2000×10 ⁻⁶	3.6×10 ⁻⁶	[28]
GCE	BiHCF	7.0-1010×10 ⁻⁶	3×10 ⁻⁶	[34]
GCE	AY/TiO ₂ NPs/Chit	10-580×10 ⁻⁶	1×10 ⁻⁶	This work

3.7. Interference effect

To evaluate the selectivity of the modified electrode, the effect of some interferences including the some inorganic ions and common phenolic complexes were studied in PBS (pH

12) containing 50 μM hydrazine. According to the results 1-fold concentration of phenol, nitrophenol and 10-fold concentration of some inorganic ions such as IO_3^- , PO_4^{3-} , I^- , Cl^- , Br^- , F^- , Na^+ , Li^+ , K^+ , Ca^{2+} , Mg^{2+} , Pb^{2+} and Zn^{2+} had no interference effect on hydrazine determination.

3.8. Application

To study the validity of GCE modified by AY/TiO₂ NPs/Chit for quantification of hydrazine in real samples, mineral, tap and lake water samples were tested via a recovery study. Table 2 shows the recoveries for different samples ranged from 98.4% to 104.5%. These satisfactory data show that the effect of matrix for studied samples is less than 5% for quantification of hydrazine in water samples.

Table 2. Quantification of hydrazine content in real water samples and its repeatability

Type of water	Added (μM)	Found (μM) ^a	RSD (%) ^b	Recovery (%)
Tap	100	99.1	2.78	99.1
Mineral	500	503	3.10	100.6
Lake	600	615	3.78	102.5

^a Mean of four measurements.

^b Relative standard deviation for n=3

4. CONCLUSION

A novel modified GCE was prepared by simple immobilizing of AYR/Chit/TiO₂ NPs on the GCE surface. Compared with GCE, the combination of unique properties of chitosan, TiO₂ nanoparticle and alizarine yellow R resulted in the improvement of both the peak potential and current responses of AYR/Chit/TiO₂ NPs /GCE. The GCE modified by a thin film of AYR/Chit/TiO₂ NPs shows stable and reproducible electrochemical behavior. This modified electrode makes evident excellent catalytic activity for hydrazine oxidation. The proposed sensor was used for determination of low levels of hydrazine by using the amperometric method.

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